DEVELOPMENT OF NEW METRICS AND A TOOL FOR SOCIAL QUANTIFICATION OF SUSTAINABLE PROCESS DESIGN

By

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DEVELOPMENT OF NEW METRICS AND A TOOL FOR SOCIAL QUANTIFICATION OF SUSTAINABLE PROCESS DESIGN

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Dedicated to the memories of all those martyrs around the world who sacrificed their invaluable lives for the sake of humanity……..

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Abstract: The concept of sustainable design has emerged as a new paradigm. Sustainability combines economic, environmental and social aspects of Process design. In our research all the available metrics, tools that are being used for social quantification with good definition, description and calculation methodology is reviewed. Then a new tool is proposed which considers both the inherent safety and occupational health quantification for sustainable process design. The method is tailored for the process research and development stage by including only such chemical properties and process operating conditions which are obtainable at early design stage. The approach is demonstrated for the two alternative processes of DME production and for the base case and optimized case Acrylonitrile production using simulation engine ASPEN PLUS^{TM}. With the help of the developed standard index scale and the retrofitted SUSTAINABILITY EVALUATOR the best socially sustainable process design is assessed.

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CHAPTER I

INTRODUCTION

With the advent of the 21st century, green chemistry is being incorporated in the design of chemical processes, eventually shifting the industrial focus from economic concerns to sustainability concerns.Sustainability can be defined as "economic well being linked to the health of environment and the success of the world citizens"(Schraz et al., 2002). According to the report of the1987 World Commision on Environment and Development, Our Common Future, sustainability is defined as "development that meets the present without compromising the ability of future generations to meet their own needs" (Bruntland,1987).Sustainability is comprised of the following dimensions: economic, environmental and social. As depicted in the Venn diagram (Figure 1.1), it can be concluded that a process that is designed for only economic and environmental concerns is classified as viable; a process that is designed for only environmental and social concerns is classified as bearable and a process that is designed for economic and social concerns is equitable"(Adams, 2006). As economics of the industrial processes was initially dictated as the main constraint in the design of chemical process plants, health and safety of the workers and public welfare (social concerns) have only recently become another main constraint (Samli, 2011). Although researchers have put forth much efforts to quantify sustainability, an important drawback is that social quantification at the early design stage has not generally been considered from both a health and safety perspective successfully. As the term 'sense making of social sustainaibility' itself is abstract, a well defined methodology is needed to quantitatively measure the social dimension of sustainability.

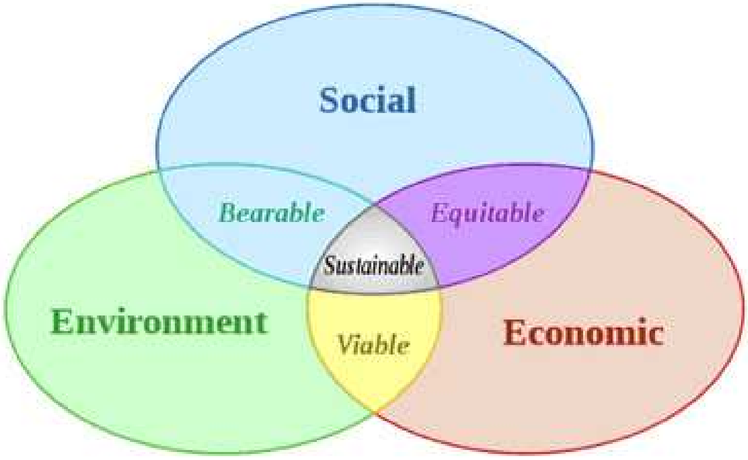


Figure 1.1: Dimensions of Sustainability (Pinter 2005; Adams 2006)

Economic and technical aspects used to be the only essential aspects influencing the decision-making of companies. However, now increasing attention is given to safety, health and environmental (SHE) criteria because of legal requirements, company image, as well as economic reasons. These aspects can be considered even as a competitive advantage (Hurme, Tuomaala, and Turunen, 2003). A safer, healthier, and environment friendlier process can be achieved through internal and external means. Internal means, widely known as the ‘inherent approach’ is considered preferable, since it relies on the fundamental properties of the process and chemicals in aiming to eliminate risks by using less hazardous chemicals, smaller inventories of chemicals, and milder process conditions. In fact, the chemical which does not exist, does not pose a danger to anybody. The inherent approach requires less add-on protective systems, which also simplify the process and makes it more easily manageable. Protective equipment may however fail and human may create errors. Therefore designing a fundamentally safer, healthier and environmentally friendlier plant is more appealing (Kletz, 1991).

There is no general answer to the question of which process is inherently safer. One problem is how to minimize it simultaneously with considering the risk associated with all of the process hazards. In the real world, the various hazards are not independent of each other, but are inextricably linked together (Hendershot, 1995). A process modification, which reduces one hazard, will always have some impact, positive or negative, on the risk resulting from another hazard (Heikkila et al, 1999). Efficiency of safety policies can be assessed by looking at accident statistics in industry. According to the US Dept. of Labor (Bureau of Labor Statistics, US Dept. of Labor, 2010), a total of 120 fatal work injuries occurred in the oil and gas extraction industry in 2008. The three most frequent fatal events in 2008 were transportation incidents (41 percent), contact with objects and equipment (25 percent), and fires and explosions (15 percent). The number of fatal work injuries associated with fires and explosions over the past five years ranged from 10 fatalities in 2007 to 21 fatalities in 2006. In 2008, there were 18 fatalities (Bureau of Labor Statistics, US Dept. of Labor, 2010).The trend is showing that the traditional approach of safety is not enough and actions should be reshuffled which necessitates more preventive strategies such as inherent safety plant design. In this study an inherent safety index will be presented to quantify the safety evaluation problems at the early design stage.

Occupational health is the promotion and maintenance of the highest degree of physical, mental, and social well-being of workers in all occupations by preventing departures from health, controlling risks, and the adaptation of work to people, and people to their jobs (ILO/WHO, 1950). In other words, occupational health is concerned with the two-way relationship between work and health. Subsequently, occupational health hazards are those factors arising in or from the occupational environment that adversely impact health (Lypton and Lynch, 1994).It is estimated that yearly over two million people worldwide die of occupational injuries and work related diseases (Eijkemans, 2005). In fact more people die from diseases caused by work than are killed in industrial accidents (Wenham, 2002). However, due to its being complex in nature, occupational health has received less importance from chemical engineers than safety issues. Health differs from safety in terms of the exposure time and the abnormality of the circumstances. Safety deals with acute i.e. major catastrophic short-term events that are unlikely to occur. Mean-while, health is more related to chronic i.e. continuous, slow, low level exposure over the time. Occupational health concerns with routine work activities carried out by employees experiencing a day-to-day workplace exposure under normal conditions. Therefore, the health effects involve a lot of work related and technical factors that result in a complicated means of assessment which compound the task of assessing occupational health in work places (Hassim et al. 2009).

The proposed framework of this work incorporates the sequential process simulator, ASPEN PLUS (version 8.1) to simulate processes and calculate mass and energy balances. As part of the methodology, a modified version of the developed Excel based tool titled the “SUSTAINABILITY EVALUATOR” (Shadiya, 2010b) has been applied for addressing specifically the social dimension of sustainability.

For a better understanding of the proposed framework and its implementation, several topics presented in Table 1.1 will be covered in the subsequent chapters. Chapter

Two will discuss the tool available to address the social dimension of sustainability. Chapter Three will deal with the survey of social metrics, indices available and the SUSTAINABILITY EVALUATOR modification. The proposed metrics and index system will also be discussed. Chapter Four will discuss the methodology for the existing framework used in this work. Case studies and the applicability of the methodology will be described in Chapter Five. The case studies are of comparing two alternate processes for DME production and base case and optimized case for Acrylonitrile process. The last chapter will discuss the conclusions and future recommendations.

Table 1.1: Subsequent chapters in summary

Chapter 2	Available tools for evaluating health and safety.
Chapter 3	Available social metrics, indices and brief overview of the modified sustainability evaluator. A new metric and index system is also proposed.
Chapter 4	Detailed description of the proposed framework
Chapter 5	Discussion of results obtained from following the proposed methodology on the case studies for DME productions and Acrylonitrile process.
Chapter 6	Conclusions and future recommendations

This research may be the first in combining both health and safety quantification elaborately using the retrofitted SUSTAINABILITY EVALUATOR. The result will help the decision makers to choose between the more socially sustainable options when implementing a process design. It is also user-friendly to help to amalgam with economic and environmental- the other two aspects of sustainability for any future research.

CHAPTER II

SAFETY AND HEALTH EVALUATION TOOLS

In this section safety and health concerns are first discussed.Then an explaination of Inherernt Safety and Inherent Occupational Health are described. Finally, the tools available for addressing health and safety are consulted.

2.1 Health and Safety Concerns

The Bhopal tragedy, the largest industrial accident ever, is approaching its 30th anniversary this year.This catastrophe, caused by the release of methyl isocyanate gas from a Union Carbide plant, led to 10,500 deaths, long term environmental issues and liabilities (Wright,2007).The review for the cause and effect of Bhopal incident rejects the conventional post-incident add-on protective systems anymore and necessitates the application of the early design SHE consideration. As another example, after the Fixborough, England cyclohexane release that killed 28 and injured 99 people due to the collapse of a pipe leading to the escape of 35 tons of cyclohexane, it was determined that calculations were not completed to determine if the pipes could withstand the process strain (Flynn and Theodore, 2002).

The importance of completing safety and health risk assessments during early process design stage is inevitable. Companies are now required to conduct safety analysis that addresses the following concerns: hazard that can occur, probability of the hazard to occur and impact of the hazard (Arendt and Lorenzo, 2000). Risks for long and short term chemical exposure to employees and surrounding public habitat must be assessed. Shadiya (2010a) discussed the different types of chemical processing plant accidents as follows:

2.1.1 Chemical Processing Plant Accidents

A safe chemical processing plant is characterized by the situation where little to no disastrous accidents occurs. Chemical processing plant accidents are unexpected events that can result in financial and personal loss. In processing plants, accidents can occur as results of the following:

- Equipment Failure: Abnormal conditions such as equipment leaks, irregular temperature and pressure ranges, equipment spills and operational failures such as vacuum problems, blocked out let valve, cooling water failure can lead to an incident.
- Human Errors: Incorrect calculations and assumptions when designing process equipment can lead to accidents. Improper use of process equipment, not grounding electrical systems and thermal hazards. When any or a combination of the events mentioned above occurs, several of the following incidents can occur at the right conditions: fires, explosion and toxic emissions and hazardous spills.

2.1.1.2 Fires

Fires occur when oxygen reacts with a fuel at the proper temperature in the presence of heat and mixing. The potential for a substance to cause fire is determined by its flammability limit, flash point temperature, burning velocity, ignition energy and auto ignition temperature (Flynn and Theodore, 2002). For most fires to occur there must be an ignition source. Figure 3.7 shows the typical ignition sources for industrial fires, according to a study completed by the Factory Mutual Engineering Corporation (Flynn and Theodore, 2002). As shown in the figure, electrical accidents are the major ignition source accounting for 23% of industrial fires while chemical action, lightening, static electricity are the lowest ignition sources causing only 1% of industrial fires.

According to the National Fire Protection Association, fire can be classified into four classes (Firenze, 1979):

- Class A Fires: These are fires that result from the burning of solid materials e.g. wood, paper, cloth, trash etc. This type of fire can be extinguished by water which reduces the ignition temperature.
- Class B Fires: These are fires that occur as a result of a vapor-air mixture over flammable liquid e.g. gasoline, diesel etc. This type of fire can be stopped by using CO_2, foam, and halogenated hydrocarbon fire extinguishers.
- Class C Fires: These are fires that result from electrical equipment failure and can be stopped by using dry chemicals, carbon dioxide, compressed gas and vaporizing liquid.

- Class D Fires: These are fires that occur in combustible metals e.g. magnesium and aluminum etc. This type of fire can be quenched by using graphite based extinguishers.

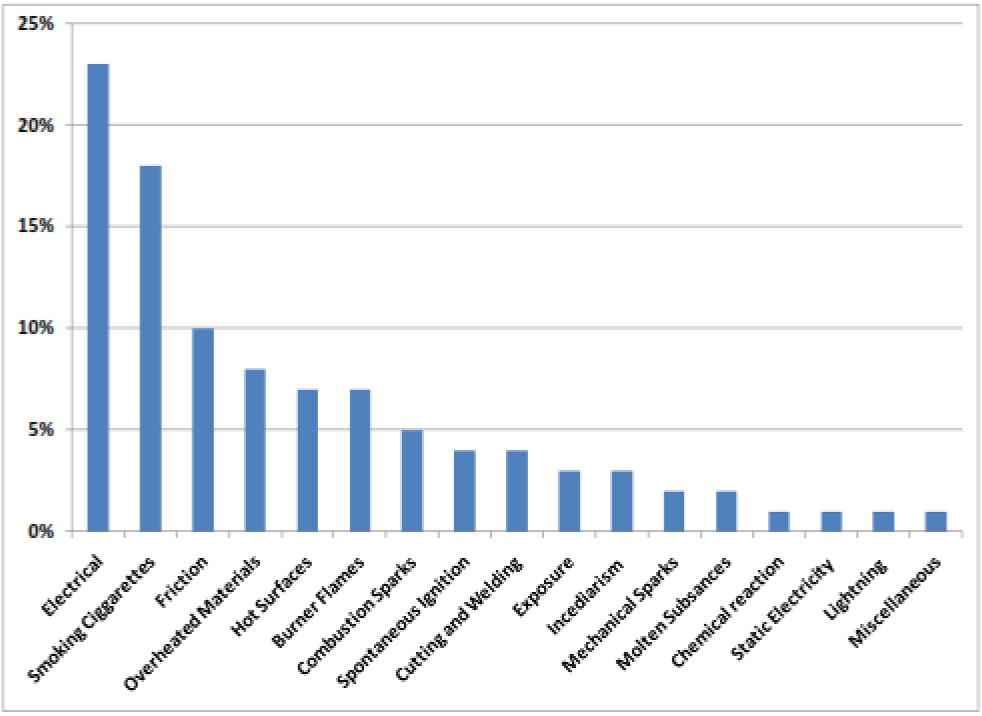


Figure 2.1: Ignition Sources of Industrial Fires (Flynn and Theodore, 2002)

2.1.1.3 Explosions

Explosions occur when there is a rapid release of energy in a constricted volume, which results in extremely high temperature and gas release. Accidental explosion include condensed phase, combustion, pressure vessel and vapor cloud explosions (Flynn and Theodore, 2002). The tendency for a substance to cause an explosion is determined by its explosion limit. The explosion limit is the range of concentration that explosion can occur. The range is bounded by the upper explosion limit (UEL) and the lower explosion limit (LEL). Plant explosions are mainly caused by equipment failures, or incorrect operational procedure. For example when two incompatible chemicals are reacted, an explosion can occur. Vessel rupturing due to pressure build up in a gaseous exothermic reactor can lead to an explosion. Inappropriate vessel material for certain toxic substance at extreme high temperatures can also lead to an explosion. Explosions can often be prevented by ensuring sound engineering practice is implemented when designing process equipment.

2.1.1.4 Toxic Exposure

Exposure of chemicals to humans can be accidental or planned. Accidental chemical exposure can cause significant threats to human life sometimes leading to death. Planned exposure of chemicals is usually controlled by an exposure limit. Some chemicals are not toxic at certain concentrations. The toxicity of most chemicals is evaluated by its toxic limit value. There are three different toxic level limits that are used in industry:

- Toxic Limit Value- Time Weighted Average: The toxic limit value-time weighted average also known as the permissible exposure limit, is defined as the average concentration of toxic chemical that a person can be exposed to in an 8 hour period.
- Toxic Limit Value- Short Term Exposure Limit: According to the American Conference of Governmental Industrial Hygienists, the toxic limit value-short term exposure limit is the concentration of toxic chemical that a person can be exposed to in a short time period without having adverse health effects.
- Toxic Limit Value-Concentration: This is defined as the maximum concentration of a toxic chemical that a person can be exposed to at any point in time.

2.1.1.5 Hazardous Spill

Hazardous chemicals which may exist in the three different states of matter are ignitable, reactive, corrosive, radioactive and infectious. Hazardous spills include the following: chlorinated oils, flammable wastes, synthetic organics, toxic metals, explosives, reactive metals, salts, acids and wastes. Uncontrolled hazardous chemical spills pose serious threats to human life, natural water, land environment and the ecosystem. An example of one of the most significant hazardous spill is the Exxon 1989 Valdez Oil Spill. The ExxonMobil 1989 Valdez Oil spill involved the accidental release of 250,000 barrels of crude oil into the Prince William Sound, Alaska ocean basin. Some of the negative impacts of this incident include the death of 375,000 sea birds, marine animals and habitat loss (Harwell and Gentile, 2006). Most recently, in April 2010, the largest marine oil spill occurred when one of BP’s offshore facilities exploded in the Gulf of Mexico as a result of a failed emergency blow out preventer. The effect of this incident has been devastating, leading to 11 death and 17 injuries (Brown, 2010; Welch and Joyne, 2010). Also for several months, more than 80,000 barrels of oil per day was gushing into the gulf, resulting in serious damage to marine life, wildlife, fishing and tourism (Mcquaid, 2010).

2.2 Inherent Safety

According to the American College Dictionary (Webster's New World Large Print Dictionary, 2004) the term “Inherent” is defined as “existing in something as a permant and inseperable element, quality or attribute”. Thus an inherently safer chemical process is safer because of its initial characteristics, those which belong to the process by its very nature. An inherently safer design is one that avoids hazards, instead of controlling them, particularly by removing or reducing the amount of hazardous material in the plant or the number of hazardous operations (Heikkila et al,1999).

Trevor Kletz was the first to express widely the concept of inherent safety in the late 1970’s.The basic principles are common sense and include avoiding the hazardous materials, minimizing the inventories of hazardous materials and aiming for simpler processes with more benign and moderate process alternatives (Kletz,1984).

Kletz (1984,1991) has given Basic Principles of Inherent Safety as follows:

* Intensification

"What you don't have, can't leak." Small inventories of hazardous materials reduce the consequencies of leaks. Inventories can often be reduced in almost all unit operations as well as storage. This also brings reductions in cost, while less material needs smaller vessels, structures and foundations.

* Substitution

If intensification is not possible, an alternative is substitution. It may be possible to replace flammable refrigerants and heat transfer with non-flammable ones, hazardous products with safer ones, and processes that use hazardous raw materials or intermediates with processes that do not. Using a safer material in place of a hazardous one decreases the need for added-on protective equipment and thus decreases plant cost and complexity.

* Attenuation

If intensification and substitution are not possible or practicable, an alternative is attenuation. This means carrying out a hazardous reaction under less hazardous conditions, or storing or transporting a hazardous material in a less hazardous form. Attenuation is sometimes the reverse of intensification, because less extreme reaction conditions may lead to a longer residence time.

* Limitation of Effects

If it is not possible to make plants safer by intensification, substitution or attenuation, the effects of a failure should be limited. For instance equipment is designed so that it can leak only at a low rate that is easy to stop or control. For example gaskets should be chosen to minimize leak rates. Also limitation of effects should be done by equipment design or change in reaction conditions rather than by adding on protective equipment.

*Simplification

Simpler plants are inherently safer than complex plants, because they provide fewer opportunities for error and contain less equipment that can go wrong. Simpler plants are usually also cheaper and more user friendly.

*Change Early

Change Early means identification of hazards as early as possible in the process design. The payback for early hazard identification can make or break the capital budget of a new process. This can be achieved by dedicated safety evaluation methodologies which are designed for preliminary process design purposes.

*Avoiding Knock-On Effects

Safer plants are designed so that those incidents, which do occur, do not produce knock-on or domino effects. For example safer plants are provided with fire breaks between sections to restrict the spread of fire, or if flammable materials are handled, the plant is built out-of-door so that leaks can be dispersed by natural ventilation.

*Making Status Clear

Equipment should be chosen so, that it can be easily seen, whether it has been installed correctly or whether it is in the open or shut position. This refers to ergonomics of the plant. Also clear explanation of the chemistry involved in the process helps operating personnel to identify possible hazards.

*Making Incorrect Assembly Impossible

Safe plants are designed so that incorrect assembly is difficult or impossible. Assembled components must meet their design requirements. A loss of containment may result from using wrong type of gaskets for example.

*Tolerance

Equipment should tolerate maloperation, poor installation or maintenance without failure. E.g. expansion loops in pipework are more tolerant to poor installation than bellows. The construction materials should be resistant to corrosion and physical conditions. For most applications metal is safer than glass or plastic.

*Ease of Control

A process should be controlled by the use of physical principles rather than added-on control equipment (i.e. the dynamics of the process should be favourable). 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.

*Administrative Controls/Procedures

Human error is the most frequent cause of the loss of containment. Training and certification of personnel on critical procedures are permanent considerations. Also some other inherent safety principles, like ease of control, making status clear, tolerance and making incorrect assembly impossible, come into play here.

In the early stages of process design these principles helps to choose the safest materials, process conditions and even process technology (Heikkila, 1999).

2.3 Inherent Occupational Health

Health differs from safety in terms of the exposure time and the abnormality of the circumstances. Safety deals with acute i.e. major catastrophic short-term events that are unlikely to recur. Mean-while, health is more related to chronic i.e. continuous, slow, low level exposure over the time. Occupational health concerns with routine work activities carried out by employees experiencing a day-to-day workplace exposure under normal conditions (Hassim and Hurme, 2010).

Inherent safety and inherent occupational health has the same background. According to Kletz (1984) all SHE aspects are interlinked. Inherent SHE can be defined e.g. as the elimination of hazards by suitable process design so that process are, by their very nature, safe, healthy, environmentally friendly, unaffected by change and stable (Gillett, 2003).

The term inherent health hazards was first introduced in the early 1990s when the EU INSIDE Project was started (2001) aiming at promoting inherent safety, health, and environmental protection(ISHE) within the European industry. Evaluation of the effects of the airborne chemicals to health was considered as inherent health aspect. Detailed discussion of the term inherent occupational health hazards were first done by Hassim and Edwards (2006). An inherent occupational health hazard can be defined here as a condition, inherent to the operation or use of material in a particular occupation , industry or work environment, that can cause death, injury, acute or chronic illness, disability, or reduced job performance of personnel by an acute or chronic exposure (Hassim and Hurme, 2010).

Elimination of the use of hazardous chemicals, process conditions, and operation procedures that may cause occupational hazards to the employees is the way in which inherent occupational health eliminates or reduces the occupational hazards. There are two fold aims (Hassim and Hurme, 2010): First, to reduce the risk of inherent properties of chemicals by using friendlier chemicals or the chemical in safer physical condition to eliminate the exposure. Second, to reduce such process steps or procedures which involves inherent danger of exposure of the chemical. Examples of such operations are some manual operations where the worker is in close contact with the material, such as the manual handling and dosing of chemical, emptying, and cleaning of the equipment, etc.

Shadiya (2010a) described the health risk assessment for a particular chemical as follows: There are four steps that are conducted in a health risk assessments and these include hazard identification, dose-response toxicity assessment, exposure assessment and risk characterization. In hazard identification, information such as chemical identity, identification of equipment that produces, transport or stores the particular hazardous chemical(s), plant design, amount of chemical produced or available and the health investigation of whether exposure to a particular chemical(s) will increase the likelihood for adverse health effect such as cancer, birth effects etc. to occur is completed in this step (Flynn and Theodore, 2002).

There are many published methods for hazard identification and these include toxicology, epidemiology, molecular and structural analysis, material safety and data sheet, fate of chemical assessments and carcinogenic or non-carcinogenic health hazard assessments.

In the dose response toxicity assessment step, the quantitative assessment of chemical(s) toxicity as a function of human exposure is completed in this step. The Environmental Protection Agency Integrated Risk Information System is an excellent source for information on health risk regulatory data. In this database of 540 chemicals, oral reference doses, and inhalation reference concentrations effects and oral slope factors and oral and inhalation for non –carcinogen risk unit risks for carcinogenic effects are available (United States Environmental Protection Agency). This information can be used to conduct a quantitative and qualitative risk assessment.

In the exposure assessment step, an evaluation is conducted to determine who will be exposed to a particular toxic chemical and for how long. In exposure assessments, the following must be addressed:

- Probability of exposure: This is an evaluation of the likelihood that a population will be exposed to a particular toxic chemical.
- Magnitude of exposure: This is a measure of the dose of chemical a population is exposed to and the frequency in which the exposure occurs.
- Route of exposure: This determines if a population is in contact with a toxic chemical via inhalation, ingestion and skin absorption.

- Population Exposed: The people who are exposed to a particular toxic substance. The health risk characterization step involves the estimation of the perceived health and ecosystem risks from a chemical exposure. Non-cancer risks for one substance can be measured by a hazard quotient which is calculated by Equation 2.1:

$$NCHQ = E/\ RFD \qquad (2.1)$$

Where

E = Exposure level

RFD = Reference dose

NCHQ= Non-cancer hazard dose

The non-cancer risks for several substances can be evaluated by calculating a hazard index as shown in Equation 2.2:

$$HI = E_1/RFD_1 + E_I/RFD2\ldots..E_I/RFD_I \qquad (2.2)$$

Hazard Index = Exposure

Low and high cancer risk as shown in Equation 2.3 and 2.4 respectively, are a measure of the probability that if one is exposed to a carcinogen, that person will be diagnosed with cancer. To evaluate the cancer risk for a mixture of substances, the risk is evaluated individually and then summed up.

$$\text{Cancer Risk} = (CDI) * (SF) \qquad (2.3)$$

Where

CDI = Chronic daily intake averaged over 70 years

SF = Slope factor (mg/kg/day)

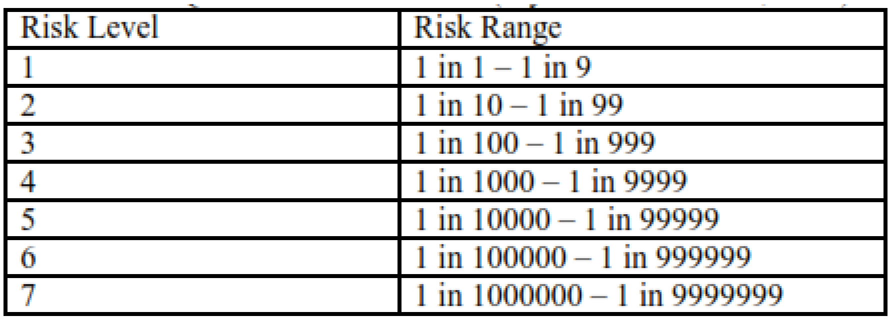
$$\text{Cancer Risk} = 1 - \exp(-CD1 * SF) \qquad (2.4)$$

There are 5 risks levels that are used to qualitatively identify adverse health effects in hazard characterization and they are listed below (Flynn and Theodore, 2002):

- Risk Level 1: No adverse health effect
- Risk Level 2: Low probability of causing adverse effect
- Risk Level 3: There is possibly that chemical is a health hazard
- Risk Level 4:There is a possibility that chemical will cause adverse health hazards
- Risk Level 5: Chemical will cause adverse health hazard.

Risk assessment on an annual or life time basis can also be expressed quantitatively as shown in Table 2.1. In this table, assessments that have a level 1 characterization are worse in terms of health impact compared to level 7.

Table 2.1: Quantitative Risk Level (Flynn and Theodore, 2002)



Risk Level	Risk Range
1	1 in 1 – 1 in 9
2	1 in 10 – 1 in 99
3	1 in 100 – 1 in 999
4	1 in 1000 – 1 in 9999
5	1 in 10000 – 1 in 99999
6	1 in 100000 – 1 in 999999
7	1 in 1000000 – 1 in 9999999

2.4 Health and Safety Screening Tools

Modern process industries passed the age of add-on protective systems already and several health and safety risk assessment methods have been developed. This section describes available screening tools for evaluating various aspects of process health and safety as follows:

2.4.1 Dow Fire and Explosion Index

The Dow Fire and Explosion Index was developed to quantify the potential damage from fire and explosion hazards in chemical processing plants that handle 1000 pounds or more of flammable, combustive and reactive toxic chemicals (Kavitha, 2003). The Dow Fire and Explosion index involves a step by step analysis as depicted in the flow chart shown in Figure 2.2 (Shadiya, 2010a).

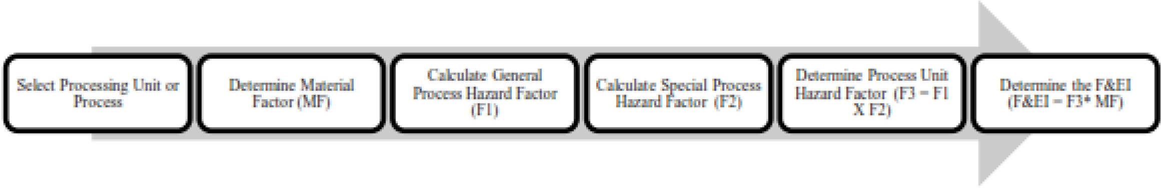


Figure 2.2: Dow Fire and Explosion Index Calculation Steps

The Dow Fire and Explosion Index have been used by many researchers to incorporate safety into chemical process design. It has been implemented into an optimization framework where technical, economic and safety considerations are being met for process design at the conceptual stage (Suardin et al., 2007). A modified version of this index which involves including credit for loss control measures has been demonstrated on an ammonia synthesis reactor (Gupta et al., 2003). The index has also been used as tool to classify hazards for the manufacture of epichlorohydrin (Khan and Abbasi, 1997). To assess the risk of fire and explosion for operations taking place in the Microbiology Laboratory at the University of Reno Nevada, the Dow Fire and Explosion Index was implemented (Kavitha, 2003).

The limitations of the Dow Fire and Explosion are that it only addresses fire and explosion safety concerns but it does not address toxicological data (Shadiya, 2010a).

2.4.2 Mond Index

The Mond Index (ICI, 1985) has been developed from the 1973 version of the Dow F&E Index. The principal modifications to the Dow method include (Lees, 1996): 1) wider range of processes and storage installations can be studied, 2) covers processing of chemicals having explosive properties, 3) improved hazard consideration for hydrogen, 4) additional special process hazards, 5) toxicity included into the assessment. It differs from the Dow fire and explosion index in that it can evaluate safety impact of wider ranges of chemicals such as explosive properties and toxicity assessments. The Mond Index also incorporates hazards credits for processes with safety control devices (Khan and Abbasi, 1998).

2.4.3 NFPA 704

NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response is a standard maintained by National Fire Protection Association of United States. First tentatively adopted as a guide in 1960 (NFPA No. 704M, 1969) and revised several times since then, it defines the "fire diamond" used by emergency personnel to quickly and easily identify the risks posed by materials. The four divisions are typically color-coded with red indicating hazardous flammability, blue indicating level of health hazard, yellow for chemical reactivity, and white containing codes for special hazards. Each of health, flammability and reactivity is rated on a scale from 0 (no hazard) to 4 (severe risk). This helps determine what, if any, special equipment should be used, procedures followed, or precautions taken during the initial stages of an emergency response.

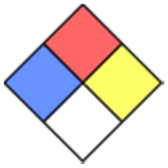


Figure2.3: NFPA 704 Fire Diamond.

Although NFPA704 has been proved to be very effective for fire safety it has some limitations in measuring the overall social sustainability. One example is the current debate regarding flame retardants. Although there is limited data available from human studies, some flame retardants are considered possible carcinogens, while other health effects may include damage to endocrine, immune, reproductive, and nervous systems. The ability of some flame retardants to bio-accumulate raises concern about the potential for harm to firefighters and the general public from even low levels of exposure (Vecchiarelli,2014).

2.4.3 Hazard and Operability Analysis(Hazop)

A HAZOP analysis is a procedure that is completed for existing and new facilities and it involves identifying all the hazards and operability issues in a chemical process. In the HAZOP study, the safety impact of all the different equipment found in a process, specifically looking at the potential hazards when the process deviates from design conditions is evaluated (Dunjó et al., 2010). Kletz (1991) has pointed out an important difference between a conventional Hazop of a line diagram and a Hazop of a flowsheet (i.e. the process concept). In a conventional Hazop deviations from design conditions are assumed to be undesirable and ways of preventing them are looked for. Also in the Hazop of a flowsheet deviations are generated but they are actually looked for to find new process alternatives. Although HAZOP analysis has been extensively used in the chemical process industry, it has some limitations. It is time consuming, as only one accident scenario can be looked at a time. It cannot be used during conceptual stages of design, as detailed process and instrumentation diagrams must be completed, requiring knowledge and expertise in order to complete the assessment accurately (Shadiya, 2010a).

2.4.4 Simulation of Chemical Industrial Accidents Software Package (SCIASP)

The Simulation of Chemical Industrial Accidents Software Package (SCIASP) was developed to evaluate the possible risk of accidents in chemical processes (El Harbawi et al., 2008). This graphical based tool is able to perform hazard analysis that determines risks and damage associated with accidental releases, fires and explosions. This newly developed software is a useful tool for risk assessment because it can be used as a decision making tool to compare the safety risks of different processes (Shadiya, 2010a).

2.4.5 Mortality Index

The Mortality Index was suggested by Marshall (1977) evaluates the fatality of lethal chemical substances. The mortality index is shown in Equation 2.5 below (Shadiya, 2010a).

$$\text{Mortality Index} = \text{Number of Deaths} / \text{Mass of Toxic Substance} \quad (2.5)$$

2.4.6 The Instantaneous Fractional Annual Loss (IFAL) Index

The Instantaneous Fractional Annual Loss (IFAL) Index, developed to identify hazards from pool fires, vapor fires, uncondensed cloud explosions, condensed cloud explosions and internal explosions is a complicated system that needs to be calculated with a computer (Singh and Munday, 1979; Munday et al., 1980). This index was proposed by the United Kingdom Insurance Technical Bureau, to access hazards for each piece of process equipment in order to estimate insurance rates (Cox, 1982).

2.4.7 Hazard Identification and Ranking (HIRA)

The Hazard Identification Racking (HIRA) methodology was developed by Khan and Abbasi (1998) to evaluate the risk of fire, explosion and toxic release. This methodology consists of two indices: the fire and explosion damage index and the toxicity damage index. This methodology has been demonstrated on the sulfolane production process and the safety risk was determined. To validate this methodology, results of other indices such as the Dow Fire and Explosion Index, IFAL Index and the Mond Fire and Explosion Index have been compared to the HIRA methodology. The results of the comparison show that HIRA is more sensitive and accurate compared to other methods (Khan and Abbasi, 1998).

One drawback of HIRA is that it does not tell if existing control systems are sufficient or need modifications. It also does not incorporate an emergency response plan such as toxic release control and firefighting equipment into the calculation (Khan et al., 2001). A new tool to improve some of the limitation of HIRA was proposed and this was called the Safety Weighted Hazard Index (sWeHI). The Safety Weighted Hazard Index was developed by Khan et al. (2001) to accurately and precisely address safety concerns in chemical industry while integrating credits for safety measures that are already in place (Shadiya,2010a).

2.4.8 Maximum Credible Rapid Risk Assessment (MAXCRED)

The Maximum Credible Rapid Risk Assessment (MAXCRED) is a computer software developed by Khan and Abbasi (1999) to simulate accident and damage potential in order to evaluate safety risk of processes in the chemical industry. It has been demonstrated on an industrial sulfolene production process (Shadiya, 2010a). Two different accident scenarios namely boiling liquid / vapor cloud explosion followed by flash fire and confined vapor cloud explosion have been modeled for the British Petroleum Texas City Refinery incident. This was developed to show that hazard assessment can prevent safety incidents and provide adequate emergency response (Khan and Amyotte, 2007). MAXCRED was also used for damage prediction for an oxidation based ethylene oxide plant (Khan et al., 2003).

2.4.9 Prototype Index of Inherent Safety (PIIS)

Edwards and Lawrence (1993) have developed a Prototype Index of Inherent Safety (PIIS) for process design. The inherent safety index is intended for analyzing the choice of process route; i.e. the raw materials used and the sequence of the reaction steps. The PIIS has been calculated as a total score, which is the sum of a chemical score and a process score. The chemical score consists of inventory, flammability, explosiveness and toxicity. The process score includes temperature, pressure and yield. It has some clear advantages over some other numerical indices in early design stages (Heikkila et al., 1999).

It has been argued that an overall inherent safety index, such as the PIIS, incorporates some kind of build-in judgment of the relative importance of the various types of hazards. The user has to defer to the judgment of the developer of the index or has to modify it to incorporate his own judgment. In the latter case the results are not any more comparable with other users (Hendershot, 1997).

2.4.10 Inherent Safety Index

The Inherent Safety Index was proposed by Heikkila (1999) to evaluate process safety. There are two categories of safety indexes presented by this researcher and they are chemical and process safety index. The summation of these two indices yields the Inherent Safety Index. The chemical index describes how raw materials, products, by-products, and intermediates interactions affect safety of a process. While the process safety index depicts how equipment configuration and operating conditions can impact the safety of a process (Shadiya, 2010a).

In spite of its limitation to model safety risks resulting from deviations in operation conditions, other researchers used the inherent safety index. It was integrated into an expert system called iSafe for ranking safety of process flow sheet structure (Palaniappan et al., 2002). It was used to select the safest production route from 10 different options for acetic acid (Palaniappan et al., 2004). This index was used to access the safety of simulated chemical and mechanical heat pump systems and the safest option was selected based on the inherent safety index (Ajah et al., 2008). This inherent safety methodology has been incorporated into the modified SUSTAINABILITY EVALUATOR for this research and will be discussed in details in section 4.3.1.

2.4.11The Dow Chemical Exposure Index

CEI (1998) gives a very comprehensive method of assessing health hazards caused by acute exposure to chemicals. The assessment is carried out for each source identified to have a potential for releasing chemicals (Hassim and Hurme, 2010).

One drawback of CEI is that it evaluates acute health hazard risk to people based on chemical release incidents and failed to measure the long term effects on workers which is essential from occupational health point of view.

2.4.12 Toxicity Hazard Index

Toxicity Hazard Index was introduced by Tyler, Doran, and Greig (1996). It ranks the relative acute toxic hazards of different chemical production units. This Mond-like index evaluates the toxicity potential of a unit, considering only short term events and acute effects based on inhalation route of exposure. It has been constructed so that the overall pattern closely follows the framework of the Mond index (Hassim and Hurme, 2010).

Like HIRA method (Khan and Abbasi, 1998), THI is also a safety-type assessment method which deals with acute toxicity alone and only treats the short-term accidental events, but not the low level and continuous releases.

2.4.12 UK Scheme

This was the model developed by a working group established by the Health and Safety Commission’s Advisory Committee on toxic substances (Maidment, 1998; Russel, Maidmetnt, Brooke, and Topping, 1998). The scheme scrutinizes both the intrinsic health hazard of substances used at work and surrogates for exposure potential particularly to employees with the ultimate target of appropriate control strategies identification.

The shortcomings of the scheme is in its applicability for design stage implementation as it is targeted particularly for existing small and medium size plants.

2.4.13 INSET Toolkit

This toolkit was an outcome of INSIDE Project (2001) capable of assessing SHE aspects as well as other feasibility factors. The four stages implementation of the toolkit is shown below:

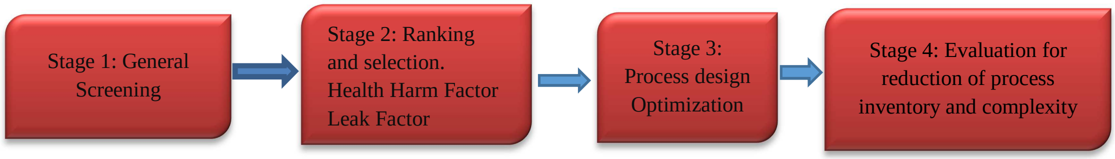


Figure 2.4: Four stages of INSET Toolkit

Only stage 2 deals directly with the ranking and selection of SHE aspects (Hassim and Hurme, 2010). The health performance of the routes is evaluated based on the hazardous materials properties relating to health effects, the likely fugitive emission rate of that material as well as the chance that people are exposed to this. For chemical properties the Health Harm Factor (HHF) is determined from R-phrase and qualitative classification. The Leak Factor (LF) is provided to estimate the fugitive release rate from process equipment and manual activities. The potential exposure is assessed only by estimating the number of locations where manual-handling operation will be carried out. The overall health index is calculated from these scores (Hassim and Hurme, 2010).

Malmen (1997) and Ellis (1997) who applied the toolkit identified some difficulties such as long time required in index calculation, the need to screen a large number of alternatives, and the requirement for analyzing complex issues at early stages.

2.4.14 Occupational Health Hazard Index

OHHI was developed by Johnson (2001) in her Master’s thesis for assessing the health hazards in design concepts. The disadvantage of the OHHI method is that some factors for example very concise and questionable evaluation of fugitive emissions and over evaluation of some factors requiring excessive data for example material properties and operational maintenance activities.

2.4.15 Process Route Healthiness Index

Hassim and Edwards (2006) proposed the PRHI methodology which is complicated and lengthy. Some disadvantages of this index system as described by Hassim and Hurme (2010) are: firstly, PRHI requires plenty of information some of which not available at early design stage. It is also inflexible as a result of ‘throughout the process’ data requirements. Besides, the index has the disadvantage of indirectly assessing several factors such as propensity for chemical emissions repeatedly.

2.4.16 Inherent Occupational Health Index

The Inherent Occupational Health Index (IOHI) was developed by Hassim and Hurme (2010) for assessing the health risks of process routes during process research and development stage by including only such properties of chemical and operating conditions of process, which are available already in this early stage. An inherent occupational health hazard has been defined here as a condition, inherent to the operation or use of material in a particular occuapation, industry or work environment, that can cause death, injury, acute or chronic illness, disability, or reduced job performance of personnel by an acute or chronic exposure (Hassim and Edwards, 2006). As described by Hassim and Hurme (2010), inherent occupational health strives to eliminate or reduce occupational health hazards by trying to eliminate the use of hazardous chemicals, process conditions, and operating procedures that may cause occupational hazards to the employees. The objective has two facades: Firstly to minimize the risk of inherent properties of chemicals (toxicity and high vapor pressure for example) by using friendlier chemicals or the chemicals in safer physical condition (such as lower temperature) to eliminate the exposure. Secondly to reduce such process steps or procedures which involve inherent danger of exposure of the chemical. Examples of such operations are some manual operations where the worker is in close contact with the material such as manual handling and dosing of chemical, emptying, and cleaning of the equipment etc. (Hassim and Hurme, 2010).

The method considers both the hazard from the chemicals present and the potential exposure of workers to the chemicals. The index can be used either for determining the level of inherent occupational health hazards or comparing alternative process routes for these risks. A quantitative standard scale for the index is developed to allow health assessment of a single process. The approach is demonstrated for six methyl methacrylate process routes using three different types of index calculations; additive-type, average-type, and worst case-type. This methodology is incorporated in the modified SUSTAINABILITY EVALUATOR in this research.

CHAPTER III

SOCIAL SUSTAINABILITY METRICS AND INDICATORS AND SUSTAINABILITY EVALUATOR TOOL.

3.1 Introduction

There have been very few attempts to define social sustainability as an independent dimension of sustainable development. Furthermore, no consensus seems to exist on what criteria and perspectives should be adopted in defining social sustainability. From a sociological standpoint (Littig and Grießler, 2005: 72) define social sustainability as "…a quality of societies. It signifies the nature-society relationships, mediated by work, as well as relationships within the society. Social sustainability is given, if work within a society and the related institutional arrangements satisfy an extended set of human needs [and] are shaped in a way that nature and its reproductive capabilities are preserved over a long period of time and the normative claims of social justice, human dignity and participation are fulfilled". From a process design standpoint the author of this thesis defines the social sustainability as " A socially sustainable process is one which is both internally and externally safer, healthier aiming to eliminate short and long term risks by using less hazardous chemicals, smaller inventories and milder process conditions."

Metrics and indicators are vital to convert the sustainability concerns into qualitative and / or quantitative measures. Though often used interchangeably to quantify sustainability, metrics and indicators are quite different from performance goals. According to a document titled "Indicators and Measures of Sustainability", a sustainability indicator can be defined as "observable world changes that indicate progress towards increased sustainability" (Alberta Round Table on the Environment and the Economy, 1993). Tanzil and Beloff (2006) noted that an indicator defines a quantitative measure as well as a narrative description of issues, while metrics refers to "quantitative or semi-quantitative measures."

3.2 Survey of Social Metrics and Indicators

3.2.1 Social Metrics

Atlee and Kirchain (2006) suggested the following characteristics of sustainability metrics which is applicable for social metrics as well.

- Simple and easily accessible by any audience
- Predictive and consistent
- Serve as decision making tool
- Economical efficient: data collection should be easily
- Unbiased
- Applicable to several process

Examples of social metrics are such as reaction temperature, pressure, process inventories, toxicity etc.

3.2.2 Social Indicators

Social indicators measure issues that relate to the health, safety and well-being of the society or community being observed. They target social concerns and address societal benefits over a period of time (Shadiya, 2010a). Examples of social indicators include the following (Anderson et al., 2001):

- Number of health issues as a result of environmental pollutants
- Number of students that are enlightened on environmental issues in an environmental education class
- Number of community members addressing environmental issues such as global warming
- Number of families who are living below the poverty line

Indicators, like metrics, are useful in measuring sustainability progress. Indicators help in explaining sustainability to individuals who might not be very knowledgeable on the subject matter. It can also be used to educate the community on sustainability by linking noticeable progress. With sustainability progress being measured quantitatively, individuals can stay focused and motivated because they are able to see noticeable changes (Shadiya, 2010a).

3.3 Proposed Social Sustainability Metrics and Indicator Systems

A summary of the key social sustainability qualitative and/or quantitative assessment systems that have been proposed by researchers is presented in Table 3.1

Table 3.1: Summary of the Metric, Tools, Indicator and Index Systems

Initiative	Organization/ Year	Brief Description	Inclusion of social sustainability issues	Analysis
The Dow Chemical Exposure Index	AIChE,1998	The index uses a methodology for estimating airborne quantity released	Guide to rating the relative acute health hazard potential of a chemical release to workers and the neighboring community	It evaluates the acute health hazard risk to people from chemical release incidents, and not the long-term effects on workers during normal operation.
CSD Indicators for sustainable Development	UN, 1995	50 core indicators part of a set of 96 indicators. The framework contains 15 themes, which are no longer explicitly categorized into four pillars of sustainable development	Social indicators include (1) Poverty, (2) Governance, (3) Health, (4) Education and (5) Demographics	Not applicable for process sustainability.
Well-being assessment	IUCN –The World Conservation Union and the International Development Research Centre (IDRC), mid 1990s	It is based in the Well-being of Nations survey, introducing the "Egg of Well-being" formed by the Ecosystem Well-being Index (EWI) and Human Well-being Index (HWI)	HWI focuses on (i) health and population (ii) wealth; (iii) knowledge and culture; (iv) Community; (v) Equity. Aggregation uses several techniques (unweighted averages, weighted, and lowest value)	Concept of 'Barometer of sustainability' and sustainability assessment flowchart is significant. May help to choose indicators and performance criteria.
Toxicity Hazard Index	Tyler, Thomas, Doran, and Greig (1996)	Ranks the relative acute toxic hazards of different chemical production units.	Evaluates the toxicity potential of a unit, considering only short-term events and acute effects based on inhalation route of exposure developed.	It deals with acute toxicity alone rather than the overall aspect of health hazards.
UK Scheme	(Maidment, 1998; Brooke, 1998; Russell,	Accounts for effects of chemicals exposure particularly to	The developed model scrutinizes both the intrinsic health hazard of substances used at work as well as	Targeting on existing plants thus making it inconvenient for design stage implementation.

	Maidment, Brooke, & Topping, 1998)	employees, with the ultimate goal of identifying appropriate control strategies	surrogates for exposure potential.	
The INSET Toolkit	INSIDE Project, (2001)	The toolkit incorporates four stages of implementation. Stage 1 involves general screening, Stage 2 deals directly with the ranking and selection of process routes based on the SHE aspects, Stage 3 concerns with process design optimization of the route(s), Finally, the initial process design is developed in Stage 4	For chemical properties, the Health Harm Factor (HHF) is determined from R-phrase and qualitative classification. The Leak Factor (LF) is provided to estimate the fugitive release rate from process equipment and manual activities	The health performance of the routes is evaluated based on the hazardous material properties relating to health effects, the likely fugitive emission rate of that material as well as the chance that people are exposed to this. Aside from being complex, this method requires massive detailed information.
City Development Index	Habitat, 2001	Formed by five indices: Infrastructure, Waste, Health, Education and City Product	Three indices measure aspects of social sustainability, but relevant issues are left out. The overall aggregation considers all the indices to have the same weighting.	Not applicable for process social quantification.
Process Route Healthiness Index (PRHI)	Hassim & Edwards (2006)	The index includes wide range of factors in a single evaluation stage, requires plenty of information	PRHI, the work still serves as the first methodology, formally published in this area	Not suitable for a simple and quick application. It is also inflexible as a result of the data requirements for the application. Index has the disadvantage of indirectly assessing several factors.
Occupational Health Hazard Index (OHHI)	Johnson (2001)	Different factors considered for assessments	Earlier version of the method PRHI	Some factors are evaluated very concisely so that the accuracy is questionable. Some factors are over-

				evaluated requiring excessive data
Mortality Index	Marshall (1977)	Mortality Index =Number of Deaths / Mass of Toxic Substance	Evaluates the fatality of lethal chemical substances	Not directly applicable at process design stage.
Safety and Health Evaluation Tools	Shadiya ,2010	Economic, environmental and social all three are quantified and sustainability measured through the 'SUSTAINABILITY EVALUATOR'	Two categories of metrics are discussed: 1.Process Safety Risks and 2.Health Risks	Disease risk assessment is incorporated in our research. A modified version of the SUSTAINABILITY EVALUATOR is also incorporated.
Inherent Process Safety Index	Heikkila, 1999	Chemical inherent safety index and process inherent safety index.	Only addresses safety concerns. Applicable for assessing the safety of a chemical process at all stages of design	Inherent safety index is incorporated in our research.
Sustainability Indicators	Afgan et al., 2000	Sustainability indicators	Indicator system has limited applications as it has been tailored towards accessing the impact of energy systems.	The assessment formula proposed may be adopted for social quantification. But not much applicable for process social sustainability.
Dow Jones Sustainability Index	Knoepfel, 2001	Sustainability index	Most of the indices are qualitative measures and are not applicable to early stages of design.	Not applicable for process social quantification.
BASF Socio-Eco-efficiency Metrics	Saling et al., 2002; Saling et al., 2005	SEE Balance	Useful in evaluate the impact of products and process during detailed design.	The social metrics presented, pose difficulty in terms of correlation with process design parameters.
IChemE Sustainability Metrics	Tallis, 2002	Sustainability metrics	For the social metrics presented, it is difficult to correlate them with process design parameters. Useful in assessing the sustainability of production processes	Potency Factor Concept for health quantification may be applicable.

Indicators of sustainable production	Krajnc and Glavič, 2003	Social indicators	Too many metrics were suggested and not all of them are applicable to early stages of design. Useful in assessing the sustainability of an operating unit	10 social indicators with quantification is proposed. Strategy may be develop to incorporate them in future research.
Global Environmental Risk Assessment (GERA) Index	Achour et al., 2005	GERA index	Useful in addressing health and safety risks of an operating unit and stream	Not Applicable for process social quantification
BRIDGES to Sustainability Metrics	Tanzil and Beloff, 2006	Sustainability Metrics	Metric categorizes environmental impact of pollution into one metric versus breaking it down into individual concerns such as global warming, acidification	Not Applicable for process social quantification
Three Dimensional Sustainability Metrics	Martins et al., 2007	Sustainability metrics	Two metrics have been presented for environmental impact and health and safety risk, the direct correlation between operating conditions, chemical process risk and environmental impact was not addressed.	Useful in evaluating the sustainability of an industrial process. Determination of Hazard Class proposed in this paper may be used to calculate the safety factors for different chemicals used in the process.
Sustainability Indices	Tugnoli et al., 2008b	Sustainability indices.	Useful in evaluating the sustainability of chemical process alternatives.	Quantitative assessment of the inherent safety during early process design was developed. Not all metrics are applicable to early stages of design.
AIChE Sustainability Index	"AIChE Sustainability Index: Strategic Commitment to Sustainability ," 2008	Sustainability index	Most of the indices are qualitative measures and are not applicable to early stages of design.	Applicable for comparing different companies ‘performance .Not Applicable for process social quantification
Systematic Modular	Othman et al., 2010	1.safety during Operation	Effect of chemical emissions on human	Useful in assessing the impact of a process

Framework		2.operability of the plant 3.safe start-up and shutdown 4. design should meet location specific demands.	health was not presented.	during early stages of design.
Dow Fire and Explosion Hazard Index	Dow, 1987	The Unit Hazard Factor and the Material Factor	1) Quantify the expected damage of potential fire and explosion incidents in realistic terms, 2) identify equipment that would be likely to contribute to the creation or escalation of an incident and 3) communicate the fire and explosion risk potential to management.	They are best suited to later design stages when process equipment, chemical substances and process conditions are known.
The Mond Index	ICI, 1985	The Unit Hazard Factor and the Material and Layout Factor	1) Wider range of processes and storage installations can be studied, 2) covers processing of chemicals having explosive properties, 3) improved hazard consideration for hydrogen, 4) additional special process hazards, 5) toxicity included into the assessment.	Modifications to improve the applicability of Dow method
Hazard and Operability Analysis (Hazop)	Kletz, 1992	Guide words: No, not; more, less; as well as; part of; reverse; other than; sooner, later; other place	Identification of process disturbances with the guide words	Qualitative technique.
Prototype Index of Inherent Safety (PIIS)	Edwards and Lawrence (1993)	Chemical score Process score	Chemical score: inventory, flammability, explosiveness and toxicity Process score: temperature, pressure and yield	This method is very reaction oriented, has some clear advantages over some other numerical indices in early design stages

			Total score: sum of the chemical and process scores	
Hazard Identification and Ranking (HIRA)	Khan and Abbasi (1998).	The fire and explosion damage index and the toxicity damage index Safety Weighted Hazard Index (sWeHI)	A five step procedure has been suggested.	sWeHI accurately and precisely address safety concerns in chemical industry while integrating credits for safety measures that are already in place.
Maximum Credible Rapid Risk Assessment (MAXCRED)	Khan and Abbasi (1999)	Computer software	A number of different risk assessment models for fire, explosion, toxic release and dispersion have been incorporated.	This was developed to show that hazard assessment can prevent safety incidents and provide adequate emergency response
Inherent occupational health assessment during process research and development stage.	M. H. Hassim and M. Hurme. 2010	Index for Physical and Process Hazards(I PPH) and Index for Health Hazards (I HH)	1. Hazard from the chemicals present and the potential for the exposure of Worker to the chemicals 2. Additive type, average-type, and worst case-type index calculations.	A quantitative standard scale for the index is developed to allow health level assessment of a single process. Inherent Occupational Health Index is incorporated in our quantification approach.

Social sustainability metrics, indicators and indices were introduced in this chapter. Although they are useful in tracking progress, not all of them are applicable to early stages of process design. However, the ability to measure social sustainability using indicators or metrics are important because it will assist in comparing processes as well as assessing positive change towards health and safety sustainability over a period of time. It could be used to evaluate alternatives such as technical alternatives e.g. different raw materials and process improvement options and/or business alternatives, for example, different supplier and acquisition options (Shadiya, 2010a). Furthermore, it can identify the means of combining the health and safety consideration along with economic impacts and environmental effects.

One thing to be mentioned is that sense making of social sustainability by quantification is a complex issue. This is because it is difficult to transform social issues into scientific vision (Shadiya, 2010a). As the focus of this research is to develop new metrics and a tool for weighing of process social sustainability, selected metrics and indices adopted by different researchers have been incorporated into the methodology developed.

CHAPTER IV

METHODOLOGY FOR DESIGNING PROCESSES FOR SOCIAL SUSTAINABILITY DURING EARLY DESIGN STAGE.

4.1 Introduction

This chapter describes the methodology that was adopted for this work which incorporates social sustainability at early design stages. For quantification the framework incorporates the novel screening tool, the “SUSTAINABILITY EVALUATOR” (Shadiya, 2010a). As the focus of this research is specifically on the social dimension of sustainability, a modified version of the “SUSTAINABILITY EVALUATOR” tool is developed in this study which identifies social sustainability concerns and evaluates improvements after processes have been optimized.

To design a socially sustainable process, the methodology shown in Figure 4.1 is proposed.

4.2 Simulation of the Base Case Process Model

According to information from the literature the base case process model is simulated. The ASPEN PLUS^{TM} process simulator version 8.1 was used. ASPEN has phase equilibrium data available for regular chemicals, electrolytes, polymers, etc. The database is regularly updated from the National Institute of Standards and Technology

(NIST). To predict phase behavior a solver is included which contains thermodynamic models. Selected process equipment and flow streams can be rigorously sized, tracked, repeated according to designers discretion. Mass and energy balance and other design calculations can be done by using built-in computational modeling tools.

Figure 4.1 Proposed Methodology for Addressing Sustainability Concerns during Early Design Stage

Some of the basic inputs into the simulator are as follows (Samli, 2011):

- Listing possible components in the process.
- Choosing the thermodynamic model representation of the molecular behavior of the fluids.
- Selecting the feed flow rates and initial operating conditions such as the temperature and pressure.
- Identifying the necessary unit operation blocks and their inputs including operating conditions.

The ASPEN process simulator is available at Oklahoma State University and it is useful for sensitivity analysis through sequential-modular(SM) and equation-oriented (EO) strategies. Sensitivity and the optimization block can be defined by an optional FORTRAN statements. In this work ASPEN PLUS will be used to simulate, optimize processes for social sustainability concerns.

4.3 Assessment of the Process Using the Retrofitted SUSTAINABILITY EVALUATOR

In this work the SUSTAINABILITY EVALUATOR (Shadiya, 2010a) is retrofitted for evaluating only the social dimension of sustainability. But it is easily amalgamable with the other two dimensions of sustainability for any future research. The inputs of the Retrofitted SUSTAINABILITY EVALUATOR are the following:

- ➢ Mass and enthalpy of feed inlet
- ➢ Mass and enthalpy of feed outlet
- ➢ Other input flow rate

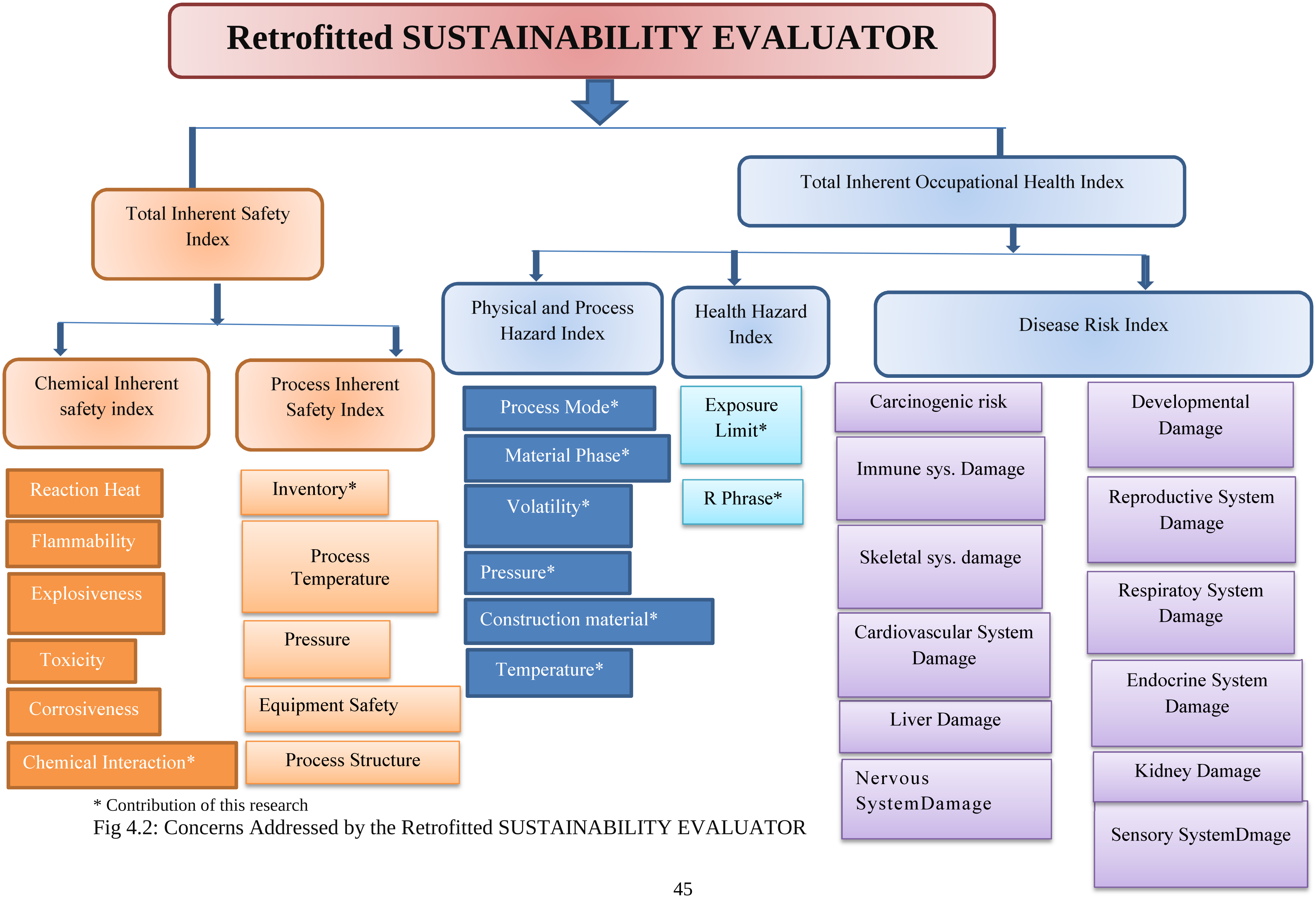
- Energy usage
- Feed flow rate
- Product flow rate
- Waste streams flow rates
- Component flow rate

The outputs from the Retrofitted SUSTAINABILITY EVALUATOR are the following:

- Process safety evaluation: Inherent safety for chemicals, operating conditions, inventories.
- Health evaluation: Occupational health for physical and process hazards, health hazards and disease risk
- Overall social sustainability impact

Health and safety has been an area of concern in industry for several years and researchers have put forth efforts towards quantifying it (Heikkila, 1999; Tugnoli et al., 2008b). In this work, we incorporated the inherent process safety index by Heikkila (1999) for process safety risk evaluation. Inherent occupational health index by Hassim and Hurme (2010) and data from International Agency for Research on Cancer (2009) and Score Card (2005) was adopted for health risks assessment. So in broader perspective, two categories of metrics as listed below are discussed for social quantification:

- Process Safety risks
- Health risks



* Contribution of this research

Fig 4.2: Concerns Addressed by the Retrofitted SUSTAINABILITY EVALUATOR

4.3.1 Process Safety Risk

Total Inherent safety index determines the process safety risks evaluation which can be comprised of the following metrics as shown below:

Table 4.1: Inherent safety index and its subindices (Hurme and Heikkilä, 1998).

Total inherent safety index

a. Chemical inherent safety index	b. Process inherent safety index
1. Subindices for reaction hazards	1. Subindices for process conditions
➢ Heat of the main reaction	# Inventory
➢ Heat of the side reactions	# Process temperature
➢ Chemical interaction	# Process pressure
2. Subindices for hazardous substances	2. Subindices for process system
➢ Flammability	# Equipment
➢ Explosiveness	# Process structure
➢ Toxicity	
➢ Corrosivity	

4.3.1.1 Heat of Main and Side Reaction

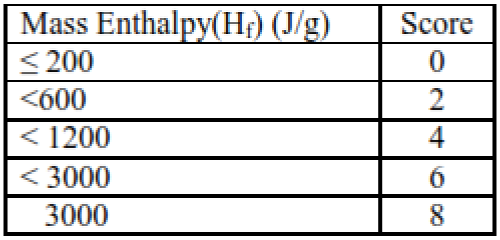
Since the possible violence of reactions lies in the heat liberated and the temperature which may be reached, the energy change during the reaction has been selected to present the reaction safety in the ISI. This is a feasible approach since the formation enthalpies are known for most substances.

The enthalpy released or absorbed in a process can be described by Equation 4.1 for constant volume conditions and an isobaric process. (Heikkila, 1999: Jensen et al., 2003).

$$\Delta H_r = \sum_{\text{products}} (H_f)_{\text{products}} - \sum_{\text{reactants}} (H_f)_{\text{reactants}} \qquad (4.1)$$

The index score ranges from 0-8 with 8 being the worse safety scenario as suggested by Shadiya (2010a)

Table 4.2: Index Score for Heat of Reaction



Mass Enthalpy(H_f) (J/g)	Score
$\leq$ 200	0
<600	2
< 1200	4
< 3000	6
3000	8

4.3.1.2 Chemical Interaction

According to Heikkila (1999) Chemical interaction considers the unwanted reactions of process substances with materials in the plant area. These reactions are not expected to take place in the reactor and therefore they are not discussed in the side reaction subindex. The Inherent Safety Index has utilized EPA's matrix (Hatayama et al., 1980) to classify the hazards of the chemical interaction in a process. The worst interaction that appears between the substances present in the plant area is used in the calculations for the Chemical Inherent Safety Index.

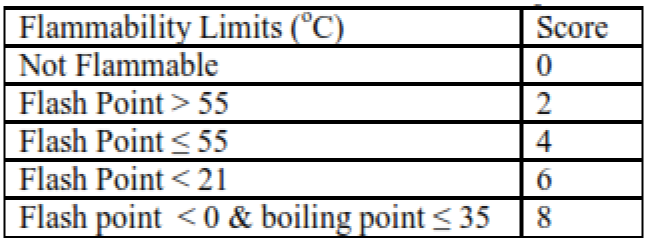
Table 4.3: Index Score for Chemical Interaction (suggested by the author)

Chemical Interaction	Score
Heat formation	2-6
Fire	8
Formation of harmless, nonflammable gas	2
Formation of toxic gas	4-6
Formation of flammable gas	4-6
Explosion	8
Rapid Polymerization	4-6
Soluble toxic chemicals	2

4.3.1.3 Flammability

Flammability measures the potential for chemicals to burn with air in the case of a leakage. The index is measured by their flash points and boiling points. The classification adopted has been obtained from EU Directive (Pyotsia, 1994). The index score is ranges from 0-8 as suggested by Shadiya (2010).

Table 4.4: Index Score for Flammability Index

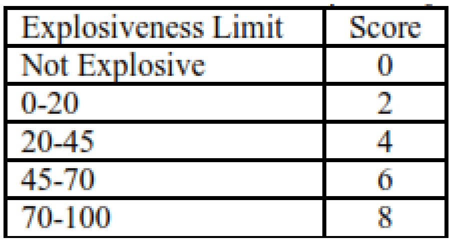


Flammability Limits (°C)	Score
Not Flammable	0
Flash Point > 55	2
Flash Point ≤ 55	4
Flash Point < 21	6
Flash point < 0 & boiling point ≤ 35	8

4.3.1.4 Explosivity

Not directly same as process explosion hazard the metric measures the potential for a gas to form an explosive mixture with air. The explosiveness is determined by the difference between the upper explosive limit (UEL) and lower explosive limit (LEL). Substances with a large explosive limit difference are classified to be more explosive. UEL and LEL for explosive chemicals have been obtained from Crowl and Louvar (1989), material data safety sheets and Dow Fire & Explosive Hazard Classification (American Institute of Chemical Engineers (AIChE), 1994). The index score for this metric as suggested by Shadiya (2010) is shown in Table 4.5.

Table 4.5: Index Score for Explosivity Index

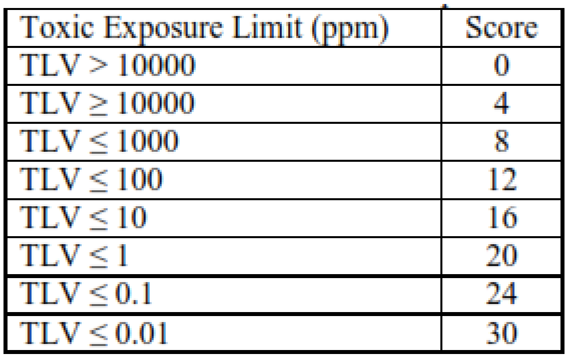


Explosiveness Limit	Score
Not Explosive	0
0-20	2
20-45	4
45-70	6
70-100	8

4.3.1.5 Toxic Exposure

The evaluation of the toxic exposure is based on the Threshold Limit Values (TLV).The lower the TLV value the more harmful the substance is. TLVs can be obtained from the American Conference of Governmental Industrial Hygienists (2009). The index score for this metric as suggested by Shadiya (2010a) is shown in Table 4.6

Table 4.6: Index Score for Toxic Exposure Index

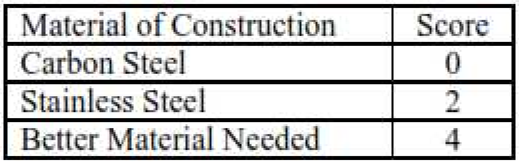


Toxic Exposure Limit (ppm)	Score
TLV > 10000	0
TLV ≥ 10000	4
TLV ≤ 1000	8
TLV ≤ 100	12
TLV ≤ 10	16
TLV ≤ 1	20
TLV ≤ 0.1	24
TLV ≤ 0.01	30

4.3.1.6 Corrosivity

Corrosiveness is determined on the basis of required construction material to resist possibility of corrosion by acids, acid anhydrides and bases. Plant equipment succumb to corrosion can be disastrous leading to toxic exposure due to leakages, explosion and fires. The corrosive index is as suggested by Shadiya (2010a) is shown in the Table 4.7

Table 4.7: Index Score Corrosive Index



Material of Construction	Score
Carbon Steel	0
Stainless Steel	2
Better Material Needed	4

4.3.1.7 Inventory

Any material when present in large quantity may be classified as hazardous (Wells, 1980). The amount of a substance present in the plant (i.e. inventory) has a large effect on the degree of hazard. Potential severity can be reduced by keeping inventories low, by minimizing the reactor size and by avoiding storage of potentially hazardous materials in the synthesis train (CCPS, 1995a). At the conceptual design phase it is practical to base the estimation of inventory on mass flows and an estimated residence time. Therefore the inventory has been included to the safety risk assessment as a mass flow in the ISBL (inside battery limits area) and OSBL (outside battery limits area) equipment including recycles with one hour nominal residence time for each process vessel (e.g. reactor, distillation column etc.).

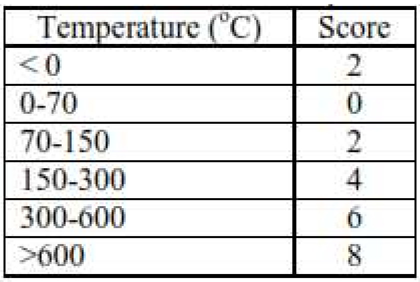
Table 4.8: Index Score for Inventory Index (suggested by the author)

Inventory	Score
0-1 t	0
1-10 t	2
10-50 t	4
50-200 t	6
200-500 t	8
500-1000 t	10

4.3.1.8 Process Temperature

The temperature is a direct measure of the heat energy available at release (Edwards and Lawrence, 1993). The hazard increases in higher temperatures because of the energy content itself and also because the strength of materials becomes weaker in high or very low (cryogenic) temperatures. The index score as suggested by Shadiya (2010a) is shown below.

Table 4.9: Index Score for Temperature Index

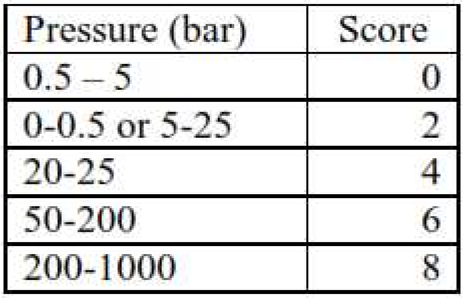


Temperature (^{o}C)	Score
< 0	2
0-70	0
70-150	2
150-300	4
300-600	6
>600	8

4.3.1.9 Process Pressure

Pressure is an indicator which measures the risk associated with the process based on available equipment in a process. Pressure is a very important parameter because high pressure conditions affect leakage rates and vessel strength (Heikkila, 1999). The index score as suggested by Shadiya (2010a) according to the pressure range is shown below.

Table 4.10: Index Score for Pressure Index



Pressure (bar)	Score
0.5 – 5	0
0-0.5 or 5-25	2
20-25	4
50-200	6
200-1000	8

4.3.1.10 Equipment Safety

Equipment safety tries to measure the possibility that a piece of equipment is unsafe (Heikkilä and Hurme, 1998a). Experience base quantitative accident and failure data and information from layout recommendations are the sources of equipment safety evaluation. Equipment safety index is separately measured for inside battery limits area (ISBL) and outside battery limits area (OSBL). The score for both the area equipment safety index evaluation is suggested by the author of this thesis as shown in Table 4.11 and Table 4.12

Table 4.11: Index Score for Equipment Safety Index for ISBL

Types of Equipment	Score
Equipment handling nonflammable, nontoxic materials	0
Heat exchangers, pumps, towers, drums	2
Air coolers, reactors, high hazard pumps	4
Compressors, high hazard reactors	6
Furnaces, fired heaters	8

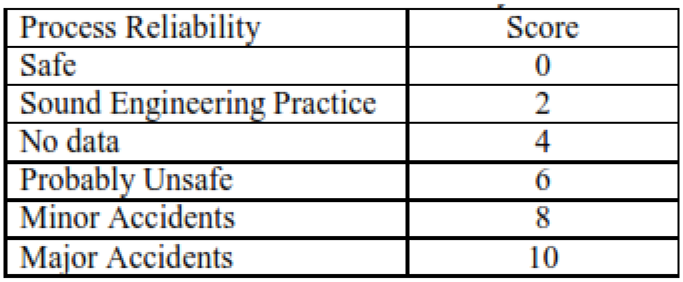
Table 4.12: Index Score for Equipment Safety Index for OSBL

Types of Equipment	Score
Equipment handling nonflammable, nontoxic materials	0
Atmospheric storage tanks, pumps	2
Cooling towers, compressors, blowdown systems, pressurized of refrigerated storage tanks	4
Flares, boilers, furnaces	6

4.3.1.11 Safe Process Structure

The safe process structure describes how well certain unit operations or other process items work together, how they should be connected and controlled together. It also describes how auxiliary systems such as cooling, heating or relief systems should be configured and connected to the main process (Heikkilä et al., 1998).The measurement relies on standards, recommendations and accident reports. The index score as suggested by Shadiya (2010a) is shown in Table 4.13

Table 4.13: Index Score for Safe Process Structure Index



Process Reliability	Score
Safe	0
Sound Engineering Practice	2
No data	4
Probably Unsafe	6
Minor Accidents	8
Major Accidents	10

4.3.2 Health risks

Total Inherent occupational health index determines the process health risks evaluation which can be comprised of the following metrics as shown below:

Table 4.14: Inherent Occupational Health Index and Its subindices

Inherent occupational health index

a. Physical and process hazard index	b. Health hazard index	c. Disease risk index
➢ Mode of Process	* Exposure limit	# Carcinogenic risk
➢ Material phase	* R-phrase	# Developmental damage
➢ Volatility		# Reproductive system damage
➢ Pressure		# Circulatory system damage
➢ Corrosiveness		# Skeletal system damage
➢ Temperature		# Endocrine system damage
		# Gastrointestinal and lever damage
		# Immune system damage
		# Kidney damage
		# Skeletal system damage
		# Nervous system damage
		# Respiratory system damage
		# Sensory system damage

4.3.2.1 Physical and Process Hazard

The physical and process hazard index measures the possibility of chemical exposure for workers. Materials’ physical properties and the operating conditions express this exposure potential. The metrics are adopted from Hassim and Hurme (2010) and the scores suggested for this research is shown in Table 4.15.

4.3.2.1.1 Process Operation Mode

Workplace exposure is affected by process operation mode. Batch processes appeared to be the most hazardous operation because it usually requires more frequent manual operations, higher number of employees, frequent start-up and shutdown and maintenance works, extra equipment strain and has the tendency to produce more fugitive emissions (Hassim and Hurme, 2010). So batch process is given the highest penalty.

4.3.2.1.2 Material Phase

A chemical's phase affects the frequency and types of exposure. The highest penalty is assigned to solid materials because while transportation and processing, solids have a higher trend of exposure compared to liquid and gas.

4.3.2.1.3 Volatility

Volatility is characterized in this index approach as atmospheric boiling point. Lower boiling point liquids and smaller sized particles are given higher penalty due to their higher exposure. The score formation has followed the criteria described by COSHH Essentials (Maidment, 1998).

4.3.2.1.4 Pressure

A higher pressure is risky for chemical exposure due to fugitive emissions through leakages and also hazardous for workers when engage in maintenance operation. The penalty range is mainly incorporated from the Inherent Safety Index by Heikkila (1999).

Table 4.15 Index Score for Physical and Process Hazards Index

Factor	Score Information	Score
Mode of process	Continuous with recycle	2
	Continuous	4
	Semi-continuous/semi-batch	6
	Batch	8
Material phase	Gas	2
	Liquid	4
	Solid	6
Volatility	liquid and gas	
	Very low volatility(bp>150°C)	0
	Low(150°C≥bp>50°C)	2
	Medium(50°C≥bp>0°C)	4
	High (bp<0°C)	6
	Solid	
	Non-dusty solids	0
	Pellet-like, nonfriable solids	2
	Crystalline, granular solids	4
	Fine, light powders	6
Pressure(bar)	.5-5	0
	5 - 50.0	2
	50-200	4
	>200	6
Corrosiveness-based on construction material	Carbon steel	0
	Stainless steel	2
	Better material	4
Temperature(°C)	<70	0
	70-150	2
	150-200	4
	>200	6

4.3.2.1.5 Corrosion

Chemical releases and exposure in workplaces are common phenomena. Following the similar classification used by Heikkila (1999), a chemical is regarded as highly corrosive if it requires a material better than stainless steel for either its processing or transportation.

4.3.2.1.6 Temperature

Temperature indicates the heat energy of the system. Increased heat energy increases the trend of fugitive emission through enhanced vaporization. Higher temperature also increases the possibility of accidental burns. Burns are damage to skin and the underlying tissue caused by heat, chemicals and electricity. The temperature penalty range is formed based on the occurrence of first, second and third degree burns. Here two causes of burns are considered, which are due to steam and surface contact (Hassim and Hurme, 2010). The score criteria is formed based on steam exposure event (Lawton & Laired, 2003: Ng and Chua, 2002: Encyclopedia of Human Biology, 1997).

4.3.2.2 Health Hazard

The health hazard index characterizes the health impacts and dangers of exposure. Exposure limit based subindex gives information on the chronic hazards of the chemicals in the working air The R-phrase based subindex on the other hand, describes the types of health effect that might be caused by the chemical (Hassim and Hurme,2010). The metrics are adopted from Hassim and Hurme (2010) and the scores are suggested in his research.

4.3.2.2.1 Occupational Exposure Limit

The Occupational Exposure Limit (OEL) is a health-based standard that are established following a rigorous evaluation of the available toxicological data (Brooke, 1998). The exposure limit based on the 8-h daily exposure time is used for the evaluation. The lower the OEL value of a substance, the harmful it is to human health. Occupational Exposure Limit set by the UK Health and Safety Commission is adopted for chronic toxic exposure evaluation. The exposure limits classification for solid and gas are based on COSHH Essentials (Maidment, 1998; Brooke, 1998; Russell et al., 1998 and Mond Index (ICI, 1985)).

4.3.2.2.2 R-Phrases

The European Union R-phrases describe the human health risk associated with the chemicals (Risk Phrases2001). Acute and chronic toxicity are the two groups of R-phrases based on the severity of adverse health effects. Chemicals with a chronic toxicity effect have a higher range of penalty because of its more problematic nature. The R-phrases have an advantage of being readily available to users at early phase of process development (Hassim and Hurme, 2010).

4.3.2.3 Disease Risk

This index measures the possibility of chemical exposure possessing risk of selected diseases for workers.The metrics and scores are adopted from Shadiya (2010a). To calculate the impact of the metric the index value is multiplied by the amount of the substances emitted.

Impact value for disease metrics = (index value) x (amount of emitted substance).

Table 4.16: Index Score for Health Hazard Index

Factor	Score Information	Score
Exposure limit	Vapor(ppm)	
	OEL>1000	0
	OEL≤1000	2
	OEL≤100	4
	OEL≤10	6
	OEL≤1	8
	Solid(mg/m^3)	
	OEL>10	0
	OEL≤10	2
	OEL≤1	4
	OEL≤.1	6
	OEL≤.01	8
R-Phrase		
	Acute	
	No acute toxicity effect	0
	R36.R37,R38,R67	2
	R20.R21,R22,R65	4
	R23, R24,R25, R29,R31,R41,R42,R43	6
	R26, R27,R28,R32,R34,R35	8
	Chronic	
	No chronic toxicity effect	0
	R66	2
	R33,R68/20/21/22	4
	R62,R63,R3/23/24/25,R48/20/21/22	6
	R40,R60,R61,R64,R39/26/27/28,R48/23/24/25	8
	R45,R46,R49	10

4.3.2.3.1 Carcinogenic risk

Carcinogenic risk index is a measurement of the carcinogenic risk for the workers of a process based on chemicals present in the process. There are four major classification carcinogenic chemicals (International Agency for Research on Cancer, 2009):

1. Carcinogenic to humans
2. Probably carcinogenic to humans
3. Possibly carcinogenic to humans
4. Carcinogenic to animals but not humans and probably not carcinogenic to humans

The index value as suggested by Shadiya (2010) is shown in Table 4.17.Impact value is calculated as:

Impact value for carcinogenic risks = (index value) x (amount of emitted substance).

Table 4.17: Index Score for Carcinogenic risk

Types of Carcinogen	Group	Score
Not Carcinogenic	N/A	0
Probably not carcinogenic to humans	4	0.2
Not classifiable as to its carcinogenicity to humans	3	0.4
Possibly carcinogenic	2B	0.6
Probably carcinogenic to humans	2A	0.8
Carcinogenic to humans	1	1

4.3.2.3.2 Developmental System Risk

The developmental risk index measures the eexposure risks to a developing child in its mother’s womb. Birth defects, low birth weight, biological dysfunctions, psychological or behavioral deficit and even brain damage may be the effects in development. Lists of known and suspected developmental toxicants and the respective index value of 0.6 and 1 was selected as suggested by Shadiya (2010a). The logic behind this is to keep harmony while comparing with the suspected and known carcinogens (Shadiya, 2010a). The impact value is calculated as:

Impact value for Developmental risks = (index value) x (amount of emitted substance).

4.3.2.3.3 Reproductive System Risk

The reproductive risk index measures the reproductive toxicants exposure risk to an adult's reproductive system. Abnormal sexual behavior, decreases in fertility, loss of fetus during pregnancy etc. are the typical reproductive system problems that may arise. Lists of known and suspected reproductive toxicants and the respective index value of 0.6 and 1 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected and known carcinogens (Shadiya, 2010a). The impact value is calculated as:

Impact value for reproductive risks = (index value) x (amount of emitted substance).

4.3.2.3.4 Circulatory System Damage Risk

This risk index measures the cardiovascular toxicants exposure to an adult's circulatory system. Hypertension, arteriosclerosis, cardiac arrhythmia, and decreased coronary ischemia are the typical cardiovascular system problems that may arise. . Lists of suspected reproductive toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for circulatory system damage risks = (index value) x (amount of emitted substance).

4.3.2.3.5 Endocrine System Damage Risk

This risk index measures the endocrine toxicants exposure to an adult's endocrine system. Hypothyroidism, diabetes mellitus, hypoglycemia, reproductive disorders, and cancer are the typical endocrine system problem that may arise. Lists of suspected endocrine toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for endocrine system damage risks = (index value) x (amount of emitted substance).

4.3.2.3.6 Gastrointestinal and Liver Damage Risk

This risk index measures the toxicants exposure to an adult's gastrointestinal tract, liver, or gall bladder. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. Impact value is calculated as:

Impact value for Gastrointestinal and Lever damage risks = (index value) x (amount of emitted substance).

4.3.2.3.7 Immune System Damage Risk

This risk index measures the immunotoxicants exposure and subsequent risk of infectious diseases and cancer to an adult's immune system. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya

(2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for immune system damage risk = (index value) x (amount of emitted substance).

4.3.2.3.8 Kidney Damage Risk

This risk index measures the toxic exposure to an adult's kidney, uterus and bladder. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for kidney damage risks = (index value) x (amount of emitted substance).

4.3.2.3.9 Skeletal System Damage Risk

This risk index measures the toxic exposure to an adult's bones, muscles and joints. Arthritis, fluorosis and osteomalacia are the typical skeletal system problem that may arise. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for skeletal system damage risks = (index value) x (amount of emitted substance).

4.3.2.3.10 Nervous System Damage Risk

This risk index measures the toxic exposure to an adult's nervous system. Confusion, fatigue, irritability, brain damage and loss of coordination are the typical skeletal system problem that may arise. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for nervous system damage risks = (index value) x (amount of emitted substance).

4.3.2.3.11 Respiratory System Damage Risk

This risk index measures the toxicants exposure to an adult's nasal passages, pharynx, trachea, bronchi, and lungs. Acute and pulmonary edema, irritation, bronchitis irritations, emphysema and cancer are the typical respiratory system problem that may arise. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for respiratory system damage risks = (index value) x (amount of emitted substance).

4.3.2.3.12 Skin and Sensory Organ Damage Risk

This risk index measures the toxic exposure to an adult's skin or sensory organ. Hearing losses, sense of smell, eye irritations etc. are the typical sensory organ damage problem that may arise. Lists of suspected toxicants and the respective index value of 0.6 was selected as suggested by Shadiya (2010a). The logic behind is to keep harmony while comparing with the suspected carcinogens. The impact value is calculated as:

Impact value for skin and sensory system damage risk = (index value) x (amount of emitted substance).

4.4 Sensitivity Analysis

Sensitivity analysis is the investigation of effect on a certain targeted objective or goal by changing the variation of variable parameters. These variables can be of two types-independent and dependent variables. As the goal of this research is to find the most socially sustainable option so the health and safety metrics are the dependent variable and mass flow rate, reactor temperature and pressure, number of stages in separation columns, reflux ratio etc. are the independent variables.

After conducting sensitivity analysis and significant variables being found reconfiguration needs to be carried out. Process reconfiguration is not process specific and can include a wide range of activities which include the following (Shadiya, 2010a):

- Incorporating recycle streams
- Adding additional separation equipment
- Including energy efficient technology to the process
- Improving the efficiency of the reactions by considering alternative reaction synthesis

- Modifying reactor operating conditions to improve conversion and reduce the production of by products
- Changing separator mechanics such as reflux ratio

4.5 Process Optimization

Optimization of the process was carried out in ASPEN PLUS process simulator. Optimization block, similar to sensitivity analysis is a ‘Model Analysis Tool’ that is available for finding optimum process operating conditions. The objective function in this case is maximizing production of desired chemicals and minimizing wastes by varying parameters on a certain range while operating as sustainable safe conditions. Unlike the sensitivity analysis, the built-in ASPEN PLUS optimization may have multiple varying parameters included to determine the optimal point of all varying conditions (Samli, 2011).

4.6 Re-evaluate Social Sustainability Using the Retrofitted Sustainability Evaluator

After optimization is done the newly optimized process is re-evaluated using the Retrofitted SUSTAINABILITY EVALUATOR. If the overall social sustainability is obtained with a low impact value, the optimized process can be accepted. Otherwise, if a high impact value is measured indicating the process not socially sustainable, the user may choose to reconfigure the process based on the results of sensitivity analysis. Than the decision maker needs to re-optimize the process and re-evaluate the social sustainability. The user must keep re-optimizing the process until an overall satisfactory solution is finalized.

4.7 Summary

In this chapter, a novel methodology proposed for this research was presented. The proposed social quantification methodology is novel for two reasons. The first is that impact assessments can be evaluated by one tool making it easier for engineers to see how process improvements affect social sustainability of a process. Secondly a holistic incorporation of social metrics, i.e. both occupational health and inherent safety metrics for the same process is quite new as many researchers don't incorporate both the aspects of social dimension applicable at the early design stage. Also, a framework which is useful in identifying and improving social sustainability concerns was discussed. The approach proposed can be summarized as follows:

- Simulate the process in Aspen Plus process simulator.
- Evaluate social sustainability of the simulated base case process using the retrofitted SUSTAINABILITY EVALUATOR.
- Conduct sensitivity analysis on the base case process to determine the parameters affecting the objective.
- Formulate the objective function.
- Optimize the process based on the parameters ranges from the sensitivity analysis
- Re-evaluate the social impact using the retrofitted SUSTAINABILITY EVALUATOR.
- Accept the social sustainability results or reconfigure the process and repeat the process until satisfying result is obtained.

The proposed methodology is implemented and demonstrated on two case studies presented in the next section.

CHAPTER V

DEMONSTRATION OF THE PROPOSED METHODOLOGY

The previous chapter explained the methodology incorporated in this research. This methodology is useful in quantifying social dimension of sustainability at early design stage. In this chapter the applicability of the tool will be discussed for two case studies. First, efficacy of the retrofitted SUSTAINABILITY EVALUATOR tool and the testing of overall methodology were demonstrated for the acrylonitrile process. Second, the usability of the evaluator tool to select the most socially sustainable process option by comparing two process alternatives for the dimethyl ether (DME) production is examined.

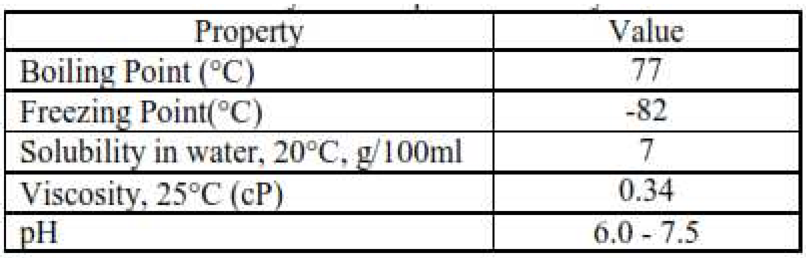
5.1 Case Study: Acrylonitrile Production Process

Acrylonitrile with the formula C_3H_3N is a colorless liquid with a slightly sharp, irritating odor. The chemical is a monomer used in the synthesis of those polymers which are utilized in the manufacturing of polyacrylonitrile, acrylic fibers, rubber and nylons. It is also acts as an intermediate in the manufacture of adiponitrile and acrylamide. The physical properties are shown in the following table 5.1.

Acrylonitrile is considered one of the top 50 highest volume chemicals produced in the United States (Kanuri, 2000; Fechter et al., 2004). Although synthesis from the acetylene hydrocyanation is an option, it is mainly produced by the BP America Sohio

Process. The Sohio Process involves a catalytic ammoxidation of propylyne. The production of acrylonitrile results in several toxic waste streams and byproducts such as acetonitrile, acrolein, carbon monoxide and hydrogen cyanide.

Table 5.1: Physical Properties of Acrylonitrile (Shadiya, 2010a)



Property	Value
Boiling Point (°C)	77
Freezing Point(°C)	-82
Solubility in water, 20°C, g/100ml	7
Viscosity, 25°C (cP)	0.34
pH	6.0 - 7.5

Acrylonitrile is listed in the toxic release inventory compiled by the Environmental Protection Agency, as one on the top toxic chemicals (United States Environmental Protection Agency, 2009). Presence of tremendous toxic waste streams which possess threat to the human health and safety eventually makes the acrylonitrile production as an excellent manufacturing process to demonstrate the proposed methodology. Contamination of water via hazardous waste sites and occupational exposure has caused human exposure to acrylonitrile.

Acrylonitrile is highly flammable and undergoes explosive polymerization if exposed to light(Reed Business Information Limited, 2010). The burning material releases fumes of hydrogen cyanide and oxides of nitrogen. Acrylonitrile is classified as a Class 2B carcinogen (possibly carcinogenic) and other health problems such as nervous system damage, kidney damage etc. are linked to it. Handling the waste stream in a sustainable manner to minimize human exposure is a challenge. The methodology discussed in Chapter IV are delineated in Figure 5.1 which is the application towards handling the sustainibility concerns of the acrylonitrile process.

- **ACRYLONITRILE BASE CASE PROCESS MODELING**
- Collection of input data from literature
- Simulate process on a process simulator e.g. Aspen Plus

- **SUSTAINABILITY ASSESSMENT OF THE BASE CASE USING THE "RETROFITTED SUSTAINABILITY EVALUATOR"**

- **SENSITIVITY ANALYSIS OF THE ACRYLONITRILE PROCESS**
- Identify process parameters that affect process sustainability
- Re-configuring process structure

- **OPTIMIZE PROCESS BASED ON THE RESULT OF THE SENSITIVITY ANALYSIS**
- By minimizing health and safety concerns

- **EVALUATE THE SUSTAINABILITY OF THE OPTIMIZED ACRYLONITRILE PROCESS USING THE "RETROFITTED SUSTAINABILITY EVALUATOR"**
- If the design is acceptable move to step 6, otherwise repeat step 5

- **IF PROCESS IS SUSTAINABLE BASED ON STEP 5, ACCEPT DESIGN OTHERWISE REPEAT STEP 4**

Figure5.1: Proposed Methodology for Addressing Social Sustainability Concerns of the Acrylonitrile Process

5.1.1 Acrylonitrile Base Case Process Modeling

The acrylonitrile base case is modeled based on literature data (Venkataraman, 1996; de Haes et al., 1999; Kanuri, 2000). The information compiled from literature is simulated in ASPEN PLUS version 8.1 using the Electrolyte Non-Random Two Liquid model with Redlich-Kwong (ELECNRTL) thermodynamic package. The ELECNRTL-RK option which provides an improved implementation for aqueous electrolytes is based on the traditional unsymmetrical reference state, e.g., aqueous phase infinite dilution. As the acrylonitrile production reaction is an aqueous electrolyte system, so the chosen model can predict the simulation results with greater accuracy.

The block flow diagram and the schematic for this process are shown in Figure 5.2 and Figure B1 (APPENDIX B) respectively. The ASPEN PLUS input file is shown in APPENDIX A.

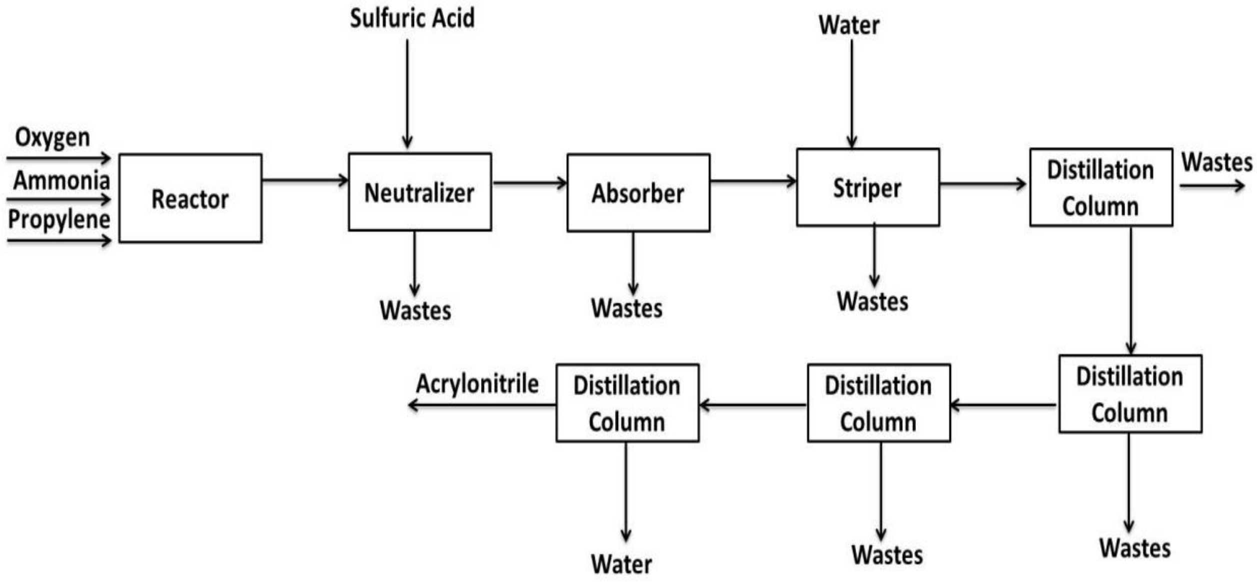


Figure 5.2: Block Flow Diagram for the Base Case Acrylonitrile Process

The production process can be divided into two sections namely propane ammoxidation and acrylonitrile separation. In the propane ammoxidation step, ammonia, propane and oxygen at 14 psia and 80^o F are fed to a mixer (M-301), which combines the three streams into one stream. The mixture is sent to R-301, a plug flow reactor (PFR). The PFR is operated at 852^o F and 28.9 psia. Propylene and ammonia are reacted with oxygen to produce acrylonitrile in the PFR. Although, acrylonitrile is synthesized as shown in Equation 5.1 in this reactor, several side reactions take place resulting in other by products (acetonitrile, acrolein, carbon dioxide, carbon monoxide and hydrogen cyanide) as shown in Equations 5.1-5.6.The kinetics or the reactions taking place in the reactor is presented in Table 5.3 and the rate constant are presented in Equation 5.8-5.13

$$C_3H_6 + NH3 + 3/2\ O_2 \longrightarrow C_3H_3N + 3H_2O \tag{5.1}$$

Propylene Ammonia Oxygen Acrylonitrile Water

$$C_3H_6 + O_2 \longrightarrow C_3H_4O + H_2O \tag{5.2}$$

Propylene Acrolein

$$C_3H_6 + NH_3 + 9/4\ O_2 \longrightarrow CH_3CN + ½\ CO + ½\ CO_2 + 3H_2O \tag{5.3}$$

Acrylonitrile

$$C_3H_4O + NH_3 + ½\ O_2 \longrightarrow C_3H_3N + 2H_2O \tag{5.4}$$

$$C_3H_3N + 2O_2 \longrightarrow CO_2 + CO + HCN + H_2O \tag{5.5}$$

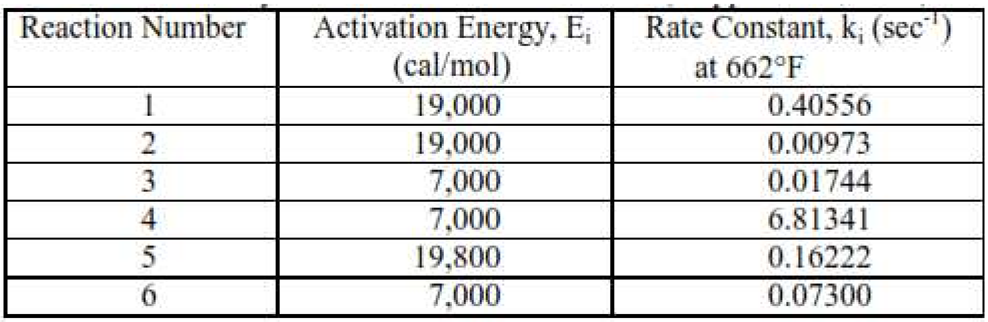
$$CH_3CN + 3/2\ O_2 \longrightarrow CO_2 + HCN + H_2O \tag{5.6}$$

After the reaction process, a sulfuric acid stream at 80 ^{o} F and 14.7 psia is introduced and sent along with the reacted mixture to another mixer (M-302). Next the separation of acrylonitrile from byproducts and the un-reacted raw materials occurs. First the mixture is sent to a neutralizer (R-302), where ammonia reacts with sulfuric acid and ammonium sulfate is produced as shown in Equation 5.7. This reaction aids in the removal of un-reacted ammonia. Next the steam exiting the neutralizer is sent to a separator (T-301) where the ammonium sulfate and sulfuric acid are separated from the mixture as the bottoms of the separator.

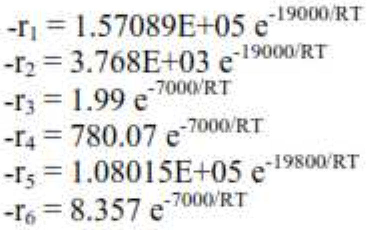
$$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{5.7}$$

Ammonium Sulphate

Table 5.3: Acrylonitrile Process Kinetic Data (Hopper et al., 1993)



Reaction Number	Activation Energy, E_i (cal/mol)	Rate Constant, k_i (sec^{-1}) at 662°F
1	19,000	0.40556
2	19,000	0.00973
3	7,000	0.01744
4	7,000	6.81341
5	19,800	0.16222
6	7,000	0.07300



$$-r_1 = 1.57089E{+}05\ e^{-19000/RT} \quad (5.8)$$
$$-r_2 = 3.768E{+}03\ e^{-19000/RT} \quad (5.9)$$
$$-r_3 = 1.99\ e^{-7000/RT} \quad (5.10)$$
$$-r_4 = 780.07\ e^{-7000/RT} \quad (5.11)$$
$$-r_5 = 1.08015E{+}05\ e^{-19800/RT} \quad (5.12)$$
$$-r_6 = 8.357\ e^{-7000/RT} \quad (5.13)$$

The un-separated distillate stream is cooled via a cooler (E-301) to 40 psia and a water stream operating at 161^{o} F and 20 ^{o} F and are sent to an absorber (T-302), where carbon monoxide, propylene and oxygen are separated as the distillate stream and aqueous solution of acrylonitrile, acetonitrile and hydrocyanic acid are present in the bottoms of the distillation column. The bottoms stream is heated by heat exchanger E-202 to 173^{o} F and 15 psia. The heated stream is sent to a stripper (T-303) where excess water is removed from the nitrile mixture. The nitrile mixture is cooled to 126 ^{o} F 14.7 psia by heat exchanger E-303. The heated stream is sent to two distillation columns (T-304 and T-305) where waste hydrocyanic acid and acrolein are removed. Finally in the last column (T-306), acrylonitrile is separated from acetonitrile. The schematic for this process, the equipment specification and stream summary tables are presented in Figure B1, Table B5 and Table B6 respectively in APPENDIX B.

5.1.2 Social Sustainability Assessment of the Acrylonitrile Base Case

For social quantification of acrylonitrile process both health and safety aspects are measured. For the safety assessment, the operating conditions, chemicals present and equipment present are selected in the input section of the software. Also, the mass enthalpy is entered to estimate the heat of reaction index (Shadiya, 2010a).The result of the safety assessment is presented in Table 5.4. The overall total inherent safety index for this process was around 90.The maximum overall safety index i.e. the worst case scenario for any process is 126.

Table 5.4: Safety Assessment Results from the SUSTAINABILITY EVALUATOR for the Base Case Acrylonitrile Process

Safety Assessment	Results	Maximum
Heat of main reaction index	8	8
Heat of side reaction index	6	8
Chemical interaction	8	8
Flammability index	8	8
Explosiveness index	6	8
Toxic Exposure Index	24	30
Corrosiveness index	4	6
Temperature index	6	8
Pressure index	2	8
inventory index	4	8
Equipment safety index,ISBL	4	8
Equipment safety index,OSBL	2	8
Safety Level of Process Structure index	8	10
Total Inherent Safety index	90	126

For health risk assessment, the physical and process hazard index and health hazard index both are measured based on the primary and side reactions of the process. The result of the health risk assessment is presented in Table 5.5. The overall total inherent safety index for this process was around 236.

Table 5.5: Health Assessment Results from the SUSTAINABILITY EVALUATOR for the Base Case Acrylonitrile Process

Reaction No.	Physical and process hazard index Ipph	Health hazard Index Ihh	Occupational health index	Maximum value
1	16	14	34	63%
2	16	16	36	67%
3	16	12	32	59%
4	16	16	36	67%
5	16	16	36	67%
6	16	14	34	63%
7	12	12	28	52%
Total			236	

Table 5.6: Disease Risk Assessment Results from the Retrofitted SUSTAINABILITY EVALUATOR for the Base Case Acrylonitrile Process

Impact Category	Impact Value (Tonns/year)	Chemicals Present
Carcinogenic Risk	105.0516	Acrolein & Acrylonitrile
Immune Sys. Damage	104.5743	Acrylonitrile
Skeletal System Damage	123.6061	Sulfuric Acid
Developmental Damage	3815.2679	Acrolein, Acetonitrile, Acrylonitrile, Ammonia, Carbon Dioxide &Carbon Monoxide
Reproductive System Damage	4056.2843	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Dioxide, Carbon Monoxide & Hydrogen Cyanide
Kidney Damage	104.5743	Acrylonitrile
Respiratory System Damage	9654.0008	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Dioxide, Carbon Monoxide, Hydrogen Cyanide, propylene, Sulfuric acid & Ammonium Sulphate
Cardiovascular System Damage	2198.7899	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Monoxide & Hydrogen Cyanide
Endocrine System Damage	960.1273	Acrylonitrile

Liver Damage	4395.6041	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Hydrogen Cyanide, Propylene, Sulfuric acid & Ammonium Sulphate
Nervous System Damage	7349.0786	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Dioxide, Carbon Monoxide, Hydrogen Cyanide & Ammonium Sulphate
Sensory System Damage	1179.665	Acrolein, Acrylonitrile & Ammonia

5.1.3 Acrylonitrile Base Case Sensitivity Analysis

To optimize the acrylonitrile process after base case impacts have been measured, we need to figure out the parameters that affect the selected social metrics. Sensitivity analysis was carried out using ASPEN PLUS with the operating conditions, variation of inlet flow-rates and equipment configuration as the direct variables to study the effect on acrylonitrile mass flow rate, propylene conversion, and total waste produced as the dependent variable.

5.1.3.1 Effect of Varying Inlet Flow rates

Propylene, ammonia and oxygen are the key raw materials involved in the manufacture of acrylonitrile. Literature data recommends using the following feed ratio range (Venkataraman, 1996; Kanuri, 2000):

- Propylene / Ammonia: 1-2
- Oxygen / Propylene: 0.5-3

Since this was a range, it was therefore important to investigate how varying the feed ratio affected acrylonitrile production rate and total waste. The inlet feed flow rate were varied as listed below:

- Ammonia: 60 -120 lbmole/hr

- Oxygen: 60-180 lbmole/hr
- Propylene: 60-120 lbmole/hr

The total number of runs for this analysis was 1376 runs and the results of the 20 best scenarios are presented in Table 5.7. These runs were selected because they had the lowest waste production with threshold acrynlonitrile production of 46 lbmol/hr and threshold material value added value of $10M. The best case scenario, case 1 has a total waste of $1131.42 lb-mol/hr.

Table 5.7: Results of Top 20 cases for Sensitivity Analysis of Varying Feed Ratio

Ammonia flow rate lb-mol/hr	oxygen flowrate lb-mol/hr	propylene flowrate lb-mol/hr	Total waste lb-mol/hr	Annual Material Value added $MM	Oxygen/ propylene feed ratio	propylene/ ammonia feed ratio
65	125	105	1131.42	22.15	1.19	1.62
70	140	90	1387.80	23.61	1.56	1.29
65	125	75	1656.00	23.72	1.67	1.15
115	125	75	1798.91	13.02	1.67	0.65
120	125	75	1803.45	11.58	1.67	0.63
105	125	75	1816.54	15.90	1.67	0.71
110	125	75	1937.93	15.96	1.67	0.68
70	140	75	1949.77	25.19	1.87	1.07
120	140	75	2102.19	13.18	1.87	0.63
65	125	120	2137.69	22.42	1.04	1.85
70	140	120	2188.47	23.18	1.17	1.71
115	140	75	2193.51	15.07	1.87	0.65
75	130	70	2207.05	26.27	1.86	0.93
105	140	75	2234.72	18.08	1.87	0.71
100	140	75	2284.70	20.01	1.87	0.75
110	140	75	2326.09	18.12	1.87	0.68
95	140	75	2346.54	22.08	1.87	0.79

90	140	75	2371.37	24.38	1.87	0.83
70	140	105	2429.99	23.55	1.33	1.50
65	125	90	2439.21	22.89	1.39	1.38

5.1.3.2 Effect of Varying Plug Flow Reactor Temperature

The reactor temperature was studied to investigate how variations of it affected propylene conversion and acrylonitrile production. The higher the conversion, the lower waste produced and the higher the acrylonitrile production value would be. According to literature, typical reactor temperature range for the acrylonitrile process ranges from 600-1111°F (Kanuri, 2000). Therefore, the reactor temperature was varied at that range as shown in Figure 5.3. As the reactor temperature is varied, propylene conversion increases as well as acrylonitrile formation. However, after 860° F, the increase in both parameters comes to a halt, there by resulting in the conclusion that the optimum temperature range is from 800-860°F, where a maximum conversion of 74.5% is attained.

5.1.3.3 Effects of Varying Plug Flow Reactor Pressure

The reactor pressure was studied to investigate how variations of it affected propylene conversion. According to literature, typical reactor pressure range for the acrylonitrile production process ranges from 5-45 psia (Venkataraman, 1996; Kanuri, 2000). Therefore, the reactor pressure was varied at that range as shown in Figure 5.4.

As the reactor pressure is varied, it can be concluded that conversion of propylene to acrylonitrile increases. However, 15 psia is the recommended operating pressure as a maximum conversion of 74% was attained.

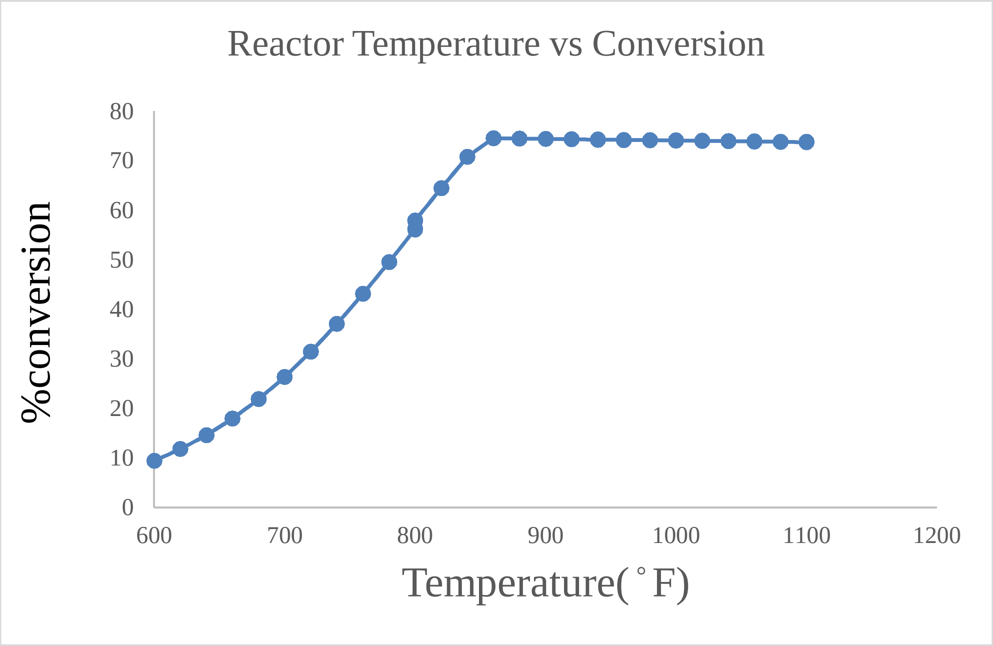


Figure 5.3: Effect of Plug Flow Reactor Temperature on Conversion

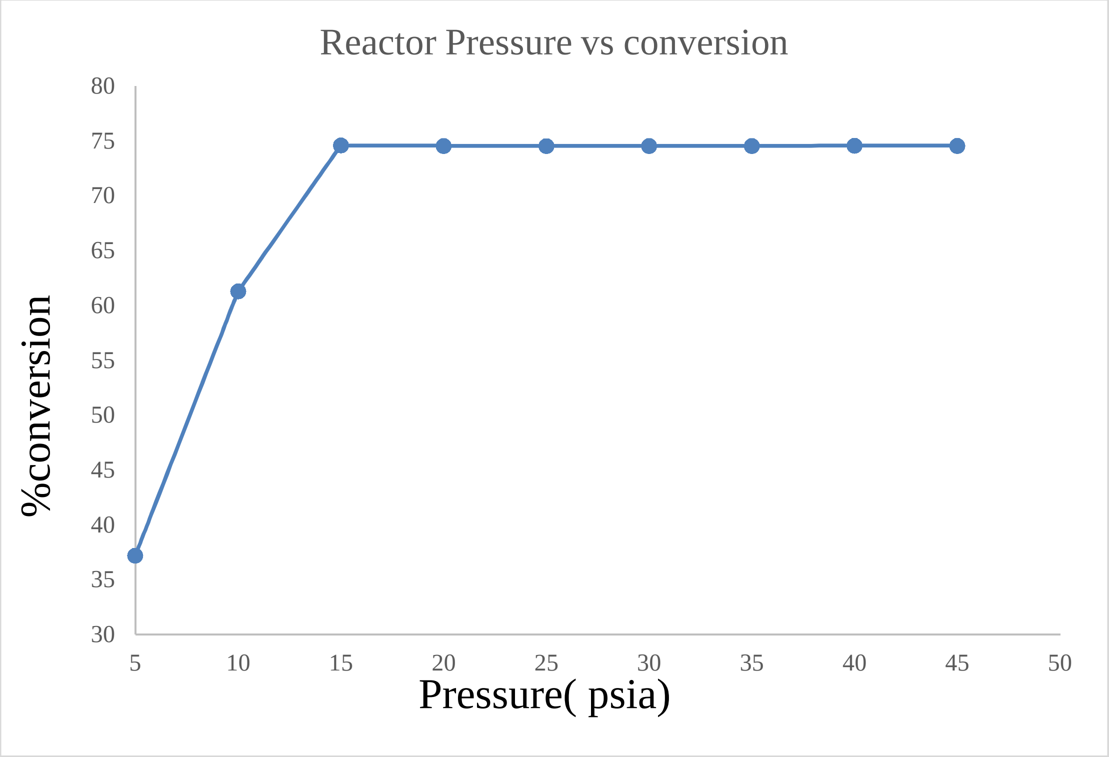


Figure 5.4: Effect of Plug flow Reactor Pressure on Conversion

5.1.3.4 Effect of Varying Plug Flow Reactor Length and Diameter on Conversion

The reactor length is varied from 3-30ft as shown in Figure 6.18. At first, conversion increases from 32-74.5% the length is varied from 0 -18ft but after 12ft, the conversion remains constant even when the length is increased. The reactor diameter is also varied from 0.2-3ft. As shown in Figure 6.19, as reactor diameter is increased conversion increases until 2.2 ft where the maximum conversion is attained.

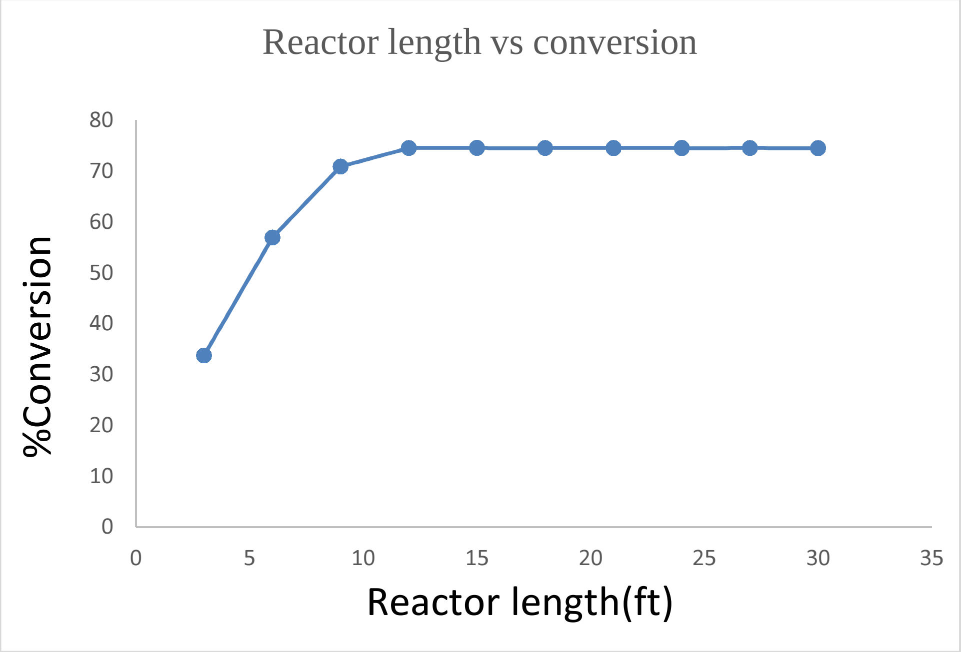


Figure 5.5: Effect of Plug Flow Reactor Length on Conversion

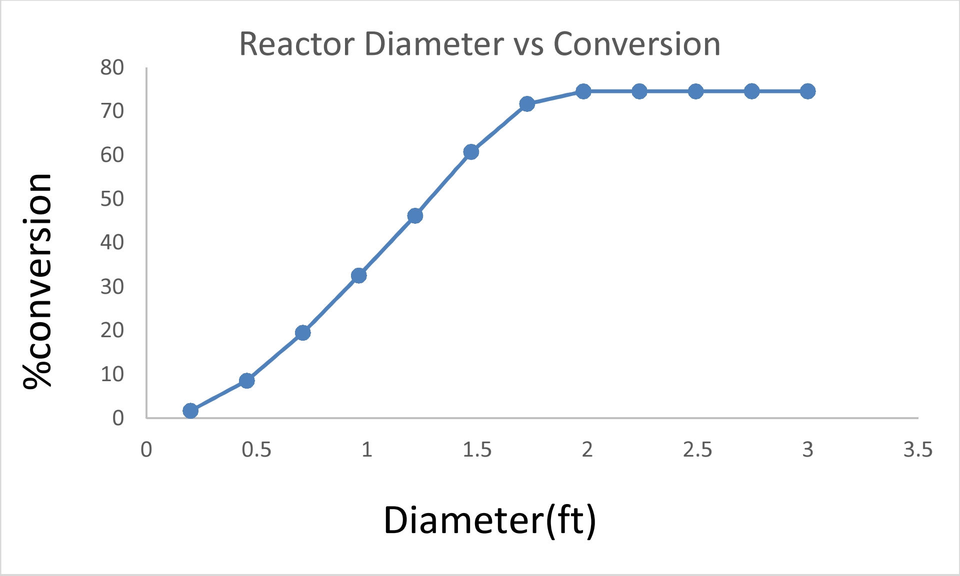


Figure 5.6: Effect of Varying Plug Flow Reactor Diameter on Conversion

5.1.3.5 Effect of Varying Stripper Feed Tray (T- 303)

The objective of the stripper is to remove water from the by-products while ensuring that there is almost complete recovery of acrylonitrile. The feed stage was noticed to impact this objective. The stripper has 30 stages, thus in order to determine the optimum feed stage, it is varied from 2-30. As shown in Figure 5.7, the ideal feed stage was found to be feed stage of 10 with a water removal flow rate of 329 lbmole/hr and acrylonitrile recovery of 99.2%.

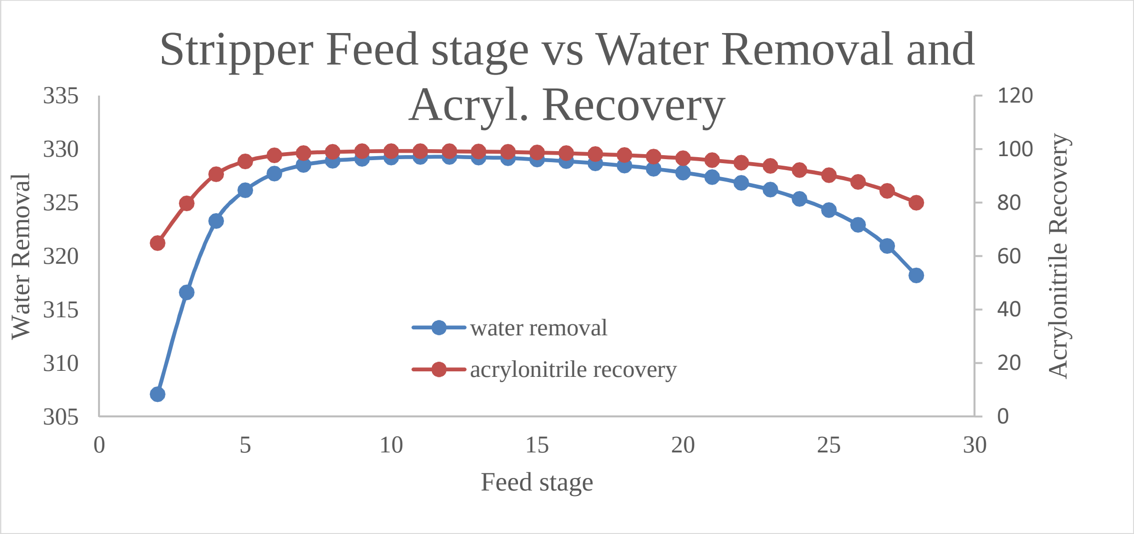


Figure 5.7: Effect of Varying Feed Stage on Water Removal and Acrylonitrile Recovery

5.1.3.6 Effect of Varying Absorber Reflux Ratio (T- 302)

The absorber separates the gases from the liquid products. The absorber reflux ratio was varied from 2 -4 to determine if it had an effect on acrylonitrile recovery. It was noted that it not have an effect on acrylonitrile recovery but it did have an effect on the condenser and re-boiler duty as shown in Figure 6.21.The lower the reflux ratio, the lower the condenser and re-boiler duty. Hence the optimum re-boiler duty and condenser duty have optimum values at a reflux ratio of 3.

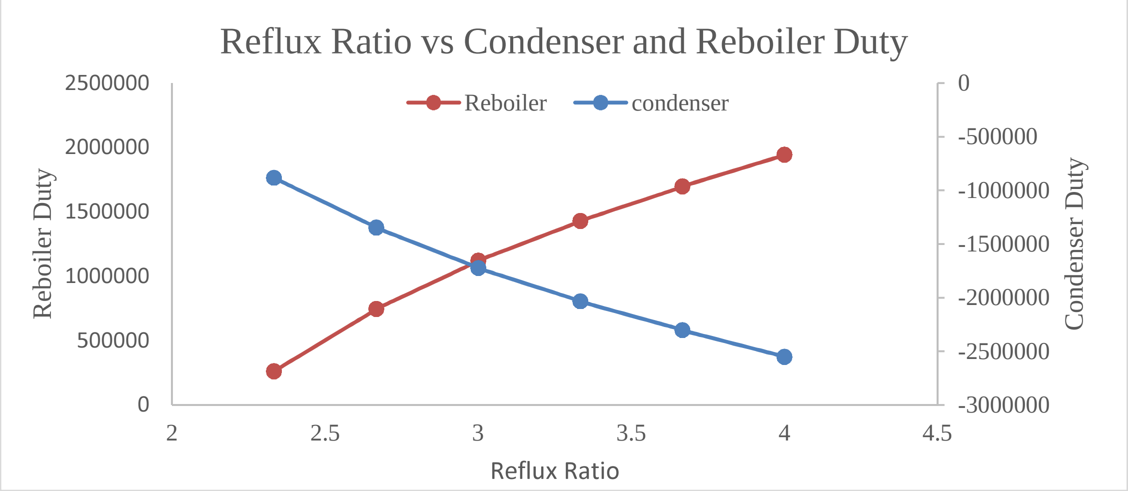


Figure 5.8: Effect of Absorber Reflux Ratio on Condenser and Re-boiler Duty

5.1.3.7 Reconfiguration

The first step of reconfiguration was to investigate if some of the waste streams could be converted to recycle streams so that it will increase acrylonitrile production as well as reduce the health and safety impacts by minimizing waste streams. To aid this objective (Shadiya 2010a), two distillation columns are incorporated into the process. The distillate stream leaving the absorber which contains carbon dioxide, carbon monoxide, propylene and hydrogen cyanide are sent to two distillation columns, T-307 and T-308. T-307 separates carbon monoxide and carbon dioxide from the mixture. The bottom stream is sent to T-308 where the recovery of propylene takes place and hydrogen cyanide is also separated. The recovered propylene is recycled back to reactor (R-301). This distillation column (T-307) recovers some of the un-reacted propylene. Since HCN is being recovered in T-307, one of the earlier HCN separator columns, T-304 is eliminated. Since water is being produced in the process, water recovered from the stripper (T-303) is recycled back to the absorber eliminating the need for process stream 6. The modified process is presented in the block flow diagram shown in Figure 5.9.

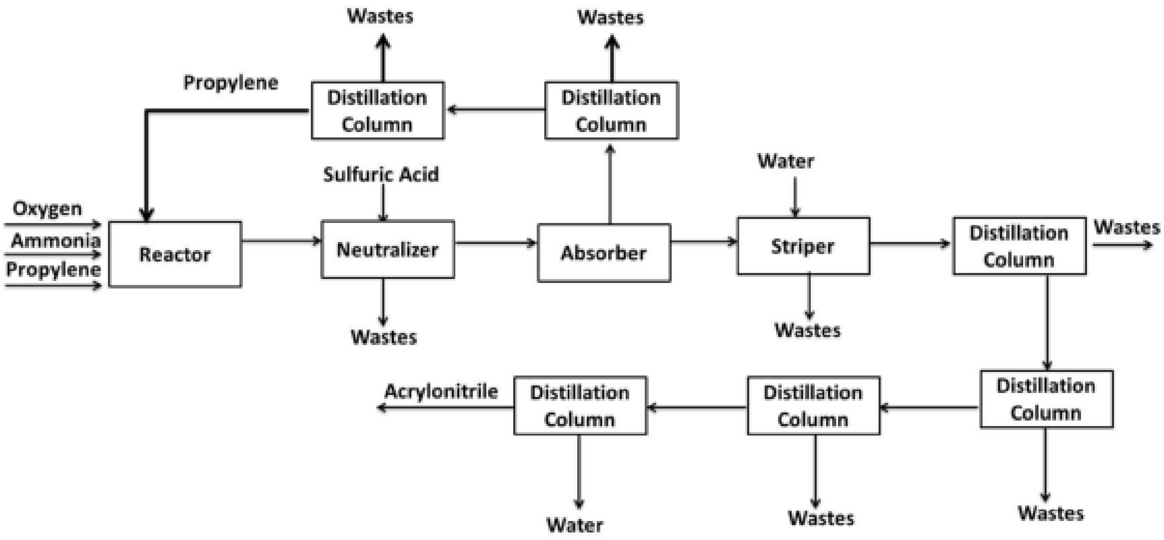


Figure 5.9: Block Flow Diagram of the Reconfigured Acrylonitrile Process (Shadiya 2010a)

5.1.4 Optimization of the Base Case Acrylonitrile

The key goal in this step is to maximize acrylonitrile production while minimizing waste (kg/yr). The waste streams as shown in Figure C.2 (Appendix C) include stream 5, 14, 19 and 23. Thus total waste is presented in Equation 5.15. Thus the optimization equations for this problem are shown below are described in Equation 5.14-5.19. The process is optimized based on the different ranges shown in Table 5.8.

Profit = Product Revenue + By-product Revenue – (Raw Material Cost
+ Waste Treatment Cost + Operating Cost +Annualized Capital Cost) (5.14)

Total Waste= Mass Flow Rates of Stream 9+ Mass Flow Rates of Stream 14
+ Mass Flow Rates of Stream 23+ Mass Flow Rates of Stream 24 (5.15)

Maximize acrylonitrile production, Minimize Waste

Subject to the following constraints:

Operating Temperature $\geq 600^{\circ}$C (5.16)

Operating Pressure ≤ 25 bar (5.17)

Waste Streams ≤ 4 (5.18)

Conversion $\geq 60\%$ (5.19)

Table 5.8: Variables used in the Optimization of the Acrylonitrile Process

Variable Description	Base Case Value	Optimization Range
Feed Flow Rate	NH_3= 85 lbmole/hr O_2 = 129 lbmole/hr C_3H_6 = 85 lbmole/hr	NH_3= 60-90 lbmole/hr O_2= 120-140 lbmole/hr C_3H_6= 75-90 lbmole/hr
PFR Reactor Temperature	852° F	800-1112 ° F
PFR Reactor Pressure	15 psia	10-45 psia
PFR Diameter	1.08ft	1-2ft
PFR Length	19ft	8-20ft
PFR Number of Tubes	17	10-20
H_2SO_4 flow rate	11.20 lbmole/hr	1-60 lbmole/hr
T-302 (Absorber) Reflux Ratio	4	1-10
T-302 (Absorber) Feed Stage	15	2-14
T-302 (Absorber) Bottoms to Feed Ratio	0.85	0.75-0.85
T-303 (Stripper) Reflux Ratio	7	1-10
T-303 (Stripper) Distillate to Feed Ratio	0.17	0.10-0.20
T-303 (Stripper) Feed Stage	10	2-28
T-305 (Separator) Feed Stage	11	2-11
T-305 (Separator) Reflux Ratio	4	2-10
T-305 (Separator) Distillate to Feed Ratio	0.0015	0.005-0.2
T-306 (Separator) Distillate to Feed Ratio	0.78	0.7-0.9
T-306 (Separator) Reflux Ratio	4	1-5
T-306 (Separator) Feed Stage	15	2-34

The modified optimized acrylonitrile process is presented in the schematic shown in Figure C.3. The stream summary and the equipment specification table for the optimized acrylonitrile process are presented in Table C, 9 and Table C.10 respectively in APPENDIX C.

5.1.5 Social Sustainability Assessment of the Optimized Acrylonitrile Process

The optimization of the acrylonitrile process resulted in the changes presented in Table 6.31. The first key change was the reduction in raw material flow rate. This was possible because some of un-reacted raw material was recycled back to reactor (R-301). Another important change was the fact that acrylonitrile production increased from 43 lb -mole/hr to 46.3 lb-mole/hr. The optimization of the acrylonitrile process led to an increase in acrylonitrile productions of 9% while waste reduction to 43%.

Table 5.9: Key Differences between the Base and Optimized Acrylonitrile Processes

Major Change	Base Case Value	Optimized Value
Feed Flow Rate	Ammonia = 85 lbmole/hr Oxygen = 129 lbmole/hr Propylene = 85 lbmole/hr	Ammonia = 67 lbmole/hr Oxygen = 129 lbmole/hr Propylene = 66 lbmole/hr
Sulfuric Acid	11 lbmole/hr	2.097 lbmole/hr
Number of Recycle Streams	0	2 (propylene to the reactor and water to the absorber)
Acrylonitrile Production	42.62 lb-mole/hr	46.32 lb-mole/hr
Stream Elimination	N/A	Water Stream Elimination
Waste	1.65 E+07 lb/year	9.44 E+06 lb/year
Total Inherent Safety index	90	83
Occupational health risk index	236	222
Disease risk reduction	N/A	46%

The safety of the optimized acrylonitrile process was evaluated and compared with the base case. As shown in Table 5.10, the results of the optimized acrylonitrile process shows that there are small changes in overall inherent safety index. It was difficult to really improve safety impact values because most of the other impact values are based on the chemicals present in the process and the operating temperature and pressure (Shadiya, 2010a). Chemical interaction is assumed to be improved to the extent that the chance of explosion has been reduced to soluble toxic exposure by taking necessary safety steps in the optimized process. Inventory is also assumed to be improved due to recycling in the optimized process.

Table 5.10: Summary of Results of Safety Metrics for the Base and Optimized Acrylonitrile Processes

Inherent safety Metrics	Index			
	base	max value	optimized	max value
Heat of main reaction index	8	100%	8	100%
Heat of side reaction index	6	75%	6	75%
Chemical interaction	8	100%	2	25%
Flammability index	8	100%	8	100%
Explosiveness index	6	75%	6	75%
Toxic Exposure Index	24	80%	24	80%
Corrosiveness index	4	50%	4	50%
Temperature index	6	75%	6	75%
Pressure index	2	25%	2	25%
inventory index	4	50%	3	38%
Equipment safety index,ISBL	4	50%	4	50%
Equipment safety index,OSBL	2	25%	2	25%
Safety Level of Process Structure index	8	80%	8	80%
Total Inherent Safety index	90		83	

For occupational health index evaluation all the main and side reactions was considered. As shown in Figure 5.10, percentage of max health hazards were decreased due to all the reactions’ chemicals exposure potential and operating conditions hazards are improved in optimized conditions. Overall occupational health index was decreased from 236 to 232.The average toxic exposure impact value also decreased by 66% for all the reactions.

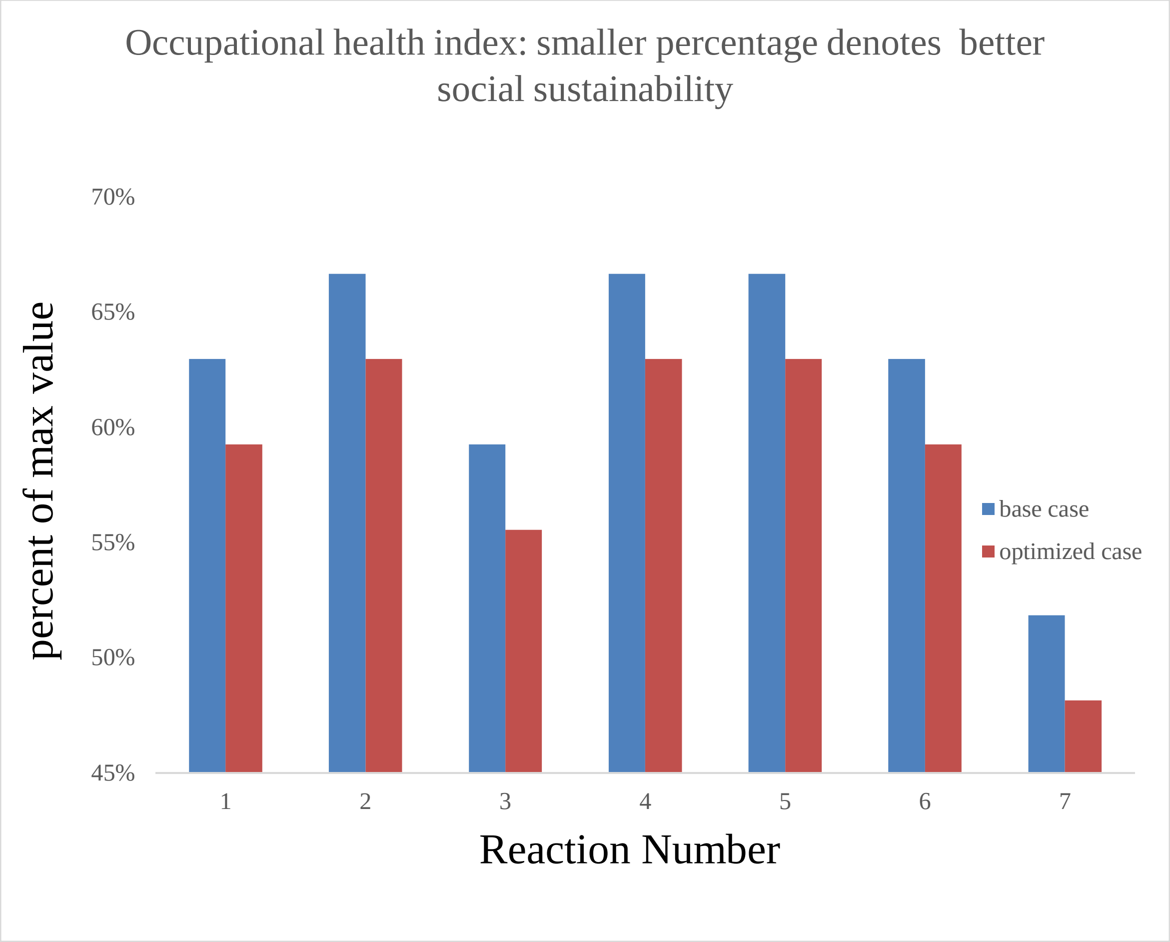


Figure 5.10: Comparison of Occupational Health Assessment for the Base and Optimized Acrylonitrile Process

Table 5.11: Summary of Results of Health Metrics for the Base and Optimized Acrylonitrile Processes

Health index	physical and process hazard index		Health hazard index		Occupational health index			
							Max value	
Reaction No.	base	optimized	base	optimized	base	optimized	base	optimized
1	16	16	14	14	34	32	63%	59%
2	16	16	16	16	36	34	67%	63%
3	16	16	12	12	32	30	59%	56%
4	16	16	16	16	36	34	67%	63%
5	16	16	16	16	36	34	67%	63%
6	16	16	14	14	34	32	63%	59%
7	12	12	12	12	28	26	52%	48%
Total					236	222		

Table 5.12: Percent Reduction of the Toxic Exposure Impact of the Acrylonitrile Optimized Case relative to the Base Case

Toxic Exposure impact value tonnes/yr		
base	optimized	decrease
174.29	24.11	86%
1.19	0.012	99%
4.61	2.89	37%
174.29	24.11	86%
174.29	24.11	86%
1600.21	1463.24	9%
58.91	23.16	61%
Average decrease		66%

The disease impact of the optimized acrylonitrile process is also evaluated and compared with the base case and this is presented in Figure 5.11. From the figure, in general the disease risk for the optimized case is lower compared to the base case. An assessment was completed to determine the percent reduction for each individual disease impact. As shown in Table 5.13, the percent reduction is highest for carcinogenic health risk (86%), immune system damage (86%), kidney damage (86%) and skeletal system damage (90%) and an average risk reduction (46%) because of improved recovery of acrylonitrile, reduction in sulfuric acid wastes as well as propylene wastes.

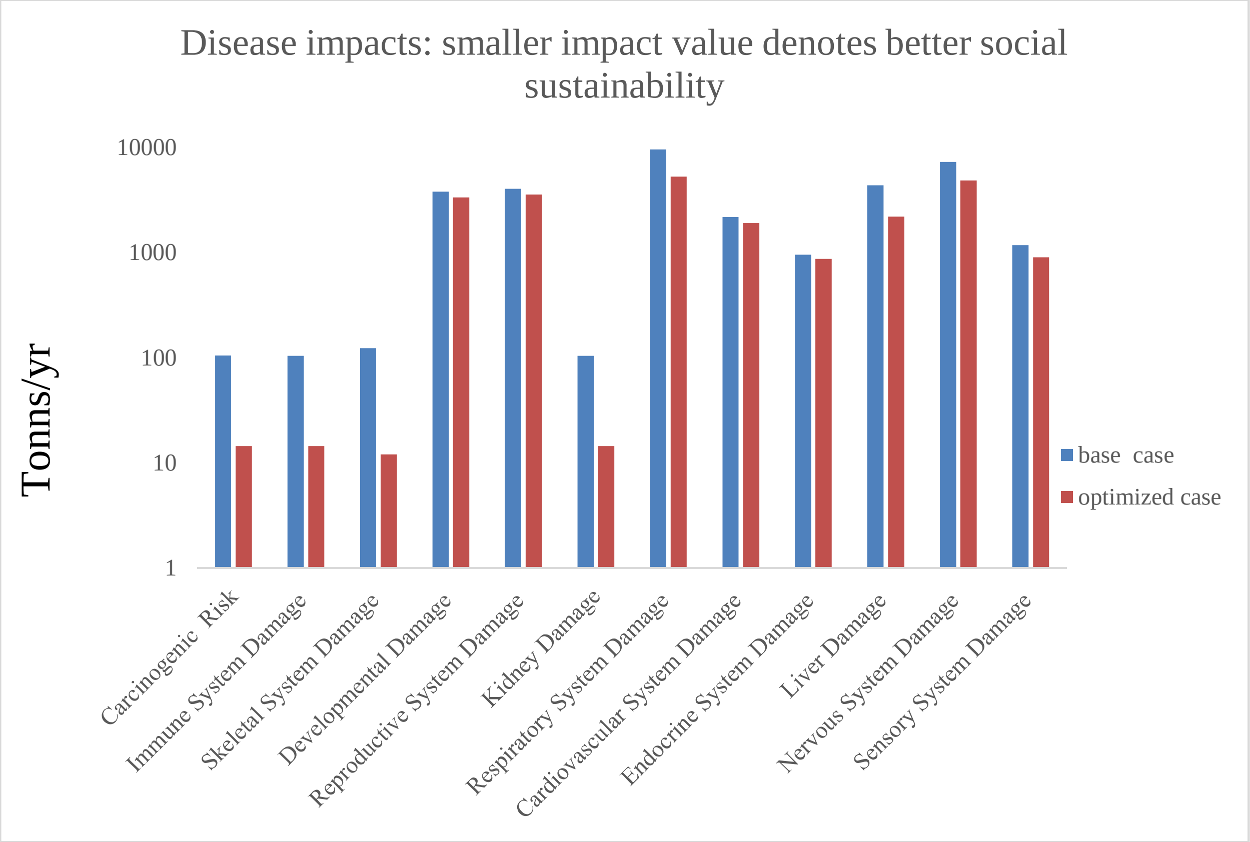


Figure 5.11: Comparison of Disease Risk Impacts Assessment the Base and Optimized Acrylonitrile Process

Table 5.13: Percent Reduction of the Disease Risk Impact of the Acrylonitrile Optimized Case relative to the Base Case

	impact value Tonnes/yr		
Disease risk evaluation	base	optimized	%decrease
Carcinogenic Risk	105.0516	14.473574	86%
Immune System Damage	104.5744	14.468893	86%
Skeletal System Damage	123.6061	12.044658	90%
Developmental Damage	3815.268	3357.4123	12%
Reproductive System Damage	4056.284	3569.6852	12%
Kidney Damage	104.5744	14.468893	86%
Respiratory System Damage	9654.001	5313.7899	45%
Cardiovascular System Damage	2198.79	1913.5037	13%
Endocrine System Damage	960.1274	877.9471	9%
Liver Damage	4395.604	2204.5575	50%
Nervous System Damage	7349.079	4866.1946	34%
Sensory System Damage	1179.665	903.89463	23%
Average decease			46%

5.1.6 Summary

The optimized acrylonitrile process differed from the base case because the following changes were made to the process:

- Addition of two distillation columns to aid in the recycle of propylene back to the reactor (R-301)
- Recycling water from the stripper (T-303) which aided in the elimination of process stream 13. The amount of sulfuric acid requirement was also reduced in optimized case.
- Optimization of operating conditions

The optimized acrylonitrile process has a safety impact of 83 compared to the base case which has a value of 90. The optimized case is reconfigured from the base case so that risk of worst chemical interactions due to fire and explosion or contact with strong acids or bases is minimized. The recycling also reduced the inventory index compared to the base case.

In terms of health concerns, the optimized acrylonitrile case has a lower health risk compared to the base case. Due to improvement of the exposure potential and process operating conditions the health risk index has been reduced and toxic exposure impact has been reduced by 66% in the optimized case compared to the base case. Disease risk impact has been reduced on an average of 46% due to fewer inventories and less waste generation in the optimized case.

Based on the results obtained from the retrofitted SUSTAINABLITY EVALUATOR, it can be concluded that optimized acrylonitrile process is a more socially sustainable compared to the base case because it is more acceptable compared to the other option from both inherent safety and occupational health impacts.

5.2 Case Study: Dimethyl Ether Production Processes

The Retrofitted SUSTAINABILITY EVALUATOR can be used to compare two process options. This was demonstrated using the Dimethyl Ether (DME) process case study. In this case study, there are two alternatives available for producing DME. These are via dehydration of methanol and via natural gas. In this section the following are discussed:

- A short description of the two DME Processes
- Social sustainability quantification of the two DME Processes
- Selection of the more socially sustainable DME Process

5.2.1 Brief Description of the DME Production Process

DME is an organic compound with the formula CH_3OCH_3. It is a colorless gas that is used as a propellant , refrigerent and as a fuel additive for diesel engines.It also acts as a precursor to produce dimethyl sulphate. Only moderate modification is needed to convert a diesel engine to burn DME. The simplicity of this short carbon chain compound leads during combustion to very low emissions of particulate matter, oxides of nitrogen and carbon monoxide. It is highly flammable but considered nontoxic. The physical properties for DME are illustrated in Table 1.

Table 5.14: Physical Properties of Dimethyl Ether (Shadiya, 2010a)

Property	Value
Boiling Point (°C)	-23.6
Freezing Point(°C)	-141.5
Solubility in water, 20°C, g/L	71
Liquid Density, g/L	1.97
Molar Mass, g/mol	46.07

Recently, because of its clean burning nature, several scholars have proposed DME as an alternative fuel for diesel engines, petrol engines and gas turbines (Horstman et al., 2005; Semelsberger et al., 2006; Arcoumanis et al., 2008; Savadkouhi et al., 2010). It could be used as fuel for transportation, power generation, cooking heating etc. (Ogawa et al., 2004). In China and Japan, DME is already being considered as a fuel because of the abundance of coal (Ogawa et al., 2004; Han et al., 2009). DME can be produced by two chemistry pathways namely: DME production via dehydration of methanol and DME production via natural gas.

5.2.1.1 DME Production via Dehydration of Methanol (Option 1)

In this pathway, DME is produced by the catalytic oxidation of methanol to form DME and water as shown in Equation 5.20 below (Turton et al., 2009). The block diagram and the schematic of the process are shown in Figure 5.12 and Figure 5.13 respectively.

$$2\ CH_3OH \rightarrow (CH_3)_2O + H_2O \qquad (5.20)$$

This process is simulated in ASPEN PLUS version 8.1.The Universal Functional Activity Coefficient (UNIFAC) is used as thermodynamic package because it predicts the properties of non-ideal mixtures well and it was recommended in literature (Jonasson et al., 1995; Kleiber, 1995). The input file for this simulated process is available in APPENDIX B.

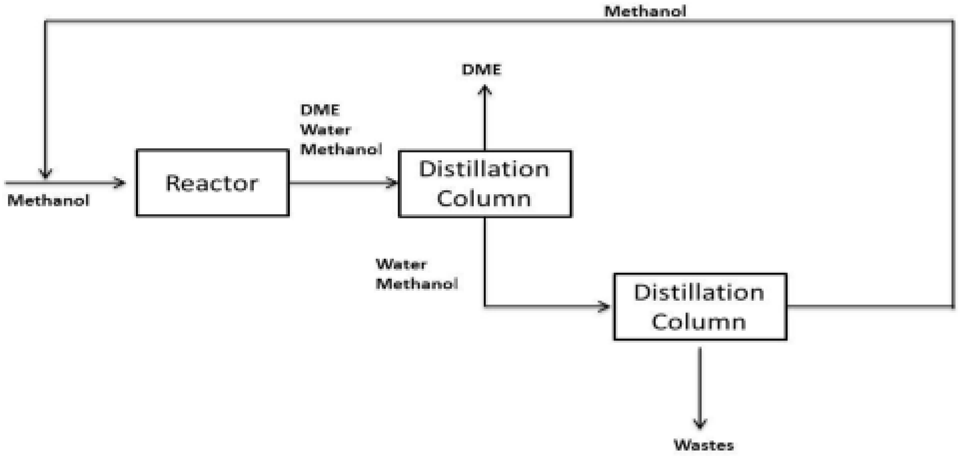


Figure 5.12: Block Diagram of DME Production via Dehydration of Methanol (Shadiya 2010a)

Methanol (Stream “Feed”) with 99.5% purity at 25°C and 1 bar is fed as a liquid stream and pumped by P-201 at 25 bars and combined with another methanol recycle stream (Stream “Recylcle”) as shown in Figure 5.13. The combined streams are sent to two heat exchanger E-201 and E-202 where it is heated to 154 °C and 220 °C respectively before being sent to a reactor. The exothermic reaction taking place is the reactor (R-201) results in 80% conversion of methanol to DME. The products exiting the reactor steam are heated to 364 °C. This exiting stream is cooled down by two coolers E-203 and E-204 to a temperature of 278 °C and 100 °C respectively, and throttled to 13.4 bar. This throttled steam is sent to the first distillation column (T-101) where the product DME (stream “DME”) is separated from the other components. Next the other components (stream S10) are sent to another distillation column (T-102) where methanol (stream S13) and water (Stream S12) are separated. The ASPEN PLUS schematic for this process is show in Figure 5.13. The stream summary and equipment specification tables for this process are presented in Table B2 and Table B1 in APPENDIX B respectively.

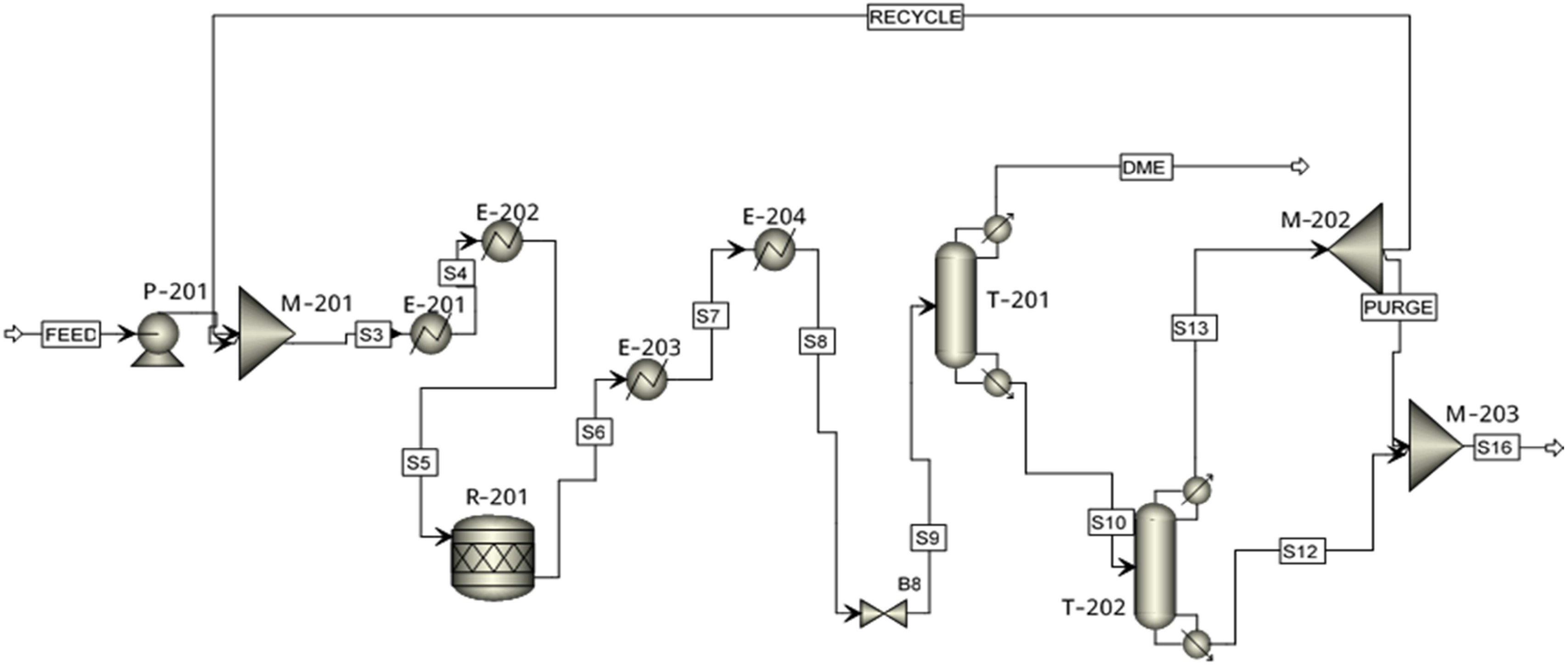


Figure 5.13: Schematic of DME Production via Dehydration of Methanol

5.2.1.2 DME Production via Natural Gas (Option 2)

DME production via natural gas is simulated in ASPEN PLUS version8.1, using UNIFAC, the same thermodynamic package as the previous option.

The block flow diagram and schematic for this process are shown in Figure 5.14 and Figure 5.15 respectively. The input file for the simulated process is available in APPENDIX A. In this approach, DME is produced by the following steps: steam reforming, methanol synthesis and DME synthesis in three isothermal reactors (Horstman et al., 2005).

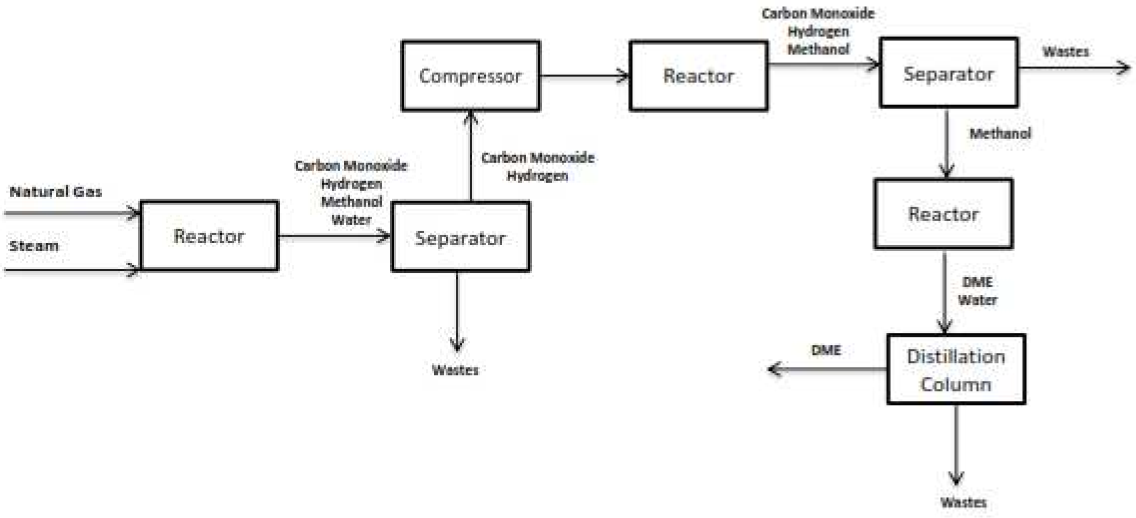


Figure 5.14: Block Diagram of DME Production via Natural Gas

In the steam reforming step, methane (stream “METHANE’) with 87.5% purity at 35^{o}C and 1 atm is heated by E-301 to 800^{o}C (stream 3) as shown in Figure 5.14. Water (stream “WATER”) at 35^{o}C and 1atm is also heated by E-302 to 800^{o}C (stream 4). Stream 3 and 4 are fed into reactor (R-301) where natural gas is reacted with steam over nickel or magnesium oxide acting as catalysts to produce synthesis gas (Stream 5) as shown in Equation 5.21.

$CH_4 + H_2O \rightarrow CO + 3H_2$ (5.21)
methane

The reaction results in a 96.6% conversion of methane to synthesis gas. The synthesis gas is cooled to 35°C by E-303 and then sent to a separator to remove excess water (stream 7). The separated synthesis gas (Stream 8) is sent to a compressor where the pressure is increased from atmospheric pressure to 40 atm (stream 9). Next, this stream is sent to a cooler to cool the stream from 644 °C to 240 °C before being sent to another reactor (R-302).

In this step, methanol is synthesized by reacting carbon monoxide and hydrogen with the aid of carbon dioxide on alumina support as shown in Equation 5.22.

$CO + 2H_2 \rightarrow CH_3OH$ (5.22)
methanol

The reaction results in a 75.5% conversion of carbon monoxide to methanol. Next the synthesized stream (stream 11) is compressed shortly before being sent to separator (T-302) where methanol is separated from the syngas mixture. The syngas (stream 14) is heated from 20 °C to 240 °C shortly before it is sent to the last reactor. Lastly, the methanol is dehydrated in reactor (R-303) to produce DME as shown in Equation 5.23.

$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ (5.23)
Methanol DME

The reaction results in a 91% conversion of methanol to DME. The DME mixture is compressed to a lower pressure and sent to distillation column (T-303). The mixture (stream S3) is also separated into two streams, a waste stream (Stream S5) and a DME

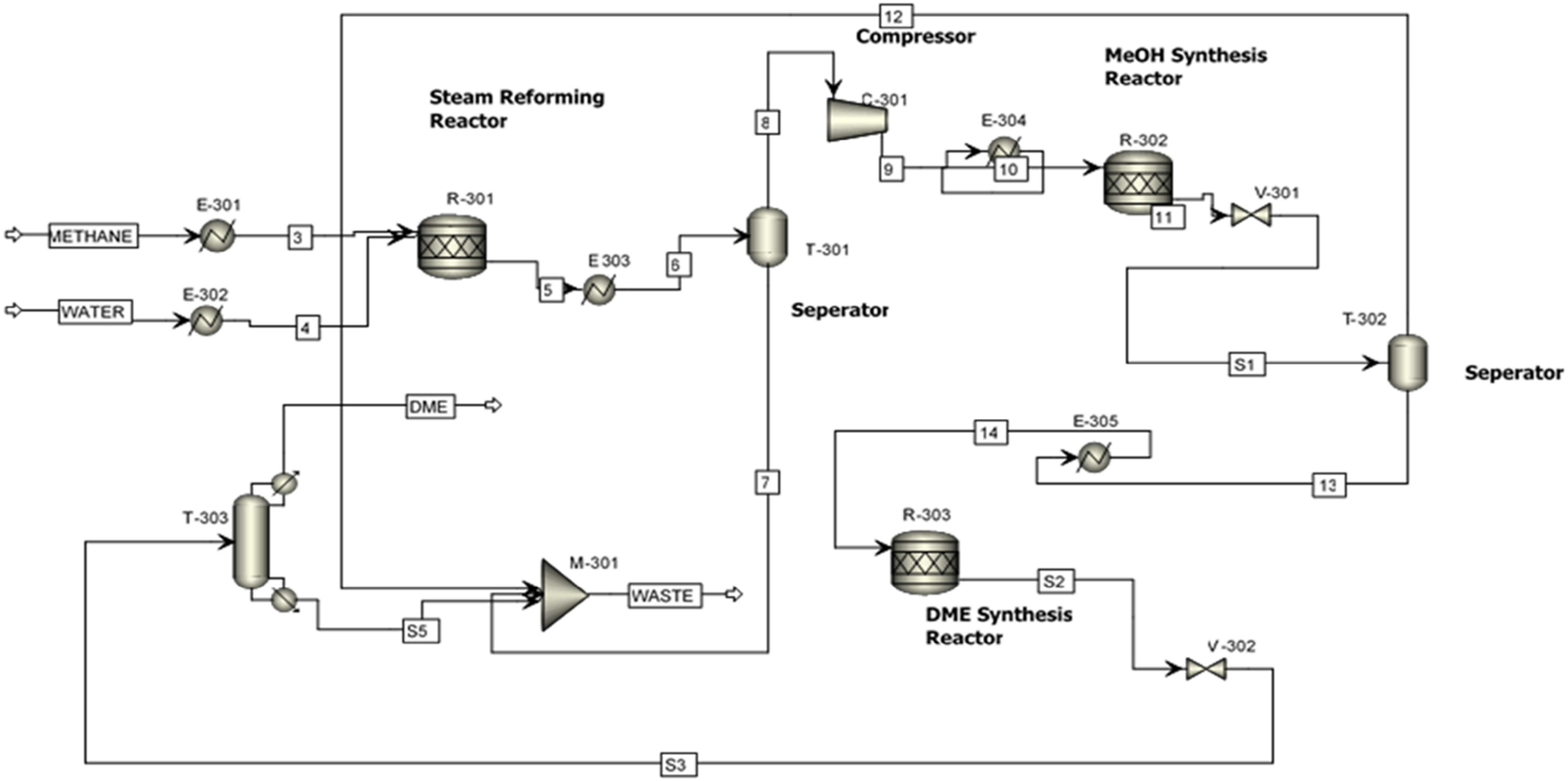


Figure 5.15: Schematic of DME Production via Natural Gas

stream (Stream “DME”). The schematic of this process is shown in Figure 5.15. The equipment specification table and stream summary table for this process are presented in Table B3 and Table B4 respectively in Appendix B.

5.2.2 Social Sustainability Evaluation of the DME Production Processes

The two DME base cases were simulated on ASPEN PLUS and set to a production rate of 129.70 kmol/hr and a purity of 99% (Shadiya 2010a). The two cases were quantified for social sustainability evaluation. Social impact can be categorized into total inherent occupational health impact and total inherent safety risk. The safety assessments of the two processes are compared in. As shown in the table 5.15, DME via methanol has a process safety index of 52 while DME via natural gas has a safety index of 84. As depicted in Fig 5.16, safety risk is much less for DME from methanol than the same from natural gas.

Table 5.15: Results of Safety Metrics from the SUSTAINABILITY EVALUATOR for the two DME Options

Inherent safety index	Index			
	MeOH	max value	NG	max value
Heat of main reaction index	0	0%	2	25%
Heat of side reaction index	0	0%	4	50%
Chemical interaction	2	25%	8	100%
Flammability index	8	100%	8	100%
Explosiveness index	4	50%	6	75%
Toxic Exposure Index	12	40%	16	53%
Corrosiveness index	4	50%	4	50%
Temperature index	6	75%	8	100%
Pressure index	2	25%	6	75%
inventory index	4	50%	6	75%
Equipment safety index,ISBL	4	50%	6	75%
Equipment safety index,OSBL	2	25%	6	75%
Safety Level of Process Structure index	4	40%	4	40%
Total Inherent Safety index	52		84	

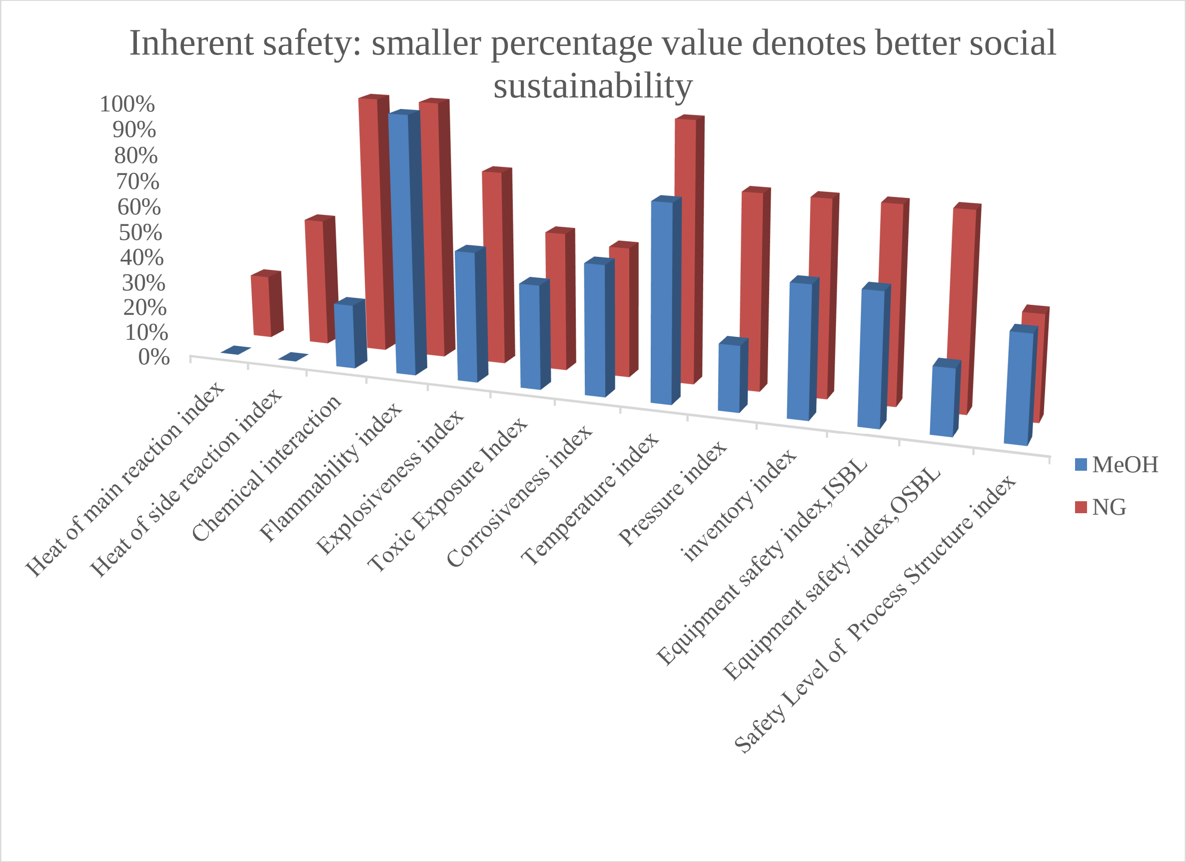


Figure 5.16: Results of Inherent Safety Risk Assessment from the SUSTAINABILITY EVALUATOR for the two DME Options

Health risk assessment was also carried out for both the chemistries of DME processes. As depicted in Table 5.16 the occupational health index for DME from MeOH and from NG are 26 and 222 respectively.

5.16: Results of the Occupational Health Indexes from the SUSTAINABILITY EVALUATOR for the Two DME Options

Health index	physical and process hazard index		Health hazard index		Occupational health index			
							Max value	
Reaction No.	MeOH	NG	MeOH	NG	MeOH	NG	MeOH	NG
1	16	18	8	12	26	34	48%	63%
2		20		12		36		67%
3		20		10		34		63%
Total					26	222		

The result of the disease impact assessment is depicted in Figure 5.17 and Table 5.17. As shown in the figure, for both options, the major disease risks from potential chemical exposure include developmental damage, respiratory system damage, nervous system damage and liver damage. DME production via natural gas has an additional health risk which is reproductive system damage. The chemicals resulting in this health risk are summarized in Table 5.17.

Table 5.17: Summary of Chemicals Contributing to Disease Risks for the Two DME Options

Disease risk evaluation	impact value Tonnes/yr		DME via MeOH	DME via NG
	MeOH	NG		
Developmental Damage	103.041	10943.034	CH_3OH	CH_3OH,CO
Reproductive System Damage	0	4246.69	None	CO
Respiratory System Damage	103.041	10589.303	CH_3OH	CH_3OH,CO,CH_4,C_2H_6,C_3H_8
Liver Damage	103.041	3865.217	CH_3OH	CH_3OH
Nervous System Damage	103.041	4469.155	CH_3OH	CH_3OH,C_3H_8,C_4H_{10}
Sensory System Damage	103.041	3865.217	CH3OH	CH3OH

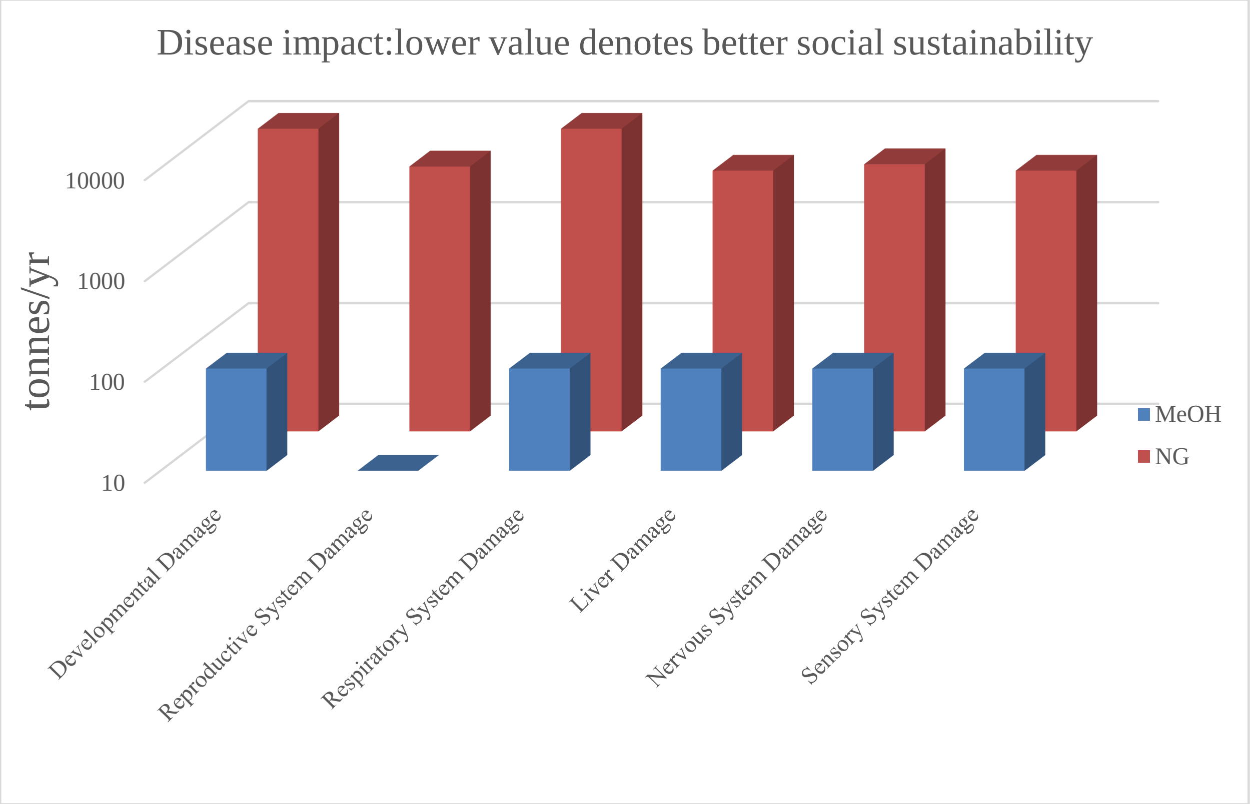


Figure 5.17: Results of Disease Impacts Assessment from the SUSTAINABILITY EVALUATOR for the two DME Options

5.2.3 Selection of More Socially Sustainable DME Production Process

In terms of social concerns, DME via methanol dehydration is more socially acceptable compared to via natural gas because the former had a lower inherent safety and inherent occupational health impact than the later. The results for safety risk evaluation as shown in Table 5.15, illustrates that DME production via methanol has a process safety index of 52 and is thus a safer process compared to DME production via natural gas which has a process safety index of 84. DME production via natural gas has a higher process safety index value due to the more exothermic reactions taking place in the process, more toxic chemicals, higher process temperature and the presence of compressors and high hazard reactors (Shadiya, 2010a). The results for health risk evaluation as shown in Table 5.16, illustrates that DME production via methanol has a process safety index of 26 and is thus a safer process compared to DME production via natural gas which has a process safety index of 222. The higher index value for DME production via natural gas is due to more reaction steps, high exposure potential for chemicals and high acute and chronic toxicity effects. As shown in Figure 5.17, DME production via natural gas (option 2) has a higher disease risk from the following impact categories: developmental damage, respiratory system damage, and liver damage, reproductive system damage, nervous system damage, sensory system damage compared to DME production via methanol.

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

In this work a methodology was developed to evaluate to the social sustainability of processes at early design stages. In acrylonitrile process study, this methodology was aimed at quantifying the social dimension and then based on the results of retrofitted SUSTAINABILITY EVALUATOR, optimizing the process to reduce waste generation maximizing desired chemical production while profit remains above a certain limit. In DME production study, this methodology tests the applicability of the retrofitted SUSTAINABILITY EVALUATOR with two different chemistries to assist the decision maker determine the superior socially adoptable alternative. The methodology discussed by this author as summarized in Table 6.1.

Table 6.1: Summary of the Proposed Methodology

Steps	Description	Tool(s)
1	Base Case Process Modeling: The process is simulated based on design specification or literature data available and mass and energy balances are calculated.	ASPEN PLUS

2	Impact Assessment of the Process: In this step, the feed, product and waste streams are identified an impact assessment is completed. The social impact of the simulated process is quantified using the modified SUSTAINABILITY EVALUATOR.	Retrofitted SUSTAINABILITY EVALUATOR and ASPEN PLUS
3	Sensitivity Analysis: The objective of this step is to identify parameters that affect the social dimension of a chemical process. The goal is to identify parameters such parameters include varying operating conditions, trying a different type of equipment and process configuration that improve production and reduce waste formation.	ASPEN PLUS
4	Optimization of the Process: Once the process has been reconfigured and parameters have been identified, the next step is to optimize the process for social sustainability. The goal of the optimization is to maximize production and minimizing wastes with a minimum threshold profit value.	ASPEN PLUS
5	Impact Assessment of the Optimized Process: After the process has been optimized it is important to evaluate the process for the inherent safety and inherent occupational health sustainability and compare the	Retrofitted SUSTAINABILITY EVALUATOR

	improvements made to the optimized process to the base case. The value of individual social category for the optimized case should be lower than that of the base case.	
6	Accept Design: If the sustainability index and impact values for all categories of social dimension are lower than the base case and the process is economic value remains above the threshold value, the decision maker can accept the design. Otherwise the repetition of the optimization step is carried out.	Decision maker's judgment

In this thesis an inherent safety index for evaluating inherent safety proposed by Heikkila (1999) in early process design stage was adopted. The inherent safety of a process index was divided into the Chemical Inherent Safety Index and the Process Inherent Safety Index. The Chemical Inherent Safety Index describes the inherent safety of chemicals in the process. The affecting factors for the Chemical Inherent Safety Index are the heat of the main reaction and the maximum heat of possible side reactions, flammability, explosiveness, toxicity, corrosiveness and the interaction of substances present in the process. The Process Inherent Safety describes maximum inventory, maximum process temperature and pressure, safety of equipment for both ISBL and OSBL and the safety of process structure.

Inherent occupational health is the measurement of occupational health hazards to the employees by the use of chemicals, process conditions and operating procedures. The Inherent Occupational Health Index presented in this research has been adopted from Hassim and Hurme (2010) and Shadiya (2010a). The metrics chosen are tailored for the information available in the early design stage namely process conditions and health and disease risk potential of chemicals. The subindexes are as follows: mode of process, temperature, pressure and chemical's material state, volatility, corrosiveness, toxicity threshold limit value, and R-phrase. There are twelve disease risk subindixes are also incorporated which includes both carcinogenic and non-carcinogenic disease risks.

The novel contribution of this research is that it quantifies both the inherent safety and inherent occupational health for processes at the same time based on the information available at the early design stage. Sustainability impacts for both inherent safety and inherent occupational health were incorporated into the retrofitted SUSTAINABILITY EVALUATOR. This aids the engineer in having a quantitative number to use in deciding the sustainability impact of a process for safety and health. It important to note that economic and environmental sustainability are not the direct concerns of this research but the methodology proposed here may easily amalgamable with the other two dimensions of sustainability for any future research. The impact assessment tool is also useful in comparing processes and selecting the best option. This has been demonstrated using the dimethyl ether (DME) and acrylonitrile processes. In the DME case study, two options with different chemistries were evaluated and the most sustainable option was selected. In the acrylonitrile process, a sensitivity analysis was first completed to detect parameters that affect the social sustainability of the process. Once the parameters have been selected, the processes are optimized with ASPEN PLUS. Next the optimized cases are evaluated and compared with their base cases using the retrofitted SUSTAINABILITY EVALUATOR.

The retrofitted SUSTAINABILITY EVALUATOR was used to compare two DME options that differed by reaction pathway and equipment configuration. DME can be manufactured via methanol or via natural gas. Based on the lower social sustainable impact obtained from the tool, DME production via methanol dehydration is the more sustainable production option. The lower impact value of safety and health for DME via methanol was a result of the fact that DME via methanol dehydration had a more efficient reaction process, was safer as less toxic chemicals and less hazardous equipment were present in the process and less wastes were generated in the process.

The overall methodology presented in Table 1.1 was demonstrated on the acrylonitrile process. The base case acrylonitrile process had several waste streams causing health risks. The acrylonitrile process was optimized to maximize profit and minimizing wastes while profit being above a threshold value of $10M- after identifying parameters that affected the sustainability of the process. The optimized acrylonitrile process differed from the base case because the following changes were made to the process: addition of separation equipment to recover raw materials, addition of water recycling stream, reduction of raw material used and optimization of operating conditions. The improvements made to the optimized acrylonitrile process led to a lower health and safety impact values.

In a nutshell, this work is significant because a novel framework that incorporates the quantification of both health and safety -the two aspects of social sustainability into early stages of chemical process design was developed. This framework involved the use of the retrofitted SUSTAINABILITY EVALUATOR, a modified impact assessment tool. This impact assessment tool, originally developed by Shadiya (2010a) and modified in this research exclusively for sense making of health and safety metrics, has aided the engineer in identifying and evaluating social sustainability concerns during early stages of chemical process design. The tool is useful comparing multiple processes and selecting the most sustainable option. Also it could be used to handle single and multiple objective optimization problems. The proposed methodology also uses ASPEN PLUS to simulate processes, calculate mass and energy balances, complete sensitivity analysis and optimize processes for sustainability. Lastly individual sustainability impact for both the health and safety was developed to quantitatively identify process improvements and select the most sustainable process options.

6.2 Future Work

While this methodology would be helpful in evaluating process' social sustainability, it could be improved upon. The future research work to be considered for the future are:

- Construct a multi-objective optimization methodology to amalgam economics, environmental with the social dimensions as objectives and their metrics as constraints.

- Figure out a more robust and effective way of entering inputs for the SUSTAINABILITY EVALUATOR from Aspen Plus e.g. linking the tool with Aspen Plus using visual basic for applications.
- Validate both the health and safety impacts for both chemistries using another tool and compare the results obtained from this study.
- Develop a rigorous model for the kinetics of DME productions. Instead of comparing only the base cases both the alternatives should be optimized based upon the results of sensitivity analysis and then the optimized processes should be compared for social sustainability.
- Classify disease risks into chronic versus acute illness. Other approaches could include evaluating the toxicology of chemicals and classifying them into carcinogenic, mutagenic and reprotoxic. The classification of non-carcinogens could also be explored by using information such as inhalation and oral reference concentrations as well as oral slope factors, oral and inhalation unit risks to classify carcinogens (Shadiya, 2010a).
- Improve the index system by additional social metrics such as land and water impact to plant location, employee welfare, job security etc. In the inherent safety measurement intermediate streams should also be considered as integral safety issue.

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APPENDIX A: INPUT FILE FOR THE FOLLOWING CASE STUDIES: DIMETHYL ETHER AND ACRYLONITRILE

DIMETHYL ETHER VIA DEHYDRATION OF METHANOL INPUT FILE

```
DYNAMICS

   DYNAMICS RESULTS=ON

TITLE 'DME SIMULATION CASE A'

IN-UNITS SI

DEF-STREAMS CONVEN ALL

SIM-OPTIONS MASS-BAL-CHE=YES OLD-DATABANK=YES

MODEL-OPTION

DATABANKS PURE28  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURE28  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
   METHANOL CH4O /
   WATER H2O /
   DIMET-01 C2H6O-1

SOLVE
   RUN-MODE MODE=SIM

FLOWSHEET
   BLOCK B1 IN=FEED OUT=S2
   BLOCK B2 IN=S2 RECYCLE OUT=S3
   BLOCK B3 IN=S3 OUT=S4
   BLOCK B4 IN=S4 OUT=S5
   BLOCK B5 IN=S5 OUT=S6
   BLOCK B6 IN=S6 OUT=S7
   BLOCK B7 IN=S7 OUT=S8
   BLOCK B8 IN=S8 OUT=S9
   BLOCK B9 IN=S9 OUT=DME S10
   BLOCK B10 IN=S10 OUT=S13 S12
   BLOCK B12 IN=PURGE S12 OUT=S16
   BLOCK B13 IN=S13 OUT=RECYCLE PURGE

PROPERTIES NRTL-RK
```

```
    PROP-DATA NRTL-1
       IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C
PDROP=bar  &
          INVERSE-PRES='1/bar'
       PROP-LIST NRTL
       BPVAL METHANOL WATER -2.626000000 828.3871000
.3000000000  &
          0.0 0.0 0.0 24.99000000 188.3000000
       BPVAL WATER METHANOL 4.824100000 -1329.543500
.3000000000  &
          0.0 0.0 0.0 24.99000000 188.3000000
       BPVAL METHANOL DIMET-01 -1.271500000 480.9184000
.3000000000  &
          0.0 0.0 0.0 60.00000000 120.0000000
       BPVAL DIMET-01 METHANOL 2.452600000 -541.8811000
.3000000000  &
          0.0 0.0 0.0 60.00000000 120.0000000

    STREAM FEED
       SUBSTREAM MIXED TEMP=298.1500000 PRES=1.00000000E+5
       MOLE-FLOW METHANOL .0721388888 / WATER 6.94444444E-4

    BLOCK B2 MIXER
       PARAM

    BLOCK B12 MIXER
       PARAM

    BLOCK B13 FSPLIT
       FRAC RECYCLE 0.992

    BLOCK B3 HEATER
       PARAM TEMP=427.1500000 PRES=1.51000000E+6

    BLOCK B4 HEATER
       PARAM TEMP=493.1500000 PRES=1.47000000E+6

    BLOCK B6 HEATER
       PARAM TEMP=551.1500000 PRES=1.38000000E+6

    BLOCK B7 HEATER
       PARAM TEMP=373.1500000 PRES=1.34000000E+6

    BLOCK B9 RADFRAC
       PARAM NSTAGE=22 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
```

```
      COL-CONFIG CONDENSER=PARTIAL-V
      FEEDS S9 12
      PRODUCTS S10 22 L / DME 1 V
      P-SPEC 1 1.02132500E+6
      COL-SPECS MOLE-D=.0360277777 MOLE-RR=0.6

   BLOCK B10 RADFRAC
      PARAM NSTAGE=26 ALGORITHM=STANDARD MAXOL=25 DAMPING=NONE
      COL-CONFIG CONDENSER=PARTIAL-V
      FEEDS S10 14
      PRODUCTS S12 26 L / S13 1 V
      P-SPEC 1 7.31325000E+5
      COL-SPECS MOLE-D=.0184166666 MOLE-RR=1.8

   BLOCK B5 RSTOIC
      PARAM TEMP=637.1500000 PRES=1.39000000E+6
      STOIC 1 MIXED METHANOL -2. / DIMET-01 1. / WATER 1.
      CONV 1 MIXED METHANOL 0.8

   BLOCK B1 PUMP
      PARAM PRES=2.50000000E+6 EFF=0.6

   BLOCK B8 VALVE
      PARAM P-OUT=1.04000000E+6

   EO-CONV-OPTI

   STREAM-REPOR MOLEFLOW MASSFLOW
   ;
   ;
   ;
   ;
   ;
```

DIMETHYL ETHER VIA NATURAL GAS INPUT FILE

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS SI

DEF-STREAMS CONVEN ALL

SIM-OPTIONS MASS-BAL-CHE=YES OLD-DATABANK=YES

MODEL-OPTION

DATABANKS PURE28 / AQUEOUS / SOLIDS / INORGANIC / &
      NOASPENPCD

PROP-SOURCES PURE28 / AQUEOUS / SOLIDS / INORGANIC

COMPONENTS
   WATER H2O /
   ETHANE C2H6 /
   PROPANE C3H8 /
   N-BUTANE C4H10-1 /
   HYDROGEN H2 /
   CARBO-01 CO /
   METHANOL CH4O /
   DIMET-01 C2H6O-1 /
   METHANE CH4 /
   OXYGEN O2

SOLVE
   RUN-MODE MODE=SIM

FLOWSHEET
   BLOCK B1 IN=METHANE OUT=3
   BLOCK B2 IN=WATER OUT=4
   BLOCK B3 IN=3 4 OUT=5
   BLOCK B4 IN=5 OUT=6
```

```
   BLOCK B5 IN=6 OUT=8 7
   BLOCK B6 IN=8 OUT=9
   BLOCK B7 IN=9 OUT=10
   BLOCK B8 IN=10 OUT=11
   BLOCK B9 IN=S1 OUT=12 13
   BLOCK B10 IN=13 OUT=14
   BLOCK B11 IN=11 OUT=S1
   BLOCK B12 IN=14 OUT=S2
   BLOCK B13 IN=S2 OUT=S3
   BLOCK B14 IN=S3 OUT=DME S5
   BLOCK B16 IN=S5 7 12 OUT=WASTE

PROPERTIES NRTL-RK
   PROPERTIES NRTL

PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar &
      INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL WATER METHANOL 2.732200000 -617.2687000 .3000000000 &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL METHANOL WATER -.6930000000 172.9871000 .3000000000 &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL N-BUTANE METHANOL 0.0 551.7243000 .3000000000 0.0 &
      0.0 0.0 50.00000000 50.00000000
   BPVAL METHANOL N-BUTANE 0.0 380.4331000 .3000000000 0.0 &
      0.0 0.0 50.00000000 50.00000000
   BPVAL METHANOL DIMET-01 0.0 653.0063000 .2951000000 0.0 &
      0.0 0.0 0.0 0.0
   BPVAL DIMET-01 METHANOL 0.0 -18.93720000 .2951000000 0.0 &
      0.0 0.0 0.0 0.0

STREAM METHANE
   SUBSTREAM MIXED TEMP=308.1500000 PRES=1.01325000E+5  &
      MASS-FLOW=1.587222222
   MASS-FRAC ETHANE 0.075 / PROPANE 0.035 / N-BUTANE 0.015 /  &
      METHANE 0.875

STREAM WATER
   SUBSTREAM MIXED TEMP=308.1500000 PRES=1.01325000E+5
   MASS-FLOW WATER 2.222222222
```

```
BLOCK B16 MIXER
   PARAM PRES=0.0

BLOCK B1 HEATER
   PARAM TEMP=1073.150000 PRES=1.01325000E+5

BLOCK B2 HEATER
   PARAM TEMP=1073.150000 PRES=1.01325000E+5

BLOCK B4 HEATER
   PARAM TEMP=308.1500000 PRES=1.01325000E+5

BLOCK B7 HEATER
   PARAM TEMP=513.1500000 PRES=4.05300000E+6

BLOCK B10 HEATER
   PARAM TEMP=513.1500000 PRES=2.02650000E+6

BLOCK B5 FLASH2
   PARAM TEMP=293.1500000 PRES=1.01325000E+5

BLOCK B9 FLASH2
   PARAM TEMP=293.1500000 PRES=2.02650000E+6

BLOCK B14 RADFRAC
   PARAM NSTAGE=41 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS S3 35 ABOVE-STAGE
   PRODUCTS DME 1 V / S5 41 L
   P-SPEC 1 8.10600000E+5
   COL-SPECS MOLE-D=0.0380277777 MOLE-RR=5.

BLOCK B3 RSTOIC
   PARAM TEMP=1073.150000 PRES=1.01325000E+5
   STOIC 1 MIXED METHANE -1. / WATER -1. / CARBO-01 1. /  &
      HYDROGEN 3.
   CONV 1 MIXED METHANE 0.966

BLOCK B8 RSTOIC
```

```
    PARAM TEMP=513.1500000 PRES=4.05300000E+6
    STOIC 1 MIXED CARBO-01 -1. / HYDROGEN -2. / METHANOL 1.
    CONV 1 MIXED CARBO-01 0.9

BLOCK B12 RSTOIC
    PARAM TEMP=513.1500000 PRES=2.02650000E+6
    STOIC 1 MIXED METHANOL -2. / DIMET-01 1. / WATER 1.
    CONV 1 MIXED METHANOL 0.92

BLOCK B6 COMPR
    PARAM TYPE=ISENTROPIC PRES=4.05300000E+6 SEFF=0.8  &
        SB-MAXIT=30 SB-TOL=0.0001

BLOCK B11 VALVE
    PARAM P-OUT=2.02650000E+6

BLOCK B13 VALVE
    PARAM P-OUT=8.10600000E+5

EO-CONV-OPTI

STREAM-REPOR MOLEFLOW MASSFLOW
;
;
;
;
;
```

ACRYLONITRILE BASE CASE INPUT FILE

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS MASS-BAL-CHE=YES OLD-DATABANK=YES

MODEL-OPTION

DATABANKS PURE28  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURE28  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
   AMMONIA H3N /
   WATER H2O /
   HYDRO-01 CHN /
   CARBO-01 CO /
   OXYGE-01 O2 /
   PROPY-01 C3H6-2 /
   CARBO-02 CO2 /
   ACETO-01 C2H3N /
   ACRYL-01 C3H3N /
   ACROL-01 C3H4O /
   SULFU-01 H2SO4 /
   AMMON-01 "(NH4)2SO4"

SOLVE
   RUN-MODE MODE=SIM

FLOWSHEET
   BLOCK B1 IN=2 3 1 OUT=4
   BLOCK B2 IN=4 OUT=5
   BLOCK B3 IN=5 7 OUT=6
   BLOCK B4 IN=6 OUT=8
   BLOCK B5 IN=8 OUT=10 9
   BLOCK B6 IN=10 OUT=11
   BLOCK B7 IN=13 OUT=12
   BLOCK B8 IN=11 12 OUT=14 15
```

```
   BLOCK B9 IN=15 OUT=16
   BLOCK B10 IN=16 OUT=17 18
   BLOCK B11 IN=17 OUT=19
   BLOCK B13 IN=19 OUT=22 21
   BLOCK B14 IN=22 OUT=23
   BLOCK B15 IN=21 OUT=24 25
   BLOCK B16 IN=25 OUT=26 27
   BLOCK B17 IN=14 9 23 24 OUT=28

PROPERTIES ELECNRTL
   PROPERTIES ENRTL-RK

PROP-DATA HOCETA-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST HOCETA
   BPVAL AMMONIA WATER .2000000000
   BPVAL AMMONIA PROPY-01 .2000000000
   BPVAL AMMONIA CARBO-02 .2000000000
   BPVAL AMMONIA ACETO-01 1.400000000
   BPVAL AMMONIA ACRYL-01 1.400000000
   BPVAL WATER WATER 1.700000000
   BPVAL WATER CARBO-02 .3000000000
   BPVAL WATER ACETO-01 1.500000000
   BPVAL WATER ACRYL-01 1.500000000
   BPVAL WATER AMMONIA .2000000000
   BPVAL PROPY-01 ACETO-01 .2000000000
   BPVAL PROPY-01 ACRYL-01 .2000000000
   BPVAL PROPY-01 AMMONIA .2000000000
   BPVAL CARBO-02 WATER .3000000000
   BPVAL CARBO-02 CARBO-02 .1600000000
   BPVAL CARBO-02 AMMONIA .2000000000
   BPVAL ACETO-01 WATER 1.500000000
   BPVAL ACETO-01 PROPY-01 .2000000000
   BPVAL ACETO-01 ACETO-01 1.650000000
   BPVAL ACETO-01 ACRYL-01 1.650000000
   BPVAL ACETO-01 AMMONIA 1.400000000
   BPVAL ACRYL-01 WATER 1.500000000
   BPVAL ACRYL-01 PROPY-01 .2000000000
   BPVAL ACRYL-01 ACETO-01 1.650000000
   BPVAL ACRYL-01 ACRYL-01 1.650000000
   BPVAL ACRYL-01 AMMONIA 1.400000000

PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
```

```
   PROP-LIST NRTL
   BPVAL AMMONIA WATER -.1642422000 -1027.525000 .2000000000  &
      0.0 0.0 0.0 0.0 200.0000000
   BPVAL WATER AMMONIA -.5440720000 1678.469000 .2000000000  &
      0.0 0.0 0.0 0.0 200.0000000
   BPVAL WATER HYDRO-01 0.0 505.5000000 .3000000000 0.0 0.0  &
      0.0 10.00000000 110.0000000
   BPVAL HYDRO-01 WATER 0.0 0.0 .3000000000 0.0 0.0 0.0  &
      10.00000000 110.0000000
   BPVAL WATER CARBO-02 10.06400000 -3268.135000 .2000000000  &
      0.0 0.0 0.0 0.0 200.0000000
   BPVAL CARBO-02 WATER 10.06400000 -3268.135000 .2000000000  &
      0.0 0.0 0.0 0.0 200.0000000

STREAM 1
   SUBSTREAM MIXED TEMP=80. PRES=14.7 <psi>
   MOLE-FLOW AMMONIA 85.

STREAM 2
   SUBSTREAM MIXED TEMP=80. PRES=14.7 <psi>
   MOLE-FLOW OXYGE-01 129.

STREAM 3
   SUBSTREAM MIXED TEMP=80. PRES=14.7 <psi>
   MOLE-FLOW PROPY-01 85.

STREAM 7
   SUBSTREAM MIXED TEMP=86. PRES=14.7 <psi>
   MOLE-FLOW WATER 0.21 / SULFU-01 11.

STREAM 13
   SUBSTREAM MIXED TEMP=45. PRES=1. <atm>
   MOLE-FLOW WATER 120.

BLOCK B1 MIXER
   PARAM

BLOCK B3 MIXER
   PARAM

BLOCK B17 MIXER
   PARAM

BLOCK B6 HEATER
   PARAM TEMP=70. PRES=20.
```

```
BLOCK B7 HEATER
   PARAM TEMP=70. PRES=20.

BLOCK B9 HEATER
   PARAM TEMP=173. PRES=20.

BLOCK B11 HEATER
   PARAM TEMP=127. PRES=15.

BLOCK B14 HEATER
   PARAM TEMP=70. PRES=15.

BLOCK B5 FLASH2
   PARAM TEMP=359. PRES=23.99

BLOCK B8 RADFRAC
   PARAM NSTAGE=15 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS 11 15 ON-STAGE / 12 1
   PRODUCTS 14 1 V / 15 15 L
   P-SPEC 1 15. / 2 20.
   COL-SPECS B:F=0.85 MOLE-RR=4.

BLOCK B10 RADFRAC
   PARAM NSTAGE=30 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 16 10 ON-STAGE
   PRODUCTS 17 1 L / 18 30 L
   P-SPEC 1 15.
   COL-SPECS D:F=0.17 MOLE-RR=7.

BLOCK B13 RADFRAC
   PARAM NSTAGE=15 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 19 7
   PRODUCTS 21 15 L / 22 1 L
   P-SPEC 1 14.7
   COL-SPECS D:F=0.08 MOLE-RR=1.18

BLOCK B15 RADFRAC
   PARAM NSTAGE=12 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
   COL-CONFIG CONDENSER=PARTIAL-V
```

```
   FEEDS 21 11
   PRODUCTS 24 1 V / 25 12 L
   P-SPEC 1 14.7
   COL-SPECS D:F=0.016 MOLE-RR=4.

BLOCK B16 RADFRAC
   PARAM NSTAGE=35 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 25 15
   PRODUCTS 26 1 L / 27 35 L
   P-SPEC 1 12.
   COL-SPECS D:F=0.78 MOLE-RR=4.

BLOCK B4 RSTOIC
   PARAM TEMP=170. PRES=15. <psi>
   STOIC 1 MIXED AMMONIA -2. / SULFU-01 -1. / AMMON-01 1.
   CONV 1 MIXED AMMONIA 0.96

BLOCK B2 RPLUG
   PARAM TYPE=T-SPEC NTUBE=20 LENGTH=19. DIAM=1.083333333
   T-SPEC 0.0 852.
   REACTIONS RXN-IDS=R-1

EO-CONV-OPTI

STREAM-REPOR MOLEFLOW

REACTIONS R-1 POWERLAW
   REAC-DATA 1 PHASE=V
   REAC-DATA 2 PHASE=V
   REAC-DATA 3 PHASE=V
   REAC-DATA 4 PHASE=V
   REAC-DATA 5 PHASE=V
   REAC-DATA 6 PHASE=V
   RATE-CON 1 PRE-EXP=157498. ACT-ENERGY=34200. TEMP-EXPONEN=0.
   RATE-CON 2 PRE-EXP=3778. ACT-ENERGY=34200.
   RATE-CON 3 PRE-EXP=1.99 ACT-ENERGY=12600.
   RATE-CON 4 PRE-EXP=780.82 ACT-ENERGY=12600.
   RATE-CON 5 PRE-EXP=108308. ACT-ENERGY=35640.
   RATE-CON 6 PRE-EXP=8.3658 ACT-ENERGY=12600.
   STOIC 1 MIXED PROPY-01 -1. / AMMONIA -1. / OXYGE-01  &
      -1.5 / ACRYL-01 1. / WATER 3.
   STOIC 2 MIXED PROPY-01 -1. / OXYGE-01 -1. / ACROL-01 1. / &
      WATER 1.
   STOIC 3 MIXED PROPY-01 -1. / AMMONIA -1. / OXYGE-01  &
```

```
        -2.25 / ACETO-01 1. / CARBO-02 0.5 / CARBO-01 0.5 /  &
        WATER 3.
    STOIC 4 MIXED ACROL-01 -1. / AMMONIA -1. / OXYGE-01  &
        -0.5 / ACRYL-01 1. / WATER 2.
    STOIC 5 MIXED ACRYL-01 -1. / OXYGE-01 -2. / CARBO-01 1. / &
        CARBO-02 1. / WATER 1. / HYDRO-01 1.
    STOIC 6 MIXED ACETO-01 -1. / OXYGE-01 -1.5 / CARBO-02  &
        1. / HYDRO-01 1. / WATER 1.
    POWLAW-EXP 1 MIXED PROPY-01 1.
    POWLAW-EXP 2 MIXED PROPY-01 1.
    POWLAW-EXP 3 MIXED PROPY-01 1.
    POWLAW-EXP 4 MIXED ACROL-01 1.
    POWLAW-EXP 5 MIXED ACRYL-01 1.
    POWLAW-EXP 6 MIXED ACETO-01 1.
;
;
;
;
;
```

OPTIMIZED ACRYLONITRILE INPUT FILE

```
DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS SI

DEF-STREAMS CONVEN ALL

SIM-OPTIONS MASS-BAL-CHE=YES OLD-DATABANK=YES

MODEL-OPTION

DATABANKS PURE28  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURE28  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    AMMONIA H3N /
    WATER H2O /
    HYDRO-01 CHN /
    CARBO-01 CO /
    OXYGE-01 O2 /
    PROPY-01 C3H6-2 /
    CARBO-02 CO2 /
```

```
    ACETO-01 C2H3N /
    ACRYL-01 C3H3N /
    ACROL-01 C3H4O /
    SULFU-01 H2SO4 /
    AMMON-01 "(NH4)2SO4"

SOLVE
    RUN-MODE MODE=SIM

FLOWSHEET
    BLOCK M-301 IN=OXYGEN PROPYLEN AMMONIA 13 OUT=4
    BLOCK R-301 IN=4 OUT=5
    BLOCK M-302 IN=5 H2SO4 OUT=6
    BLOCK R-302 IN=6 OUT=8
    BLOCK T-301 IN=8 OUT=10 9
    BLOCK E-301 IN=10 OUT=11
    BLOCK T-302 IN=11 39 OUT=14 16
    BLOCK E-303 IN=18 OUT=15
    BLOCK T-303 IN=16 OUT=21 18
    BLOCK T-305 IN=21 OUT=24 25
    BLOCK T-306 IN=25 OUT=ACRYL 27
    BLOCK B17 IN=9 24 1 20 OUT=WASTES
    BLOCK T-307 IN=14 OUT=1 2
    BLOCK B7 IN=2 OUT=3
    BLOCK T-308 IN=3 OUT=7 20
    BLOCK B9 IN=7 OUT=13
    BLOCK B5 IN=15 27 OUT=38 39
```

```
PROPERTIES ELECNRTL
    PROPERTIES ENRTL-RK

PROP-DATA HOCETA-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
    PROP-LIST HOCETA
    BPVAL AMMONIA WATER .2000000000
    BPVAL AMMONIA PROPY-01 .2000000000
    BPVAL AMMONIA CARBO-02 .2000000000
    BPVAL AMMONIA ACETO-01 1.400000000
    BPVAL AMMONIA ACRYL-01 1.400000000
    BPVAL WATER WATER 1.700000000
    BPVAL WATER CARBO-02 .3000000000
    BPVAL WATER ACETO-01 1.500000000
    BPVAL WATER ACRYL-01 1.500000000
    BPVAL WATER AMMONIA .2000000000
    BPVAL PROPY-01 ACETO-01 .2000000000
    BPVAL PROPY-01 ACRYL-01 .2000000000
    BPVAL PROPY-01 AMMONIA .2000000000
    BPVAL CARBO-02 WATER .3000000000
    BPVAL CARBO-02 CARBO-02 .1600000000
    BPVAL CARBO-02 AMMONIA .2000000000
    BPVAL ACETO-01 WATER 1.500000000
    BPVAL ACETO-01 PROPY-01 .2000000000
    BPVAL ACETO-01 ACETO-01 1.650000000
```

```
    BPVAL ACETO-01 ACRYL-01 1.650000000
    BPVAL ACETO-01 AMMONIA 1.400000000
    BPVAL ACRYL-01 WATER 1.500000000
    BPVAL ACRYL-01 PROPY-01 .2000000000
    BPVAL ACRYL-01 ACETO-01 1.650000000
    BPVAL ACRYL-01 ACRYL-01 1.650000000
    BPVAL ACRYL-01 AMMONIA 1.400000000

PROP-DATA NRTL-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
    PROP-LIST NRTL
    BPVAL AMMONIA WATER -.1642422000 -1027.525000 .2000000000  &
        0.0 0.0 0.0 0.0 200.0000000
    BPVAL WATER AMMONIA -.5440720000 1678.469000 .2000000000  &
        0.0 0.0 0.0 0.0 200.0000000
    BPVAL WATER HYDRO-01 0.0 505.5000000 .3000000000 0.0 0.0  &
        0.0 10.00000000 110.0000000
    BPVAL HYDRO-01 WATER 0.0 0.0 .3000000000 0.0 0.0 0.0  &
        10.00000000 110.0000000
    BPVAL WATER CARBO-02 10.06400000 -3268.135000 .2000000000  &
        0.0 0.0 0.0 0.0 200.0000000
    BPVAL CARBO-02 WATER 10.06400000 -3268.135000 .2000000000  &
        0.0 0.0 0.0 0.0 200.0000000

DEF-STREAMS CONVEN 38
```

```
STREAM AMMONIA
    SUBSTREAM MIXED TEMP=299.8166667 PRES=1.03421359E+5
    MOLE-FLOW AMMONIA 9.44984104E-3

STREAM H2SO4
    SUBSTREAM MIXED TEMP=303.1500000 PRES=1.01352932E+5
    MOLE-FLOW WATER 2.64595549E-5 / SULFU-01 0.00052599788

STREAM OXYGEN
    SUBSTREAM MIXED TEMP=299.8166667 PRES=1.03421359E+5
    MOLE-FLOW OXYGE-01 .0163797244

STREAM PROPYLEN
    SUBSTREAM MIXED TEMP=299.8166667 PRES=1.03421359E+5
    MOLE-FLOW PROPY-01 8.81985164E-3

BLOCK B17 MIXER
    PARAM

BLOCK M-301 MIXER
    PARAM PRES=1.01352932E+5

BLOCK M-302 MIXER
    PARAM

BLOCK B5 FSPLIT
    MOLE-FLOW 39 .0151197456
```

```
BLOCK B7 HEATER
   PARAM TEMP=299.8166667 PRES=1.03421359E+5

BLOCK B9 HEATER
   PARAM TEMP=299.8166667 PRES=1.03421359E+5

BLOCK E-301 HEATER
   PARAM TEMP=349.8166667 PRES=1.37895146E+5

BLOCK E-303 HEATER
   PARAM TEMP=349.8166667 PRES=1.37895146E+5

BLOCK T-301 FLASH2
   PARAM TEMP=449.8166667 PRES=1.03421359E+5

BLOCK T-307 DSTWU
   PARAM LIGHTKEY=CARBO-02 RECOVL=0.99 HEAVYKEY=PROPY-01  &
      RECOVH=0.01 PTOP=1.01352932E+5 PBOT=1.01352932E+5 RDV=1.0  &
      NSTAGE=10 PACK-HEIGHT=3.048000000 PLOT=YES

BLOCK T-308 DSTWU
   PARAM LIGHTKEY=PROPY-01 RECOVL=0.99 HEAVYKEY=HYDRO-01  &
      RECOVH=0.01 PTOP=1.01352932E+5 PBOT=1.01352932E+5  &
      NSTAGE=15

BLOCK T-302 RADFRAC
   PARAM NSTAGE=15 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
```

```
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 11 15 ABOVE-STAGE / 39 1
    PRODUCTS 14 1 V / 16 15 L
    P-SPEC 1 1.01352932E+5
    COL-SPECS B:F=0.85 MOLE-RR=2.4

BLOCK T-303 RADFRAC
    PARAM NSTAGE=30 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
    COL-CONFIG CONDENSER=TOTAL
    FEEDS 16 10 ABOVE-STAGE
    PRODUCTS 18 30 L / 21 1 L
    P-SPEC 1 1.03421359E+5
    COL-SPECS D:F=0.16 MOLE-RR=10.5

BLOCK T-305 RADFRAC
    PARAM NSTAGE=12 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 21 11
    PRODUCTS 24 1 V / 25 12 L
    P-SPEC 1 1.01352932E+5
    COL-SPECS D:F=0.113 MOLE-RR=10.

BLOCK T-306 RADFRAC
    PARAM NSTAGE=35 ALGORITHM=STANDARD MAXOL=25
DAMPING=NONE
    COL-CONFIG CONDENSER=TOTAL
```

```
    FEEDS 25 15
    PRODUCTS ACRYL 1 L / 27 35 L
    P-SPEC 1 82737.08752
    COL-SPECS D:F=0.87 MOLE-RR=3.

BLOCK R-302 RSTOIC
    PARAM TEMP=349.8166667 PRES=1.03421359E+5
    STOIC 1 MIXED AMMONIA -2. / SULFU-01 -1. / AMMON-01 1.
    CONV 1 MIXED AMMONIA 0.96

BLOCK R-301 RPLUG
    PARAM TYPE=T-SPEC NTUBE=20 LENGTH=3.048000000  &
        DIAM=.5486400000
    T-SPEC 0.0 728.7055556
    REACTIONS RXN-IDS=R-1

EO-CONV-OPTI

SENSITIVITY BSMILLAH
    IN-UNITS ENG
    DEFINE NH3 STREAM-VAR STREAM=AMMONIA SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE O2 STREAM-VAR STREAM=OXYGEN SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE C3H6 STREAM-VAR STREAM=PROPYLEN SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE H2O STREAM-VAR STREAM=38 SUBSTREAM=MIXED  &
```

```
    VARIABLE=MASS-FLOW
  DEFINE SULACID STREAM-VAR STREAM=H2SO4 SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE MNH3 STREAM-VAR STREAM=AMMONIA SUBSTREAM=MIXED  &
    VARIABLE=MOLE-FLOW
  DEFINE MO2 STREAM-VAR STREAM=OXYGEN SUBSTREAM=MIXED  &
    VARIABLE=MOLE-FLOW
  DEFINE  MC3H6  STREAM-VAR  STREAM=PROPYLEN  SUBSTREAM=MIXED
&
    VARIABLE=MOLE-FLOW
  DEFINE ACRYL2 MOLE-FLOW STREAM=5 SUBSTREAM=MIXED  &
    COMPONENT=ACRYL-01
  DEFINE WATERR MOLE-FLOW STREAM=18 SUBSTREAM=MIXED  &
    COMPONENT=WATER
  DEFINE ACRYL STREAM-VAR STREAM=ACRYL SUBSTREAM=MIXED  &
    VARIABLE=MASS-FLOW
  DEFINE WASTEFIN STREAM-VAR STREAM=WASTES SUBSTREAM=MIXED
&
    VARIABLE=MASS-FLOW
  DEFINE ACE MOLE-FLOW STREAM=21 SUBSTREAM=MIXED  &
    COMPONENT=ACRYL-01
  DEFINE ACE1 MOLE-FLOW STREAM=16 SUBSTREAM=MIXED  &
    COMPONENT=ACRYL-01
  DEFINE COND BLOCK-VAR BLOCK=T-302 VARIABLE=COND-DUTY  &
    SENTENCE=RESULTS
  DEFINE REB BLOCK-VAR BLOCK=T-302 VARIABLE=REB-DUTY  &
    SENTENCE=RESULTS
  DEFINE ACET MOLE-FLOW STREAM=27 SUBSTREAM=MIXED  &
```

```
        COMPONENT=ACETO-01
     DEFINE Q3 BLOCK-VAR BLOCK=R-301 VARIABLE=QCALC  &
        SENTENCE=PARAM
     DEFINE Q4 BLOCK-VAR BLOCK=T-306 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
     DEFINE Q5 BLOCK-VAR BLOCK=T-306 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
     DEFINE Q6 BLOCK-VAR BLOCK=T-305 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
     DEFINE Q7 BLOCK-VAR BLOCK=T-305 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
     DEFINE HCN MOLE-FLOW STREAM=24 SUBSTREAM=MIXED  &
        COMPONENT=HYDRO-01
     DEFINE MPROP MOLE-FLOW STREAM=5 SUBSTREAM=MIXED  &
        COMPONENT=PROPY-01
F       TWASTE =WASTEFIN
F       CNH3 = 0.17
F       C02 = 0.05
F       CPROP = 0.44
F       CH2SO4 = 0.037
F       CH2O = 3.039E-5
F       CACRYL = 1.18
F       CACETO = 0.997
F       CWASTE = 0.016364
F
F       RAW = (CNH3*NH3+ CO2*O2+CPROP*PROP+CH2SO4*H2SO4)*24*365
F       REV = (CACRYL*ACRYL+CH20*H20)*24*365
```

```
F      MVA = REV -RAW-(CWASTE*TWASTE)
F
F      OBYP=MO2/MPROP
F      PBYN=MPROP/MNH3
F      OBYN=MO2/MNH3
F
F      CONV=(MPROP-MPROP2)/MPROP*100
F
F
F      ACRR = (ACE/ACE1)*100
F      TOT = (Q5*(8.77E-6)+Q7*(8.77E-6)+Q3*(-8.77E-6))*365*24
F      TOTALQ = (( Q4* (4.31E-6)+Q6*(4.31E-6))*365*24) +TOT
F
   TABULATE 1 "TWASTE"
   TABULATE 2 "RAW"
   TABULATE 3 "REV"
   TABULATE 4 "MVA"
   TABULATE 5 "ACRYL2"
   TABULATE 6 "CONV"
   TABULATE 7 "WATERR"
   TABULATE 8 "ACRR"
   TABULATE 9 "ACE3"
   TABULATE 10 "ACET"
   TABULATE 11 "HCN"
   TABULATE 12 "COND"
   TABULATE 13 "REB"
   TABULATE 14 "TOTALQ"
```

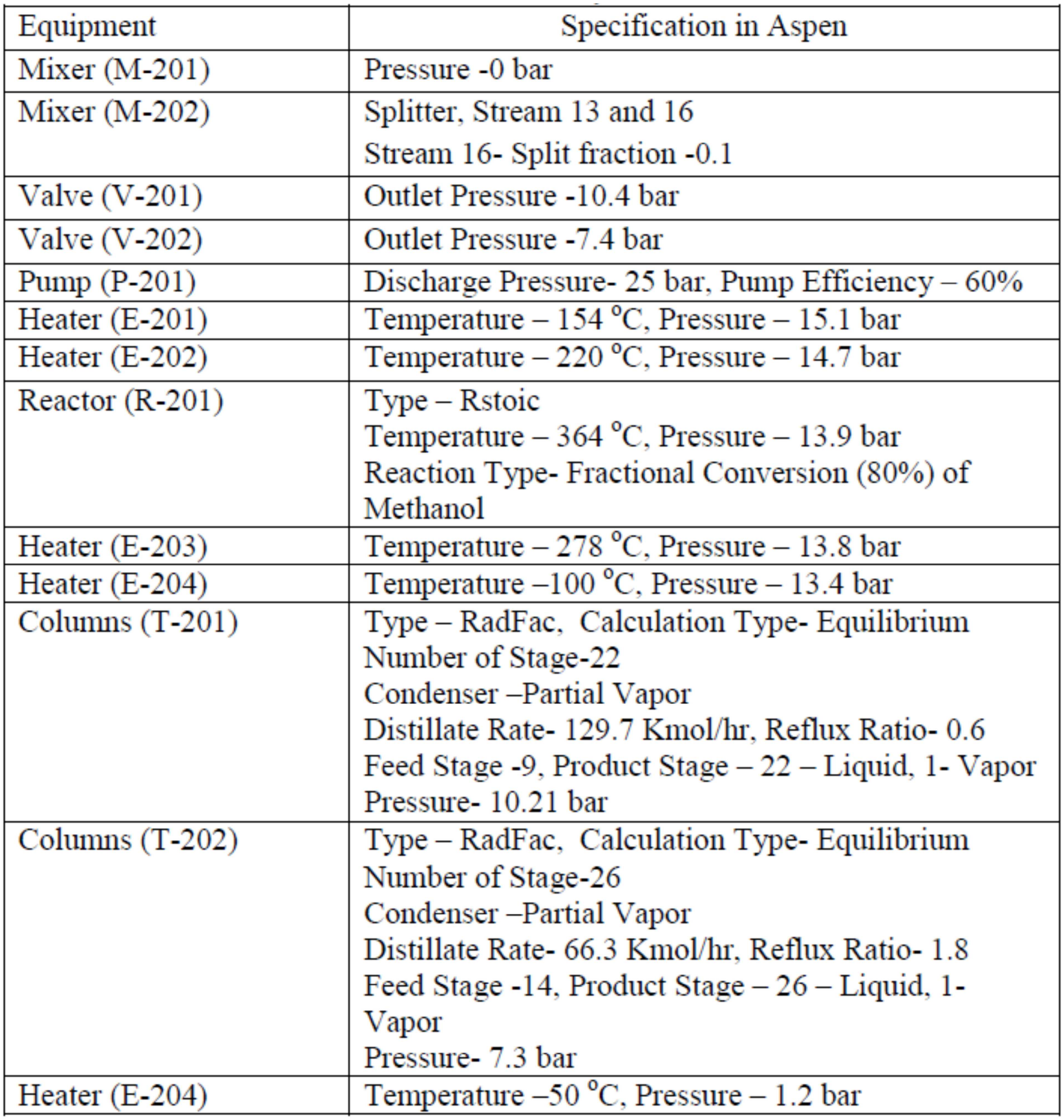
```
    VARY STREAM-VAR STREAM=AMMONIA SUBSTREAM=MIXED  &
        VARIABLE=MOLE-FLOW
    RANGE LOWER="75" UPPER="85" INCR="1"

STREAM-REPOR MOLEFLOW MASSFLOW
REACTIONS R-1 POWERLAW
    REAC-DATA 1 PHASE=V
    REAC-DATA 2 PHASE=V
    REAC-DATA 3 PHASE=V
    REAC-DATA 4 PHASE=V
    REAC-DATA 5 PHASE=V
    REAC-DATA 6 PHASE=V
    RATE-CON 1 PRE-EXP=157498. ACT-ENERGY=7.95492000E+7  &
        TEMP-EXPONEN=0.
    RATE-CON 2 PRE-EXP=3778. ACT-ENERGY=7.95492000E+7
    RATE-CON 3 PRE-EXP=1.99 ACT-ENERGY=2.93076000E+7
    RATE-CON 4 PRE-EXP=780.82 ACT-ENERGY=2.93076000E+7
    RATE-CON 5 PRE-EXP=108308. ACT-ENERGY=8.28986400E+7
    RATE-CON 6 PRE-EXP=8.3658 ACT-ENERGY=2.93076000E+7
    STOIC 1 MIXED PROPY-01 -1. / AMMONIA -1. / OXYGE-01  &
        -1.5 / ACRYL-01 1. / WATER 3.
    STOIC 2 MIXED PROPY-01 -1. / OXYGE-01 -1. / ACROL-01 1. / &
        WATER 1.
    STOIC 3 MIXED PROPY-01 -1. / AMMONIA -1. / OXYGE-01  &
        -2.25 / ACETO-01 1. / CARBO-02 0.5 / CARBO-01 0.5 /  &
        WATER 3.
    STOIC 4 MIXED ACROL-01 -1. / AMMONIA -1. / OXYGE-01  &
```

```
      -0.5 / ACRYL-01 1. / WATER 2.
   STOIC 5 MIXED ACRYL-01 -1. / OXYGE-01 -2. / CARBO-01 1. / &
      CARBO-02 1. / WATER 1. / HYDRO-01 1.
   STOIC 6 MIXED ACETO-01 -1. / OXYGE-01 -1.5 / CARBO-02  &
      1. / HYDRO-01 1. / WATER 1.
   POWLAW-EXP 1 MIXED PROPY-01 1.
   POWLAW-EXP 2 MIXED PROPY-01 1.
   POWLAW-EXP 3 MIXED PROPY-01 1.
   POWLAW-EXP 4 MIXED ACROL-01 1.
   POWLAW-EXP 5 MIXED ACRYL-01 1.
   POWLAW-EXP 6 MIXED ACETO-01 1.
;
;
;
;
;
```

APPENDIX B: PROCESS FLOW DIAGRAM, STREAM SUMMARY TABLE, EQUIPMENT SPECIFICATION FOR THE FOLLOWING CASE STUDIES: DIMETHYL ETHER AND ACRYLONITRILE

Table B1: ASPEN PLUS Equipment Specification Summary Table for DME Production via Methanol Dehydration (Shadiya, 2010a)



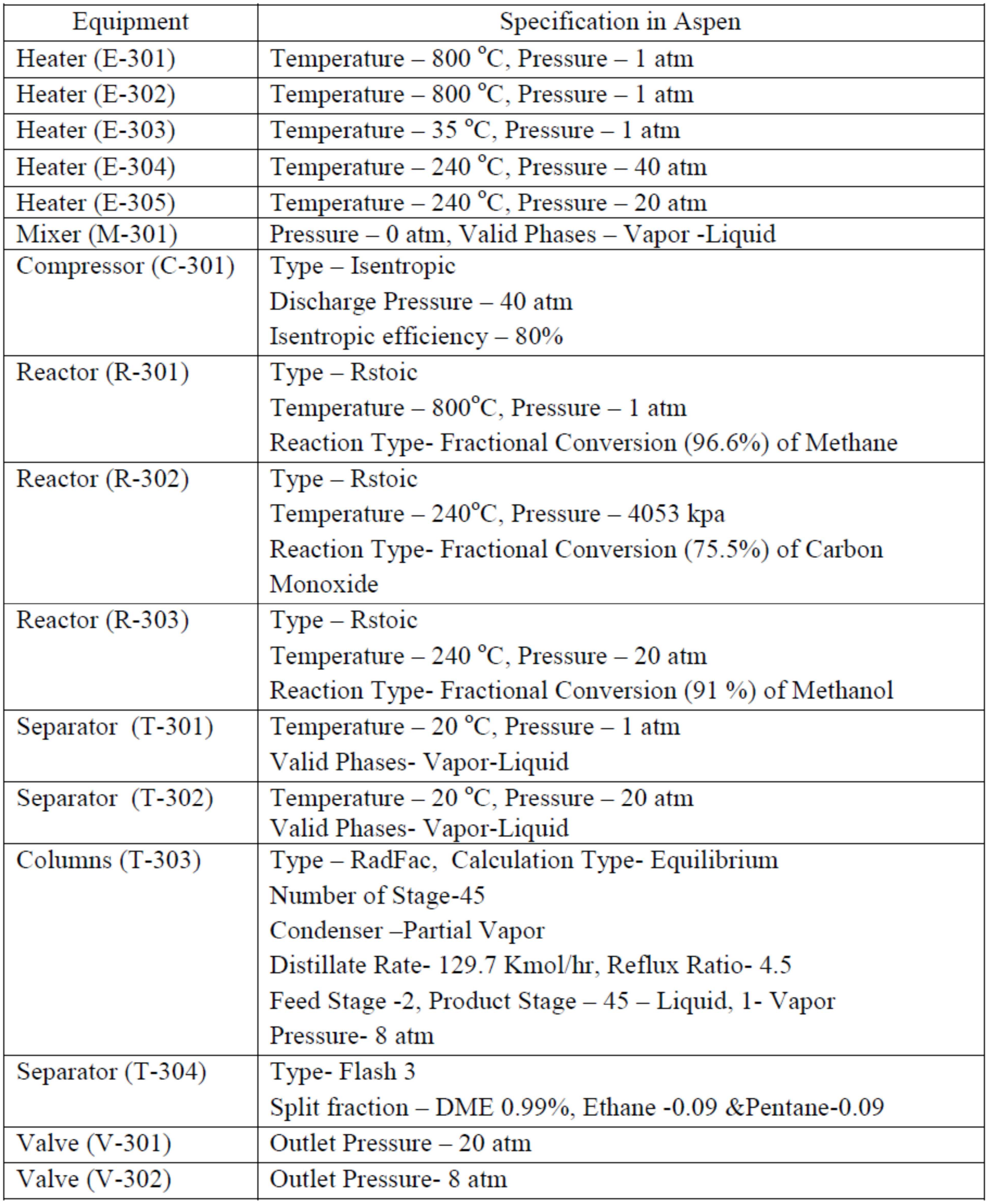
Equipment	Specification in Aspen
Mixer (M-201)	Pressure -0 bar
Mixer (M-202)	Splitter, Stream 13 and 16 Stream 16- Split fraction -0.1
Valve (V-201)	Outlet Pressure -10.4 bar
Valve (V-202)	Outlet Pressure -7.4 bar
Pump (P-201)	Discharge Pressure- 25 bar, Pump Efficiency – 60%
Heater (E-201)	Temperature – 154 ^{o}C, Pressure – 15.1 bar
Heater (E-202)	Temperature – 220 ^{o}C, Pressure – 14.7 bar
Reactor (R-201)	Type – Rstoic Temperature – 364 ^{o}C, Pressure – 13.9 bar Reaction Type- Fractional Conversion (80%) of Methanol
Heater (E-203)	Temperature – 278 ^{o}C, Pressure – 13.8 bar
Heater (E-204)	Temperature –100 ^{o}C, Pressure – 13.4 bar
Columns (T-201)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-22 Condenser –Partial Vapor Distillate Rate- 129.7 Kmol/hr, Reflux Ratio- 0.6 Feed Stage -9, Product Stage – 22 – Liquid, 1- Vapor Pressure- 10.21 bar
Columns (T-202)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-26 Condenser –Partial Vapor Distillate Rate- 66.3 Kmol/hr, Reflux Ratio- 1.8 Feed Stage -14, Product Stage – 26 – Liquid, 1- Vapor Pressure- 7.3 bar
Heater (E-204)	Temperature –50 ^{o}C, Pressure – 1.2 bar

Table B2: Stream Summary Table for DME Production via Methanol Dehydration

	DME	FEED	PURGE	RECYCLE	S2	S3	S4	S5
Substream: MIXED								
Mole Flow lbmol/hr								
METHANOL	0.72	572.54	1.13	140.55	572.54	713.09	713.09	713.09
WATER	0.00	5.51	0.02	2.47	5.51	7.98	7.98	7.98
DIMET-01	285.22	0.00	0.02	1.98	0.00	1.98	1.98	1.98
Total Flow lbmol/hr	285.94	578.05	1.17	145.00	578.05	723.05	723.05	723.05
Total Flow lb/hr	13162.86	18444.73	37.41	4639.14	18444.73	23083.86	23083.86	23083.86
Total Flow cuft/hr	10262.40	372.30	79.29	9831.49	372.91	534.94	22849.89	29967.58
Temperature F	114.77	77.00	257.35	257.35	78.98	218.66	309.20	428.00
Pressure psia	148.13	14.50	106.07	106.07	362.59	106.07	219.01	213.21

	S6	S7	S8	S9	S10	S12	S13	S16
Substream: MIXED								
Mole Flow lbmol/hr								
METHANOL	142.62	142.62	142.62	142.62	141.90	0.22	141.68	1.35
WATER	293.22	293.22	293.22	293.22	293.22	290.73	2.49	290.75
DIMET-01	287.21	287.21	287.21	287.21	1.99	0.00	1.99	0.02
Total Flow lbmol/hr	723.05	723.05	723.05	723.05	437.11	290.94	146.17	292.11
Total Flow lb/hr	23083.86	23083.86	23083.86	23083.86	9921.01	5244.47	4676.54	5281.88
Total Flow cuft/hr	43118.53	37060.54	562.93	2239.56	219.29	99.62	9910.77	203.61
Temperature F	687.20	532.40	212.00	198.63	311.06	331.98	257.35	330.58
Pressure psia	201.60	200.15	194.35	150.84	148.13	106.07	106.07	106.07

Table B3: ASPEN PLUS Equipment Specification Summary Table for DME Production via Natural Gas (Shadiya, 2010a)



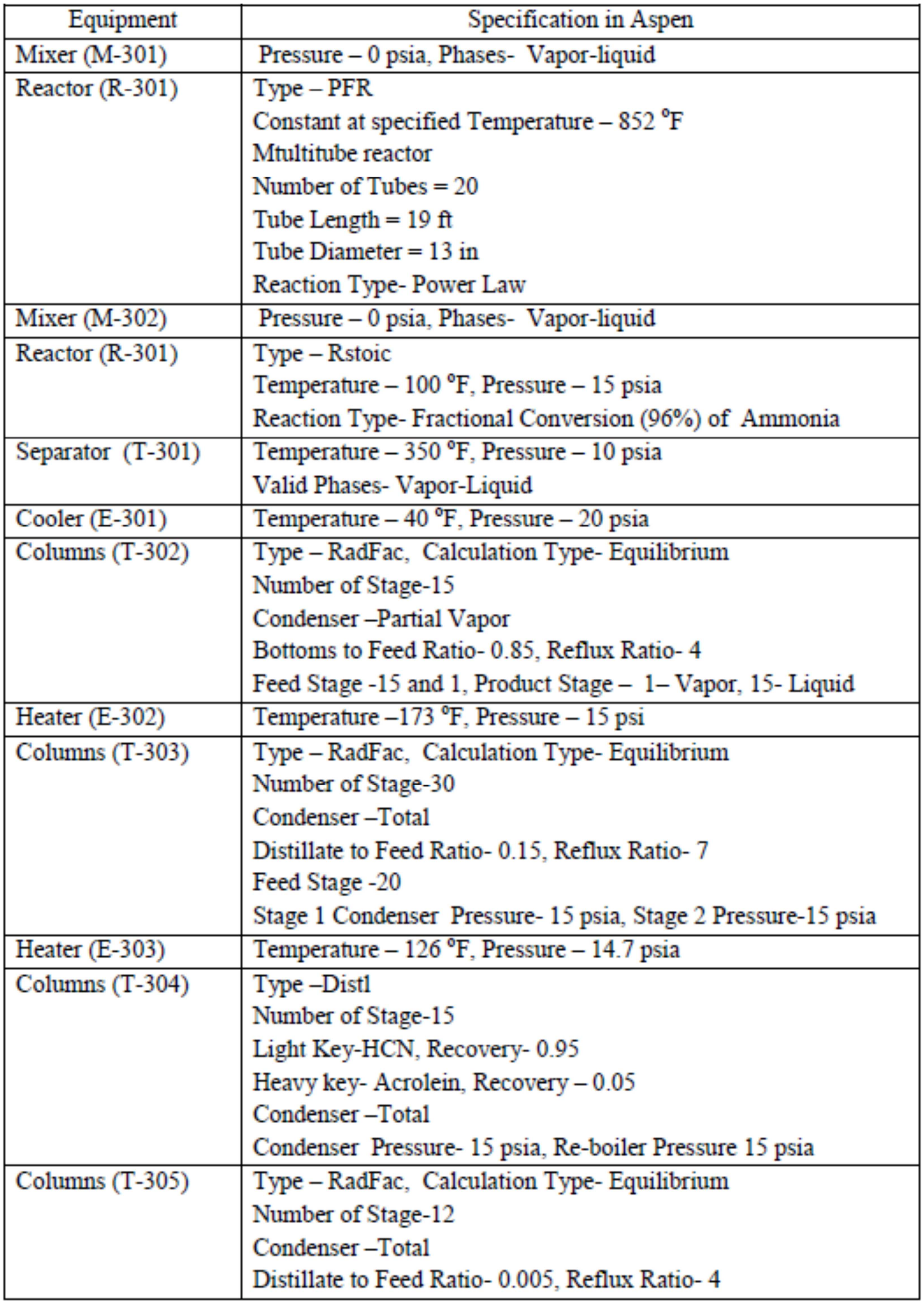
Equipment	Specification in Aspen
Heater (E-301)	Temperature – 800 °C, Pressure – 1 atm
Heater (E-302)	Temperature – 800 °C, Pressure – 1 atm
Heater (E-303)	Temperature – 35 °C, Pressure – 1 atm
Heater (E-304)	Temperature – 240 °C, Pressure – 40 atm
Heater (E-305)	Temperature – 240 °C, Pressure – 20 atm
Mixer (M-301)	Pressure – 0 atm, Valid Phases – Vapor -Liquid
Compressor (C-301)	Type – Isentropic Discharge Pressure – 40 atm Isentropic efficiency – 80%
Reactor (R-301)	Type – Rstoic Temperature – 800°C, Pressure – 1 atm Reaction Type- Fractional Conversion (96.6%) of Methane
Reactor (R-302)	Type – Rstoic Temperature – 240°C, Pressure – 4053 kpa Reaction Type- Fractional Conversion (75.5%) of Carbon Monoxide
Reactor (R-303)	Type – Rstoic Temperature – 240 °C, Pressure – 20 atm Reaction Type- Fractional Conversion (91 %) of Methanol
Separator (T-301)	Temperature – 20 °C, Pressure – 1 atm Valid Phases- Vapor-Liquid
Separator (T-302)	Temperature – 20 °C, Pressure – 20 atm Valid Phases- Vapor-Liquid
Columns (T-303)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-45 Condenser –Partial Vapor Distillate Rate- 129.7 Kmol/hr, Reflux Ratio- 4.5 Feed Stage -2, Product Stage – 45 – Liquid, 1- Vapor Pressure- 8 atm
Separator (T-304)	Type- Flash 3 Split fraction – DME 0.99%, Ethane -0.09 &Pentane-0.09
Valve (V-301)	Outlet Pressure – 20 atm
Valve (V-302)	Outlet Pressure- 8 atm

Table B4: Stream Summary Table for DME Production via Natural Gas

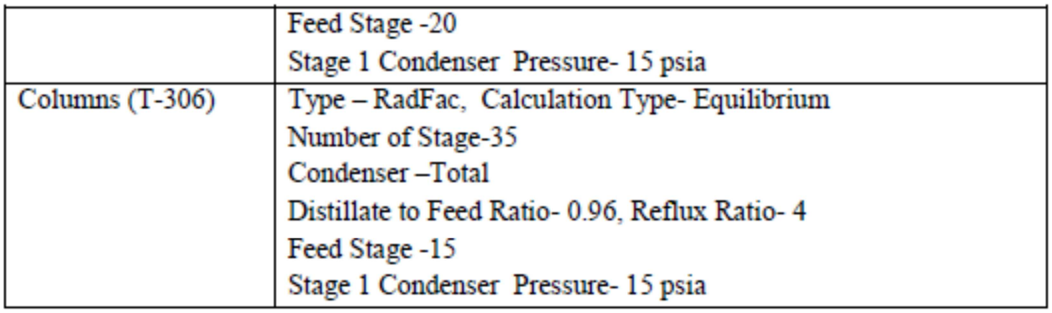
	3	4	5	6	7	8	9	10	11	12	13
Substream: MIXED											
Mole Flow lbmol/hr											
WATER	0.00	979.00	315.29	315.29	250.82	64.47	64.47	64.47	64.47	0.15	64.32
ETHANE	31.42	0.00	31.42	31.42	0.12	31.30	31.30	31.30	31.30	19.37	11.93
PROPANE	10.00	0.00	10.00	10.00	0.13	9.87	9.87	9.87	9.87	3.29	6.59
N-BUTANE	3.25	0.00	3.25	3.25	0.14	3.11	3.11	3.11	3.11	1.60	1.51
HYDROGEN	0.00	0.00	1991.14	1991.14	0.00	1991.14	1991.14	1991.14	796.80	796.80	0.00
CARBO-01	0.00	0.00	663.71	663.71	0.19	663.52	663.52	663.52	66.35	63.40	2.95
METHANOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	597.17	5.51	591.66
DIMET-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METHANE	687.07	0.00	23.36	23.36	0.04	23.32	23.32	23.32	23.32	18.72	4.60
OXYGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lbmol/hr	731.74	979.00	3038.17	3038.17	251.44	2786.74	2786.74	2786.74	1592.40	908.83	683.56
Total Flow lb/hr	12597.21	17636.98	30234.19	30234.19	4542.08	25692.12	25692.12	25692.12	25692.12	4681.82	21010.30
Total Flow cuft/hr	1032390.00	1380510.00	4286390.00	1168090.00	73.05	1074140.00	84866.15	47691.51	26309.87	17689.59	428.32
Temperature F	1472.00	1472.00	1472.00	95.00	68.00	68.00	1192.02	464.00	464.00	68.00	68.00
Pressure psia	14.70	14.70	14.70	14.70	14.70	14.70	587.84	587.84	587.84	293.92	293.92

	14	DME	METHANE	S1	S2	S3	S5	WASTE	WATER
Substream: MIXED									
Mole Flow lbmol/hr									
WATER	64.32	0.00	0.00	64.47	336.49	336.49	336.49	587.45	979.00
ETHANE	11.93	11.93	31.42	31.30	11.93	11.93	0.00	19.49	0.00
PROPANE	6.59	6.55	10.00	9.87	6.59	6.59	0.04	3.45	0.00
N-BUTANE	1.51	1.51	3.25	3.11	1.51	1.51	0.00	1.74	0.00
HYDROGEN	0.00	0.00	0.00	796.80	0.00	0.00	0.00	796.80	0.00
CARBO-01	2.95	2.95	0.00	66.35	2.95	2.95	0.00	63.59	0.00
METHANOL	591.66	2.25	0.00	597.17	47.33	47.33	45.09	50.60	0.00
DIMET-01	0.00	272.03	0.00	0.00	272.16	272.16	0.14	0.14	0.00
METHANE	4.60	4.60	687.07	23.32	4.60	4.60	0.00	18.76	0.00
OXYGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lbmol/hr	683.56	301.81	731.74	1592.40	683.56	683.56	381.75	1542.02	979.00
Total Flow lb/hr	21010.30	13495.69	12597.21	25692.12	21010.30	21010.30	7514.62	16738.51	17636.98
Total Flow cuft/hr	21116.15	13665.77	295805.00	52632.03	21612.69	55323.11	150.36	399155.00	287.04
Temperature F	464.00	97.64	95.00	455.66	464.00	450.27	309.31	96.93	95.00
Pressure psia	293.92	117.57	14.70	293.92	293.92	117.57	117.57	14.70	14.70

Table B5: Base Case Acrylonitrile Process Equipment Specification (Shadiya, 2010a)



Equipment	Specification in Aspen
Mixer (M-301)	Pressure – 0 psia, Phases- Vapor-liquid
Reactor (R-301)	Type – PFR Constant at specified Temperature – 852 °F Mtultitube reactor Number of Tubes = 20 Tube Length = 19 ft Tube Diameter = 13 in Reaction Type- Power Law
Mixer (M-302)	Pressure – 0 psia, Phases- Vapor-liquid
Reactor (R-301)	Type – Rstoic Temperature – 100 °F, Pressure – 15 psia Reaction Type- Fractional Conversion (96%) of Ammonia
Separator (T-301)	Temperature – 350 °F, Pressure – 10 psia Valid Phases- Vapor-Liquid
Cooler (E-301)	Temperature – 40 °F, Pressure – 20 psia
Columns (T-302)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-15 Condenser –Partial Vapor Bottoms to Feed Ratio- 0.85, Reflux Ratio- 4 Feed Stage -15 and 1, Product Stage – 1– Vapor, 15- Liquid
Heater (E-302)	Temperature –173 °F, Pressure – 15 psi
Columns (T-303)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-30 Condenser –Total Distillate to Feed Ratio- 0.15, Reflux Ratio- 7 Feed Stage -20 Stage 1 Condenser Pressure- 15 psia, Stage 2 Pressure-15 psia
Heater (E-303)	Temperature – 126 °F, Pressure – 14.7 psia
Columns (T-304)	Type –Distl Number of Stage-15 Light Key-HCN, Recovery- 0.95 Heavy key- Acrolein, Recovery – 0.05 Condenser –Total Condenser Pressure- 15 psia, Re-boiler Pressure 15 psia
Columns (T-305)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-12 Condenser –Total Distillate to Feed Ratio- 0.005, Reflux Ratio- 4



	Feed Stage -20 Stage 1 Condenser Pressure- 15 psia
Columns (T-306)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-35 Condenser –Total Distillate to Feed Ratio- 0.96, Reflux Ratio- 4 Feed Stage -15 Stage 1 Condenser Pressure- 15 psia

Table B6: Stream Summary Table for Acrylonitrile Production Base Case

	1	2	3	4	5	6	7	8	9	10
Substream: MIXED										
Mole Flow lbmol/hr										
AMMONIA	85	0	0	85	21.77	21.77	0	0.87	0.00	0.87
WATER	0	0	0	0	205.60	205.81	0.21	205.81	1.32	204.50
HYDRO-01	0	0	0	0	15.89	15.89	0	15.89	0.03	15.86
CARBO-01	0	0	0	0	16.93	16.93	0	16.93	0.00	16.93
OXYGE-01	0	129	0	129	0.35	0.35	0	0.35	0.00	0.35
PROPY-01	0	0	85	85	21.74	21.74	0	21.74	0.03	21.71
CARBO-02	0	0	0	0	17.37	17.37	0	17.37	0.01	17.36
ACETO-01	0	0	0	0	2.53	2.53	0	2.53	0.02	2.51
ACRYL-01	0	0	0	0	44.81	44.81	0	44.81	0.28	44.54
ACROL-01	0	0	0	0	0.03	0.03	0	0.03	0.00	0.03
SULFU-01	0	0	0	0	0.00	11.00	11	0.55	0.53	0.02
AMMON-01	0	0	0	0	0.00	0.00	0	10.45	10.45	0.00
Total Flow lbmol/hr	85	129	85	299	347.02	358.23	11.21	337.33	12.66	324.67
Total Flow lb/hr	1447.60	4127.85	3576.85	9152.30	9152.30	10234.95	1082.657	10234.95	1474.46	8760.49
Total Flow cuft/hr	33247.78	50785.02	33045.89	117153.00	331947.00	307864.00	9.65	56588.31	42.47	118018.00
Temperature F	80.00	80.00	80.00	79.65	852.00	719.51	86.00	170.00	359.00	359.00
Pressure psia	14.70	14.70	14.70	14.70	14.70	14.70	14.70	15.00	23.99	23.99

	11	12	13	14	15	16	17	18	19
Substream: MIXED									
Mole Flow lbmol/hr									
AMMONIA	0.87	0.00	0.00	0.09	0.78	0.78	0.78	0.00	0.78
WATER	204.50	120.00	120.00	0.13	324.37	324.37	11.86	312.51	11.86
HYDRO-01	15.86	0.00	0.00	12.53	3.33	3.33	3.33	0.00	3.33
CARBO-01	16.93	0.00	0.00	16.89	0.04	0.04	0.04	0.00	0.04
OXYGE-01	0.35	0.00	0.00	0.34	0.00	0.00	0.00	0.00	0.00
PROPY-01	21.71	0.00	0.00	19.49	2.22	2.22	2.22	0.00	2.22
CARBO-02	17.36	0.00	0.00	17.22	0.14	0.14	0.14	0.00	0.14
ACETO-01	2.51	0.00	0.00	0.00	2.51	2.51	2.20	0.31	2.20
ACRYL-01	44.54	0.00	0.00	0.00	44.54	44.54	43.66	0.88	43.66
ACROL-01	0.03	0.00	0.00	0.00	0.03	0.03	0.03	0.00	0.03
SULFU-01	0.02	0.00	0.00	0.00	0.02	0.02	0.00	0.02	0.00
AMMON-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lbmol/hr	324.67	120.00	120.00	66.70	377.97	377.97	64.25	313.72	64.25
Total Flow lb/hr	8760.49	2161.83	2161.83	2404.88	8517.45	8517.45	2826.13	5691.32	2826.13
Total Flow cuft/hr	10679.41	34.69	34.63	22872.38	156.38	154.23	56.18	95.48	810.88
Temperature F	70.00	70.00	45.00	24.64	195.39	173.00	93.54	212.87	127.00
Pressure psia	20.00	20.00	14.70	15	20	20	15	15	15

	21	22	23	24	25	26	27	28
Substream: MIXED								
Mole Flow lbmol/hr								
AMMONIA	0.00	0.78	0.78	0.00	0.00	0.00	0.00	0.87
WATER	11.86	0.00	0.00	0.00	11.86	0.00	11.86	1.45
HYDRO-01	1.53	1.80	1.80	0.54	0.99	0.99	0.00	14.90
CARBO-01	0.00	0.04	0.04	0.00	0.00	0.00	0.00	16.93
OXYGE-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
PROPY-01	0.00	2.22	2.22	0.00	0.00	0.00	0.00	21.74
CARBO-02	0.00	0.14	0.14	0.00	0.00	0.00	0.00	17.37
ACETO-01	2.20	0.00	0.00	0.01	2.19	1.75	0.44	0.03
ACRYL-01	43.50	0.16	0.16	0.40	43.11	42.62	0.49	0.83
ACROL-01	0.02	0.00	0.00	0.00	0.02	0.02	0.00	0.01
SULFU-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.53
AMMON-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.45
Total Flow lbmol/hr	59.11	5.14	5.14	0.95	58.17	45.37	12.80	85.45
Total Flow lb/hr	2655.01	171.12	171.12	36.02	2618.99	2360.98	258.01	4086.49
Total Flow cuft/hr	54.88	3.96	1917.20	403.55	54.21	48.91	4.53	33309.21
Temperature F	170.93	-59.11	70.00	137.29	173.52	155.53	198.73	166.53
Pressure psia	14.7	14.7	15	14.7	14.7	12	12	14.70

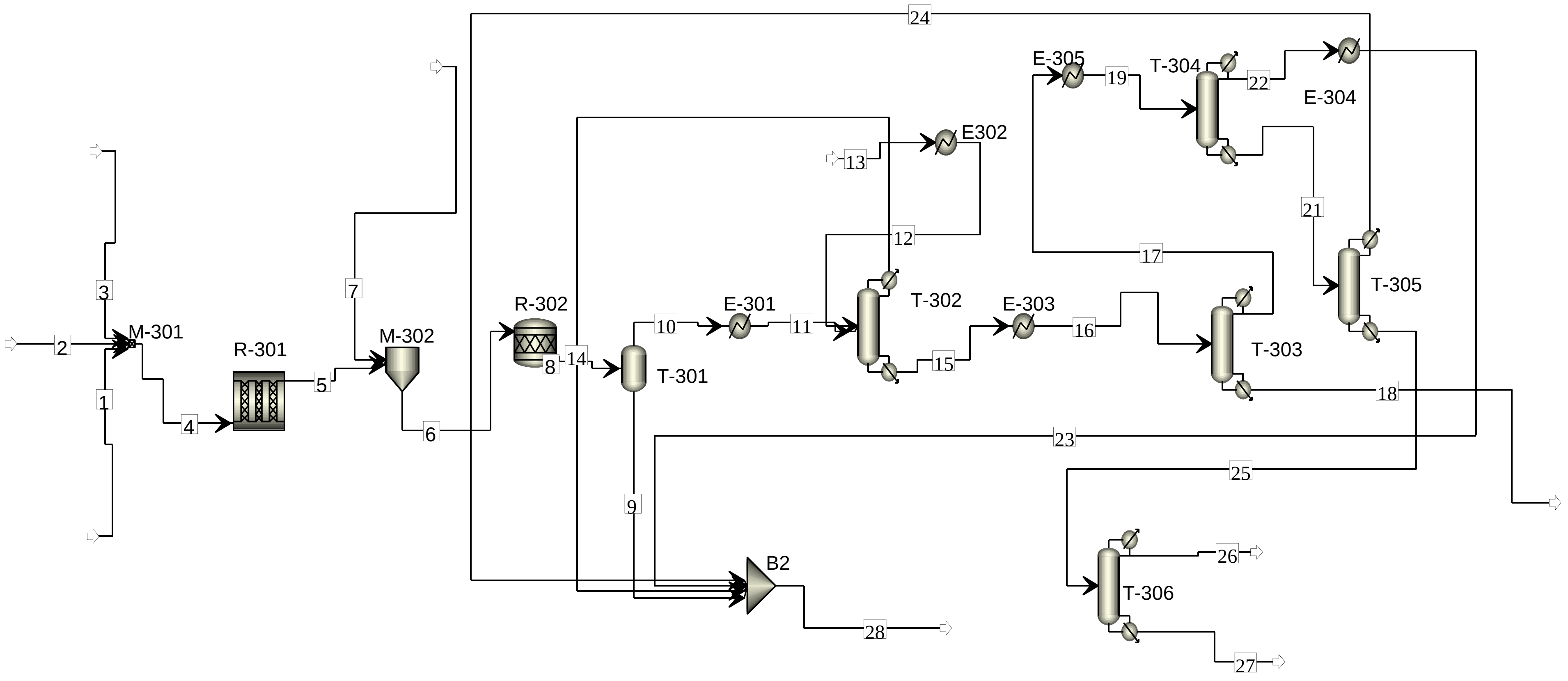
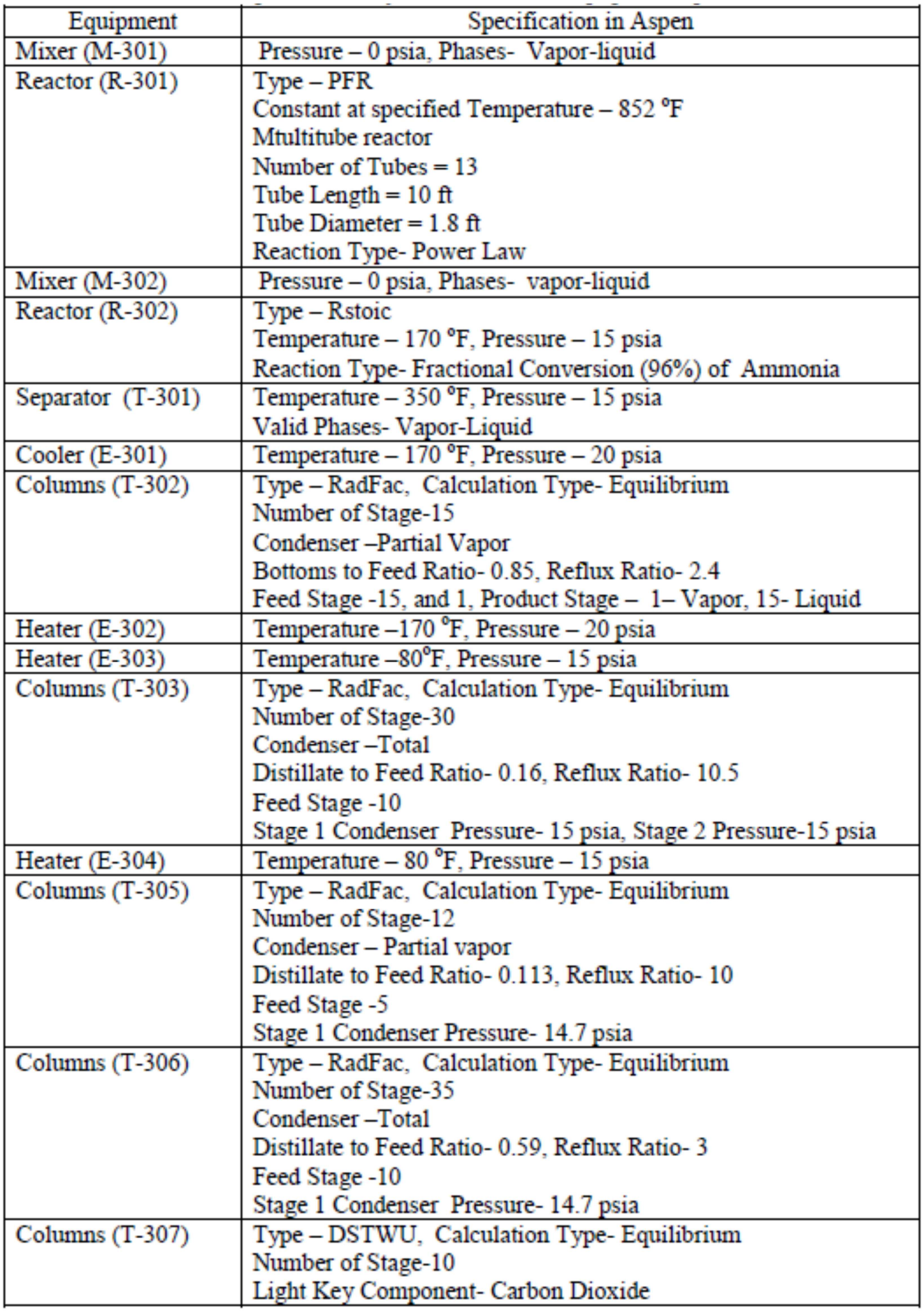
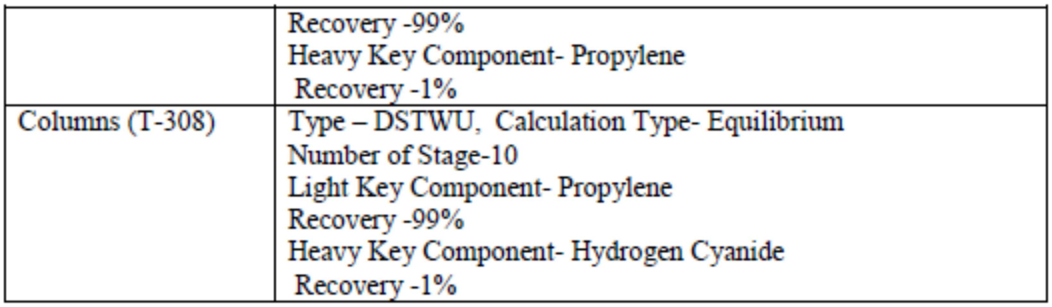


Figure B1: Schematic of the Acrylonitrile Process Base Case

Table B7: Optimized Case Acrylonitrile Process Equipment Specification (Shadiya, 2010a)



Equipment	Specification in Aspen
Mixer (M-301)	Pressure – 0 psia, Phases- Vapor-liquid
Reactor (R-301)	Type – PFR Constant at specified Temperature – 852 °F Mtultitube reactor Number of Tubes = 13 Tube Length = 10 ft Tube Diameter = 1.8 ft Reaction Type- Power Law
Mixer (M-302)	Pressure – 0 psia, Phases- vapor-liquid
Reactor (R-302)	Type – Rstoic Temperature – 170 °F, Pressure – 15 psia Reaction Type- Fractional Conversion (96%) of Ammonia
Separator (T-301)	Temperature – 350 °F, Pressure – 15 psia Valid Phases- Vapor-Liquid
Cooler (E-301)	Temperature – 170 °F, Pressure – 20 psia
Columns (T-302)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-15 Condenser –Partial Vapor Bottoms to Feed Ratio- 0.85, Reflux Ratio- 2.4 Feed Stage -15, and 1, Product Stage – 1– Vapor, 15- Liquid
Heater (E-302)	Temperature –170 °F, Pressure – 20 psia
Heater (E-303)	Temperature –80°F, Pressure – 15 psia
Columns (T-303)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-30 Condenser –Total Distillate to Feed Ratio- 0.16, Reflux Ratio- 10.5 Feed Stage -10 Stage 1 Condenser Pressure- 15 psia, Stage 2 Pressure-15 psia
Heater (E-304)	Temperature – 80 °F, Pressure – 15 psia
Columns (T-305)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-12 Condenser – Partial vapor Distillate to Feed Ratio- 0.113, Reflux Ratio- 10 Feed Stage -5 Stage 1 Condenser Pressure- 14.7 psia
Columns (T-306)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-35 Condenser –Total Distillate to Feed Ratio- 0.59, Reflux Ratio- 3 Feed Stage -10 Stage 1 Condenser Pressure- 14.7 psia
Columns (T-307)	Type – DSTWU, Calculation Type- Equilibrium Number of Stage-10 Light Key Component- Carbon Dioxide



	Recovery -99% Heavy Key Component- Propylene Recovery -1%
Columns (T-308)	Type – DSTWU, Calculation Type- Equilibrium Number of Stage-10 Light Key Component- Propylene Recovery -99% Heavy Key Component- Hydrogen Cyanide Recovery -1%

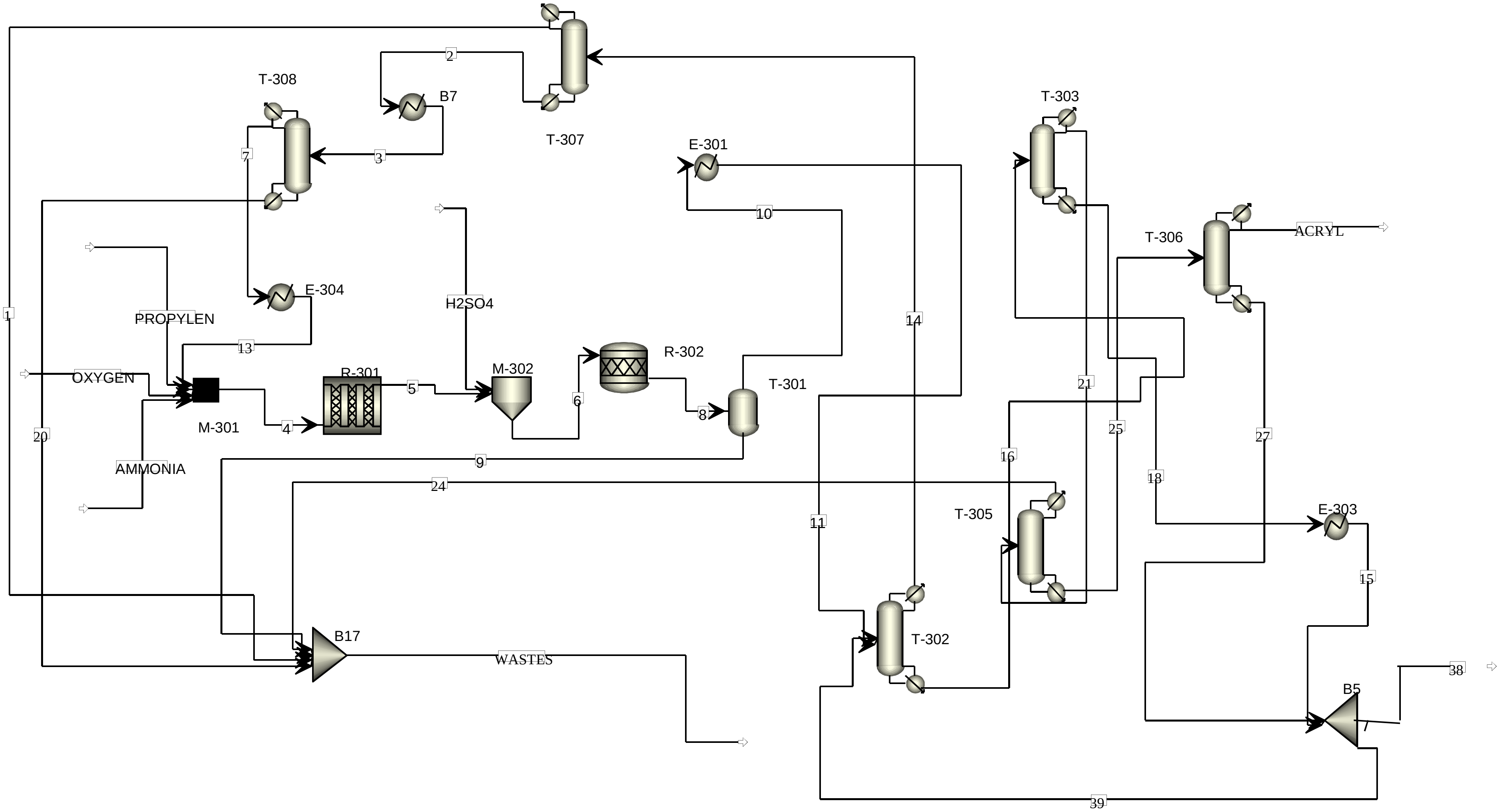


Figure B.2: Schematic of the Acrylonitrile Process Optimized Case

Table B8: Stream Summary Table for Acrylonitrile Production Optimized Case

	1	2	3	4	5	6	7	8	9	10
Substream: MIXED										
Mole Flow lbmol/hr										
AMMONIA	0.0	0.0	0.0	75.0	8.6	8.6	0.0	0.3	0.0	0.3
WATER	0.0	0.4	0.4	0.0	213.4	213.6	0.0	213.6	0.3	213.3
HYDRO-01	0.0	10.0	10.0	0.1	14.2	14.2	0.1	14.2	0.0	14.2
CARBO-01	15.3	0.0	0.0	0.0	15.3	15.3	0.0	15.3	0.0	15.3
OXYGE-01	0.0	0.0	0.0	130.0	0.0	0.0	0.0	0.0	0.0	0.0
PROPY-01	0.3	27.6	27.6	97.3	30.9	30.9	27.3	30.9	0.0	30.8
CARBO-02	15.6	0.2	0.2	0.2	15.8	15.8	0.2	15.8	0.0	15.8
ACETO-01	0.0	0.0	0.0	0.0	2.7	2.7	0.0	2.7	0.0	2.7
ACRYL-01	0.0	0.0	0.0	0.0	49.6	49.6	0.0	49.6	0.1	49.5
ACROL-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SULFU-01	0.0	0.0	0.0	0.0	0.0	4.2	0.0	0.1	0.1	0.0
AMMON-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.1	4.1	0.0
Temperature F	-141.6	-42.1	80.0	79.6	852.0	802.1	-55.0	170.0	350.0	350.0
Pressure psia	14.7	14.7	15.0	14.7	14.7	14.7	14.7	15.0	15.0	15.0

	11	13	14	15	16	18	20	21	24	25
Substream: MIXED										
Mole Flow lbmol/hr										
AMMONIA	0.3	0.0	0.0	0.0	0.3	0.0	0.0	0.3	0.3	0.00
WATER	213.3	0.0	0.4	329.3	330.6	329.3	0.4	1.3	0.0	1.31
HYDRO-01	14.2	0.1	10.0	0.0	4.2	0.0	9.9	4.2	3.7	0.47
CARBO-01	15.3	0.0	15.3	0.0	0.0	0.0	0.0	0.0	0.0	0.00
OXYGE-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00
PROPY-01	30.8	27.3	27.9	0.0	3.0	0.0	0.3	3.0	3.0	0.01
CARBO-02	15.8	0.2	15.7	0.0	0.1	0.0	0.0	0.1	0.1	0.00
ACETO-01	2.7	0.0	0.0	0.3	3.3	0.3	0.0	3.0	0.0	3.03
ACRYL-01	49.5	0.0	0.0	0.4	51.2	0.4	0.0	50.9	0.0	50.88
ACROL-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.04
SULFU-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00
AMMON-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00
Temperature F	170.0	80.0	40.7	170.0	181.1	213.0	69.4	100.9	51.6	170.14
Pressure psia	20.0	15.0	14.7	20.0	14.7	15.0	14.7	15.0	14.7	14.70

	27	38	39	ACRYL	AMMONIA	H2SO4	OXYGEN	PROPYLEN	WASTES
Substream: MIXED									
Mole Flow lbmol/hr									
AMMONIA	0.00	0.00	0.00	0.00	75.00	0.0	0.00E+00	0.00E+00	3.42E-01
WATER	1.31	212.91	117.66	0.00	0.00	0.2	0.00E+00	0.00E+00	7.29E-01
HYDRO-01	0.00	0.00	0.00	0.47	0.00	0.0	0.00E+00	0.00E+00	1.36E+01
CARBO-01	0.00	0.00	0.00	0.00	0.00	0.0	0.00E+00	0.00E+00	1.53E+01
OXYGE-01	0.00	0.00	0.00	0.00	0.00	0.0	1.30E+02	0.00E+00	0.00E+00
PROPY-01	0.00	0.00	0.00	0.01	0.00	0.0	0.00E+00	7.00E+01	3.52E+00
CARBO-02	0.00	0.00	0.00	0.00	0.00	0.0	0.00E+00	0.00E+00	1.56E+01
ACETO-01	1.38	1.06	0.59	1.65	0.00	0.0	0.00E+00	0.00E+00	1.77E-02
ACRYL-01	4.56	3.17	1.75	46.32	0.00	0.0	0.00E+00	0.00E+00	1.14E-01
ACROL-01	0.00	0.00	0.00	0.04	0.00	0.0	0.00E+00	0.00E+00	5.24E-05
SULFU-01	0.00	0.01	0.00	0.00	0.00	4.2	0.00E+00	0.00E+00	5.40E-02
AMMON-01	0.00	0.00	0.00	0.00	0.00	0.0	0.00E+00	0.00E+00	4.11E+00
Temperature F	167.71	169.94	169.94	157.78	80.00	86.0	8.00E+01	8.00E+01	2.70E+01
Pressure psia	12.00	12.00	12.00	12.00	15.00	14.7	1.50E+01	1.50E+01	1.47E+01

VITA

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