METHODOLOGY FOR COMPARISON OF CHEMICAL PROCESS ROUTES BASED ON ENVIRONMENT, HEALTH AND SAFETY ASPECTS AT EARLY STAGES OF CHEMICAL PROCESS PLANT DESIGN

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DECLARATION

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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Abstract

The chemical process route selection is one of the important decisions that needs to be taken during initial stages of plant design and development. Although conventionally the economic factor has been considered in this selection process, presently the environmental, health and safety (EHS) issues have also become main concerns as hazards related to EHS can be largely reduced by avoiding them during initial stages of plant development. Therefore, in order to select a route, the assessment of alternate chemical process routes based on EHS aspects and their comparison need to be carried out. For this assessment, comparison and selection methodologies are needed. Most of the methodologies available for chemical process routes assessment and selection, consider mainly environmental or health or safety hazards individually or in combination of two of them. Although few methodologies are available that consider all three EHS aspects, those that consider EHS hazards posed by both types of releases namely daily plant operational and accidental are lacking.

In this work fuzzy based inherent environmental, health and safety hazard index called EHS-Fuzzy Index is developed to compare chemical process routes based on integrated EHS hazards due to daily operational activities of the plant as well as accidental releases. The EHS-Fuzzy Index includes information of thirteen EHS related parameters which is available during routes selection stage. The lower the EHS-Fuzzy Index the more environmental friendly, occupational healthy and safer the chemical route. Further, this methodology can be used to compare and rank alternative chemical routes based on environmental hazard or health hazard and safety impact separately as well. The EHS-Fuzzy Index was applied in a case of six routes to manufacture methyl methacrylate (MMA). The Tertiary Butyl Alcohol (TBA) chemical route to manufacture MMA showed the least EHS-Fuzzy Index value. By applying the MMA case study in the radial polygon diagram method, the results obtained using the EHS-Fuzzy Index methodology were verified.

Keywords:
Chemical process route, Plant releases, Inherent safety, Environmental and health hazards, Fuzzy based index

DEDICATION

I dedicate this thesis to my wonderful family who have always been a great source of inspiration and support.

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Buddika Anuradha

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A_{Floor} - cumulative value of average floor area of each unit operation

ADacc - the acid deposition impact due to accidental chemical release (Kmol equivalence of SO_2)

AQacc1, AQacc2, etc. - the health impact value of each work place accidental release scenario

CEI - Chemical Exposer Index

CED_i - cumulative energy demand of chemical i (kJ/mol)

$CF_{AD\mathit{i}}$ - characterization factor for acidification of chemical i

EPA - environment protection agency

EHS - Environment Health and Safety

FEcont - health impact due to fugitive emission of a chemical route

FLAche - flammability hazard of a chemical route

Fi - flammability of chemical i (NFPA fire rating)

f_{GWPi} - global warming potential of chemical i (equivalence of CO_2)

GHG - greenhouse gases

GWIacc-fire - the global warming impact due to GHG emission of accidental fire (Kmol equivalence of CO_2)

GWIacc-che - the Global Warming Impact due to greenhouse gas emission of accidental chemical releases (Kmol equivalence of CO_2)

GWIcon - the global warming impact due to GHG emission of continuous operation (kmol equivalents of CO_2/hour)

HAQacc - health impact of work place accidental release airborne quantity of a chemical route

INVche - chemical safety impact of a chemical route (te)

LC - Lethal concentration

LD - Lethal dose

MMA - manufacture methyl methacrylate

M_i - molar mass (g/mol)

M_i - molar mass (g/mol)

m_{AQ} - airborne quantity (kg/s)

$m_{i,FE}$ - fugitive emission rate of chemical substance i (kg/s)

n - number of chemicals associated with the chemical process route

NFPA	- National fire and protection agency
$N_{i(Cl)}$ and $N_{i(Br)}$	- the number of Cl and Br atoms respectively, per molecule
$N_{i(C)}$	- the number of C atoms of substance i, per molecule
ODacc	- ozone depletion impact of a chemical route (years)
PEC	- Predicted Environmental Concentration
q_i	- molar feed rate of chemical i (kmol/hour)
Q_i	- total quantity of chemical i released to the environment (te)
$STEL_i$	- short-term exposer limit of chemical i (kg/m^3)
TLV	- threshold limit value
TWAi	- time weighted average value of substance i (kg/m^3)
Tpro	- process safety impact due to operating temperature of chemical route (K)
T_j	- difference between operating temperature and ambient temperature of reaction step j (K)
VF	- volumetric flow rate (m^3/s) of air in the work place
x_i	- mass faction of chemical i in the stream
Yi	- mass fraction of chemical i
τ_i	- atmospheric life (years) of chemical i
ΔH_{CO2}	- heat of combustion of carbon (kJ/mol)

Chapter 1

INTRODUCTION

The rapid industrialization observed today has resulted in increase of industrial accidents along with the advancement of peoples' social and economic wellbeing. The Bhopal disaster is one of the largest accidents happened at a chemical process plant which drew world attention to serious hazards involved in chemical manufacturing industry (Browing, 1993). Other such accidents happened in the world include Ludwigshafen disaster, Flixborough disaster, Houston disaster, Seveso disaster and Amoco Cadiz disaster. Not only experiences of large accidents, those accidents having smaller scale impacts also have been given attention in understanding causes and consequences (Gunasekera and De Alwis, 2008). Analysis of such accidents in chemical manufacturing industry has shown that in order to avoid or eliminate hazards involved, assessment of the chemical manufacturing process needs to be carried out during all stages of plant development (Rathnayake and Khan, 2014; Yang, Khan and Amyotte, 2015).

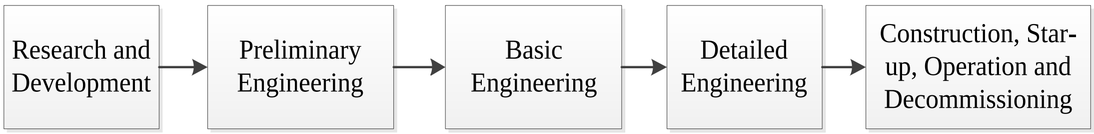

Figure 1.1: Chemical process plant development stages

The main stages of chemical process plant development are given in the Figure 1.1. Avoiding or eliminating hazards could be best achieved during early stages of process plant development (Kletz,). The process of selection of the chemical process route is carried out during preliminary engineering design stage of above process plant development stages (Kidam et al., 2016).

The chemical process route is defined as the sequence of reaction steps involved in producing a chemical using raw materials and energy (Edwards & Lawrence, 1993). There are many synthesis chemical process routes or paths to produce a specific desired chemical product or products. The hazards involved in the route could be avoided or reduced by selecting the chemical route which has the least hazard.

The route selected will fix the chemicals present and the process used in the plant and hence the associated hazards. Therefore, decision of chemical route selection at initial stages of plant design and development can eliminate or avoid most of the hazards of the chemical process plant. This will make the chemical plant inherently environmentally friendlier, healthier and safer (IEHS). In an inherently environmentally friendlier, healthier and safer chemical route, the hazards are avoided or eliminated rather than controlling them by add-on protective equipment.

Previously when selecting a chemical process route, aspects such as the cost of operation and raw materials, market availability of raw material and technology have been given more consideration. However, recently with the industrial accidents experiences, safety, health and environmental aspects have also become important aspects considered when selecting routes for developing a chemical process plant. By having chemical process plant with less hazards, sustainable development efforts are also facilitated.

In the preliminary engineering design stage of the chemical plant development the available process routes to produce the chemical are identified (Kidam et al., 2016). These routes need to be compared and the best chemical route should be selected before the basic and detailed engineering design is done (American institute of chemical engineers., 2009). This selection leads to industrial working environments with minimum hazards and with less environmental impacts (OHSA, 1986).

The information available to compare and select one process route from possible routes to manufacture a chemical during preliminary design stages is less. Therefore, the route selection methodology needs to be one that work with parameters where data are available at this stage.

Several methodologies developed for assessing chemical process routes during preliminary design stages are available in literature. In most methodologies developed, assessment covers only part of the hazards that is either environmental or health or safety hazards (Ahmad et al., 2014; Etowa et al., 2002; Gunasekera & Edwards, 2006; Hassim & Hurme, 2010; Khan & Amyotte, 2004; Rathnayaka et al., 2014; Patel et al., 2012; Cave & Edwards, 1997). There are several methods in which accidental release of the total inventory has been considered (Cave & Edwards, 1997; Hassim & Hurme, 2010; Khan et al., 2001). In few assessment methods the continuous emission due to daily operation has been considered.

Integrated chemical process routes assessment methodologies based on the three parameters environmental, health and safety hazards considering both, emissions due to daily plant operation as well as one off accidental releases are lacking. This work presents a methodology, which integrates environmental, health and safety aspects associated with one off accidental releases and with releases due to day to day operations in the plant to select the most inherently environmental friendly, occupationally healthy and safer chemical process route.

1.1 Research objective and Scope

The objective of this work is to develop a methodology to assess chemical process routes during early stage of plant design based on environmental, health and safety aspects considering impact due to emission from continuous operation of the plant as well as one off release.

Scope:

The method is generic and is able to apply for any kind of potential and established chemical process route. Further, the method will be simple and uses only the data available at preliminary engineering stage of design and development of a chemical process plant.

1.2 Thesis structure

The thesis contains five separate chapters with headings to demonstrate the background information, methodology developed and case study application and discussion. The first chapter gives introduction and object of the topic.

The available methodologies those are relevant to the environment, health and safety assessment of chemical process routes are presented under literature review in chapter two.

The third chapter presents the methodology for fuzzy based inherent environment, health and safety hazard assessment called EHS-Fuzzy Index. This includes the parameter evaluation and application of multi criteria assessment method.

The result and discussion of the EHS-Fuzzy Index application in Methyl methacrylate manufacturing routes case study and verification of the methodology are given in chapter four.

The fifth chapter, presents conclusions and the recommendations of this research study.

Chapter 2
LITERATURE REVIEW

In this chapter, the current developed methodologies to assess chemical process routes considering environmental, health and safety aspects including impact due to one off releases and continuous emission resulting from day to day plant operations are presented.

As discussed earlier, the chemical process route is considered as the way or path to achieve a particular chemical product using raw materials and energy. The EHS hazards associated with the route is considered according to the definition of “Hazard”, that is a physical situation with potential for human injury, damage to property, damage to environment or some combination of these (Crowl & Louvar, 2001).

An inherently safer, healthier and environmentally friendly chemical process route is one that has eliminated or avoided hazards by having safer chemical substances or process conditions. Application of inherent safety principles at early stages of chemical process plant development leads to avoiding or minimizing of hazards. The word ‘inherent’ means something which is intrinsic to the chemical process route. The main aim of inherently safer design is to avoid or remove hazards rather than add on protective equipment to control them. The inherent safety concept has been promoted by many researches (Kletz, 1976; Kletz, 1998; Cave & Edwards, 1997; Edwards and Lawrence, 1993).

The hazard assessment is diversified through environment, health and safety impact of chemical industry. One of the assessment methodologies based on inherent environmental hazard is the Environmental Hazard Index (EHI) (Cave & Edwards, 1997). The environmental impacts of catastrophic chemical releases are assessed in Atmospheric Hazard Index (AHI) (Gunasekera & Edwards, 2003). The inherent occupational health hazards are assessed in Process Route Healthiness Index (Hassim & Edwards, 2006). The inherent safety is assessed in Integrated Inherent Safety Index

(Khan & Amyotte, 2004). Above are some examples for hazard assessing methodologies available in literature.

2.1 Inherent environmental hazards assessment

The methodologies developed in literature to select chemical process alternatives assessing environmental impacts are discussed in this section. The manner in which the substances are released to the environment from the plant as well as the characteristics of the substances and their ecosystem characteristics are considered in this review.

2.1.1 Environmental impact assessment based on plant releases

The environmental impact could happen due to different types of releases from chemical processing plants. The release can be a raw material, end product or emissions due to accidents and daily operations in the plant. Among the hazard assessment methodologies developed to assess process alternatives based on planed or daily operational releases include works done by Hassim and Hurme (2010) and Topuz et al (2010). The methodologies developed based on accidental releases include worked such as Cave and Edwards (1997), Gunasekera and Edwards (2003) Topuz et al (2010) and Warnasooriya and Gunasekera (2017).

The process alternatives assessment methodologies developed based on environmental impacts in literature have used many impacts such as toxicity, acid deposition, ozone depletion and global warming. In order to present these impacts quantitatively, various parameters have also been used.

2.1.1.1 Toxicity

The toxicity of any chemical can affect various parts of the environment. The environment hazard index (EHI) developed by Cave and Edward (1997) describes six compartments of the environment air, water, biota, soil, sediment and suspended sediment where a toxic substance can get distributed. The toxicity is a property of chemical substances, which can affect human body (Crowl & Louvar, 2001). The parameters representing the toxicity such as LC50, LD50 and TLV have been used in various methodologies that assess the environmental hazards associated with releases of chemical process plant (Cave and Edward, 1997; Patel et al., 2012).

Human toxicity, toxicity on animal species or vegetation toxicity can be used to assess the toxicity effects of chemical substances (Cave and Edward, 1997; Gunasekera and Edwards, 2003). The acute toxicity as well as chronic toxicity data for animal species are widely available for many toxic substances.

2.1.1.2 Global warming

The emissions of greenhouse gases such as CO_2, N_2O and CH_4 from chemical processes have the potential to enhance the greenhouse gas effect. Greenhouse gases (GHGs) can be emitted in several ways such as from continuous operation, accidental fire or accidental chemical releases. Chemical process plants using energy sources have the possibility of releasing GHGs (Andraos, 2015; Patel et al., 2012). Usually, when fossil carbon products are used as the energy source, after combustion CO_2 is released.

The chemicals used in the process plant can be released in case of an accident. If these chemicals include GHGs then an impact on climate due to global warming is possible (Srinivasan and Nhan, 2008; Gunasekera and Edwards, 2003). An accidental chemicals release can give GHG emissions in two ways. One is where the accidental chemical release is a GHG and the other is where the chemical released is flammable and catches fire resulting in a release of CO_2. The global warming is expressed quantitatively using global warming potential and is in units of equivalence of CO_2 (Srinivasan and Nhan, 2008; Patel et al., 2012).

2.1.1.3 Acid deposition

An acidic substance in the atmosphere depositing in dry or wet form on the earth is known as acid deposition. The plant emission with sulfur dioxide and nitrogen oxides react with water, oxygen in the atmosphere to create acidic components (EPA, 2014). The wet form of acid deposition is widely recognized than dry deposition as it accounts for a larger portion of the total deposition.

Acid deposition can have many harmful ecological effects on water systems. Acid deposition can damage trees by changing the chemical and physical characteristics of soil. Total acid deposition of any releases is determined using SO_2 equivalent quantity (Srinivasan and Nhan, 2008). In Gunasekera and Edwards (2003) work, chemical concentration in the atmosphere and the critical concentration level for vegetation were considered in estimating the impact due to acid deposition.

2.1.1.4 Ozone depletion

Stratospheric ozone depletion is a consequence of atmospheric substances such as CO_2, CH_4, N_2O, CFC, HFC and Perfluorinated compounds. The stratospheric ozone is a natural protection layer from sun's harmful ultraviolet rays that protects human health, plant, marine ecosystems and materials. The quantification of hazard due to stratospheric ozone depletion is carried out in several implementations. The atmospheric life of a released chemical substance and the number of Cl and Br atom per mole of the released substance are used in Ullmann's Encyclopedia (1996) to quantify the ozone depletion impact. The same method has been applied in Gunasekera and Edwards' (2003) development as well. The ozone depletion potential value has been considered as a parameter for hazard assessment due to ozone depletion by Srinivasan and Nhan (2008).

2.1.2 Environmental impact assessment based on chemical characteristics

The environmental impact can be assessed considering substance characteristics such as flammability, reactivity, bioaccumulation, persistency (half –life in water) and environmental conditions such as wind velocity, humidity, temperature and soil structure. Therefore, these characteristics can be divided into two categories namely, substance characteristics and ecosystem characteristics (Topuz et al, 2011).

The environmental impact depends on the property of the substances available at the plant. For example, high toxic substance can affect more than a less toxic substance even a small quantity of chemical substance is present in the plant (Cave and Edwards, 1997). The flammability, reactivity, corrosiveness, toxicity and explosiveness are some chemical properties used in environmental impact assessment in methodologies developed for chemical process alternatives selection (Srinivasan and Nhan, 2008; Topuz et al, 2011).

Furthermore, environmental impact of chemicals released from a chemical plant depends also on the characteristics of the ecosystem. The area of ground water resource, animal population, area of forests are few ecological parameters considered for environmental impact assessment in literature (Christen et al, 1994; Topuz et al, 2011).

2.2 Inherent occupational health hazards assessment

The employee health at the working environment is considered as the occupational health. The chemical process plant operation can have effects on occupational health such as death, injury, disability and reduce personnel job performance due to acute and chronic exposure (Hassim and Hurme, 2010). The airborne quantity of accidental plant releases in work places and fugitive emission are two release scenarios selected in literature for health hazards assessment (Hassim and Edwards, 2006; Hassim and Hurme, 2010; Dow Chemicals, 1998). The Health Quotient Index (Hassim and Hurme, 2010), the Process Route Healthiness Index (Hassim and Edwards, 2006) and the Chemical Exposer Index (CEI) (Dow Chemicals, 1998) are some of available health hazards assessment methodologies in literature that are developed to select process alternates based on assessment of occupational health hazards.

2.2.1 Health impact assessment based on accidental plant releases

The chemical substances used in the process industry can be released in to work environment due to various reasons such as equipment failure. The potential health impacts on people from possible chemical releases due to failures are usually resultant from operation conditions. The process pipes, horses, pressure relief devices, vessels and tanks are some equipment that has the greatest potential for the release of significant amount of process material (Dow Chemicals, 1998).

The material entering the work place atmosphere are of three different types. They are direct vaporization, liquid flashing and pool evaporation (Dow Chemicals, 1998). These materials can be released as liquid or vapor. Liquid releases can run out simply on the ground forming a pool or part can vaporize forming a vapor cloud. The flash liquid exists in the air as small droplets that can be carried away with the vapor (Hassim and Edwards, 2006).

2.2.2 Health impact assessment based on continuous plant releases

The major continuous emission at plant environment is fugitive emission due to continuous plant operation. The chemical concentration at workplace atmosphere should be kept below the adverse worker exposer concentration levels. Hassim and Hurme (2010) developed a methodology for occupational health hazard assessment considering exposure to fugitive emission. Their method is developed to apply at early stages of chemical process plant design. It needs data related to the number of piping components of typical operation such as distillation or absorber, to estimate the total fugitive emission rate.

The emission rates of any piping component and number of piping components give the total chemical emission rates due to continuous operation (EPA, 2014; Hassim et al, 2012). The work place chemical concentration can be then calculated using volumetric flow rate (Hassim and Hurme, 2010). The chronic toxicity measurement and workplace chemical concentration are used in methodologies presented in literature to give an idea about the health impact due to fugitive emission (Hassim and Edwards, 2006; Hassim and Hurme 2010).

2.2.3 Health impact assessment based on process parameters

The health impact due to chemical process plant operation can be assessed considering various parameters. Some of these parameters which have relationship with health impact include work place transportation, type of process (batch or continuous), temperature, pressure, viscosity and phase of chemical substance (Adu et al, 2008). These parameters can be categorized into type of process operation, process condition and material property (Hassim and Edwards, 2006).

The different types of operations such as material transportation, process venting or flashing and maintenance work are involved in chemical processes. In the method developed by Hassim and Edwards (2006) each activity is assigned with a penalty value according to the potential hazard or probability of release. For example, if the type of process is continuous, semi continuous or batch operation the penalty for potential hazard increases from continuous operation to batch operation.

The process conditions such as temperature and pressure depend on the end product and the process route selected (Hassim and Edwards, 2006). Therefore, the health risk also varies with the process condition associated the process route. The penalties are allocated according to the hazards incorporated with these process conditions.

The properties of the chemical substances involved with process route are very important when evaluate the occupational health hazards. Viscosity, solubility, density and phase are few chemical properties that can be considered in health hazard assessment. Hassim and Edwards (2006) developed their method by allocating penalty values considering the hazard potential of each property.

2.2.4 Health impact assessment methodology guidelines

National fire and protection agency (NFPA) and Occupational health and safety administration (OSHA) are well reputed organizations having standards for industries methodological guidelines for them. The list of typical occupational diseases and their consequences of the all known chemicals involved with chemical processes are defined by OSHA. The OSHA guidelines in the field operations manual gives value ranges for health effects from most severe health effects to the effect becoming less sever (U.S. Department of Labor, 1989).

The NFPA health rating is developed according to reactivity, flammability and ability to cause health hazards. These ratings are developed for chemicals used in chemical process industry ranging from 1 to 4.

2.3 Inherent safety hazards assessment methodologies

The inherent safety assessing methodologies available in literature considering various parameters are discuss in this section.

Inherent safety concept is intrinsic to a plant development. A good example for inherent safety, used by Kletz (1998), the bungalow is inherently safer than a house, because stairs are the major cause of serious accident in the home. Stairs are inherently unsafe, but that can be made 'safer' by add-on protectives such as lighting, handrail and child gates.

In inherently safer process plant design, one should avoid or remove hazards from the proposed chemical route rather than add on protective equipment to control them. The important inherent safety principles can be categorized as follow (Mannan, 2012):

Intensification- that helps to reduce hazards by using less quantity of hazardous materials.

Substitution- that reduces hazards using safer materials instead of hazardous materials.

Attenuation- that can be achieved via carrying out hazardous reactions under less hazardous conditions or transporting and storing hazardous material in less hazard form.

Limitation- this is to reduce the equipment failure by better equipment design or changing reaction conditions.

Simplification- it is to reduce the opportunities for error and malfunction. A simple plant avoids the complexities such as multiproduct or multiunit operation or congested pipe or unit settings.

The above principle can be applied with the inherent safer chemical process plant developments. There are many methodologies developed for selecting chemical process routes considering inherent safety during early stages of chemical plant development.

Edwards and Lawrence (1993) developed a Prototype Index for Inherent Safety (PIIS). Gupta and Edwards (2003) presented a graphical approach for evaluating inherent safety of process routes. Heikkilä et al. (1999), Khan and Abbasi (1998), Khan and Amyotte (2005), Palaniappan et al. (2002) and Palaniappan et al. (2004) have also developed methodologies to assess chemical process routes based on inherent safety.

Other developments in inherent safety assessment methodologies include fuzzy logic based inherent safety index (Gentile et al., 2003), Integrated Inherent Safety Index (I2SI) (Khan and Amyotte, 2004), Process Route Index (PRI) (Leong and Shariff, 2009), Inherent Safety Key Performance Indicators (IS-KPIs) (Tugnoli et al., 2012), Numerical Descriptive Inherent Safety Technique (NuDIST) (Ahmad et al., 2014) and Graphical Descriptive Technique for Inherent Safety Assessment (GRAND) (Ahmad et al., 2016).

2.3.1 Inherent safety assessment parameters

The data available for any chemical operation are limited for inherent safety assessment at early stages of process plant design. In one of the very first inherent safety assessment methodologies developed by Edwards and Lawrence (1993), seven parameters have been selected out of sixteen parameters based on availability of information at preliminary stages of plant design. The parameters for inherent safety assessment include inventory of chemicals in the plant, phase, temperature, pressure, heat of reaction, toxicity and many more.

Inventory- Amount of material available at the plant has a large effect on the degree of hazard (Edwards & Lawrence, 1993). A low inventory can reduce the potential accident severity than large mass of material. Therefore, inherent safety due to inventory is assessed using scores that reflect the hazard associated with the inventory quantities (Edwards & Lawrence, 1993). However, the reaction yield information is required for quantification of inventory at early design stages (Srinivasan & Nhan, 2008).

Phase- The impact level of the accident can vary according to the reaction phase (gas, vapour or liquid). According to the Kletz (1998), the gas phase reactors are less hazardous compare to liquid phase reactors. A less amount of mass can be released from gas phase reactors compared to that of liquid phase reactors.

Temperature- The operating temperature is a direct measure of heat energy available at releases (Edwards & Lawrence, 1993). The higher temperature is inherently unsafe because it implies that plant is under thermal stress. Therefore the process with low operating temperature is less hazardous compare with a process with a high operating temperature (Srinivasan & Nhan, 2008).

Pressure- High operating pressure is a measurement of energy availability in the plant. It represents the energy availability at release and the energy available to cause a release (Edwards & Lawrence, 1993). The reactant can be leaked due to high operating pressure. Therefore, the high operating pressure process is more dangerous than the low operating pressure process (Srinivasan & Nhan, 2008). Usually, the atmospheric pressure is considered as the hazard zero level due to pressure.

Heat of reaction- This is a measurement of energy availability due to chemical reaction. A higher exothermic reaction is able to generate high temperatures. This is dangerous when a runaway reaction occurs. In an endothermic reaction energy is absorbed (Edwards & Lawrence, 1993).

New phase generation- when the phase in which the reaction occur is different to the reactant phase unsafe conditions can be generated. If the new phase is a gas evolution or a solid precipitation, it can lead to overpressurization or equipment blockage (Edwards & Lawrence, 1993).

Catalysts- the catalyst improves reaction rate and limit the formation of unwanted reactions and side reactions within or outside a reactor. Usually, catalysts are made of heavy metals and can be poisonous (Lawrence, 1996).

Side reaction- In addition to the main reaction, side reactions occurring can lead to produce unwanted chemicals. The extra products resulting from side reactions must be separated and therefore, complexity of the process increases. The side reactions are capable of limiting formation of favorable products by changing reaction conditions (Lawrence, 1996).

Reaction yield- it is the overall efficiency of the reaction that turn reactants into products. A high yield reaction is good for inherent safety than a low conversion because more reactants are turned into the required product (Edwards & Lawrence, 1993).

Reaction rate- indicates how fast the reaction happens. If the reaction is fast, the resident time of reactants is low and the required material inventory is less. Even a fast reaction can lead to unsafe conditions because high amount of heat can be generated (Edwards & Lawrence, 1993).

Viscosity- high viscos material gives poor mixing capacity and less heat transfer from chemicals to heat transfer surface (Edwards & Lawrence, 1993).

Flammability- it is a measure showing how easy something can be burnt. The criteria to measure flammable state of a substance depends upon its boiling point, flash point and its temperature (Lawrence, 1996).

Explosiveness- the explosiveness of a material is estimated from it is upper explosive limit and lower explosive limit. This indicates how much or how little of a material must be mixed with air to form an explosive mixture. The explosive range is defined from 0 to 100% (Lawrence, 1996).

Corrosiveness- This is a hazard posed by a chemical to plant material constructed or skin. Some material become more corrosive when exposed to different forms of chemical such as hydrogen chloride gas when dissolved in water is more corrosive compared to the gas (Lawrence, 1996).

Toxicity- it is a measure of physical impact of a chemical that can be measured in both short term and long term. The toxicity depends on two factors: the concentration of a chemical and the exposure period (Lawrence, 1996).

2.4 EHS hazards combined assessment methods

Although methodologies for assessing chemical routes based on environmental, health and safety aspects separately are available in literature, the methodologies assessing routes considering all three aspects simultaneously are lacking. This section discusses available methodologies in literature that assess chemical process alternatives based on integrated environmental, health and safety hazards.

The inherent benign-ness indicator proposed by Srinivasan and Nhan (2008) considers all three, EHS aspects. They have used 15 parameters that contribute to these three aspects, which include acute and chronic impact data. However, impacts due to fugitive emissions and fire emissions have not been considered in their work. The parameters are normalized first and are integrated with the assumption of equal contribution of each parameter on overall index. The lower index value indicates more environment friendly chemical route.

The SREST- layer chemical process evaluating method (Shah et al, 2005) is a software that has been developed to assess chemical process safety in early process development stages. The assessment is carried out by different layers that starts with substance and reactivity hazard identification and assessment. After that equipment assessment and safety technology assessment layers are defined. The substances assessment is done considering environment, health and safety aspects. In this methodology equipment and technology data are needed and hence application during routes selection stage is limited. The impacts due to one off releases, fugitive emissions, fires and daily operations have not been addressed.

The sustainable assessment methodology proposed by Patel et al (2012) called EHS Index also includes environmental, health and safety aspects. In this EHS assessment, the environment impact assessment considers impacts due to greenhouse gas emissions and cumulative energy demand. The methodology considers impacts due to daily plant operational emissions though impacts resulting from one off releases, fugitive emissions and fire emissions were not discussed.

Inherent Chemical Process Route index (ICPRI) presented by Warnasooriya and Gunasekera (2017) considers EHS aspects in assessing routes during chemical process routes selection stage. The parameters used in this impact assessment were relevent to daily plant operational releases.

Although several methodologies to assess chemical process routes based on all three EHS have been developed (Srinivasan and Nhan, 2008; Shah et al, 2005; Patel et al., 2012, Warnasooriya and Guasekera, 2017), the impacts considered in their works have been either one or a combination of two of one off emissions, fugitive emissions, fire emissions or plant daily operational releases. This indicates that methodologies to assess chemical process routes based on EHS considering all emissions scenarios, namely one-off emissions, fugitive emissions, fire emissions or plant daily operational releases are needed.

2.5 Multi criteria decision making

The methodologies presented in literature use many parameters to represent various hazards. These parameters need to be integrated to arrive at the final hazard representing the total hazard posed by the chemical route. In some methodologies parameters are integrated after normalizing or giving various score values (Edwards & Lawrence, 1993; Srinivasan et al, 2008). There are some methodologies that use weight factors to combine parameters (Patel et al. 2012; Warnasooriya, 2013). The weights assigned were subjective as they were based on expert opinions. The fuzzy logic approach is another integration method that is becoming more popular as it is generic in multi criteria assessments applications (Christen et al, 1994; Gentile et al, 2003; Khan and Amyotte, 2004; Topuz et al, 2011).

Chapter 3

DEVELOPMENT OF THE ASSESSMENT METHODOLOGY

This work proposes an index called EHS-Fuzzy Index to assess chemical process routes based on Environmental, Health and Safety (EHS) for accidental releases as well as releases resulting from daily plant operations. This index takes values from 0 to 1. A higher EHS-Fuzzy Index represents a chemical route with higher EHS hazard and low EHS-Fuzzy Index represents a chemical route with less EHS hazards.

3.1 Framework for proposed assessment approach

The assessment of chemical process route begins with the development of the block diagram of the chemical manufacturing process and estimating the chemical inventory in the plant based on the data available during preliminary engineering design stage of plant development. The proposed framework to rank chemical routes based on EHS-Fuzzy Index is shown in Figure 3.1.

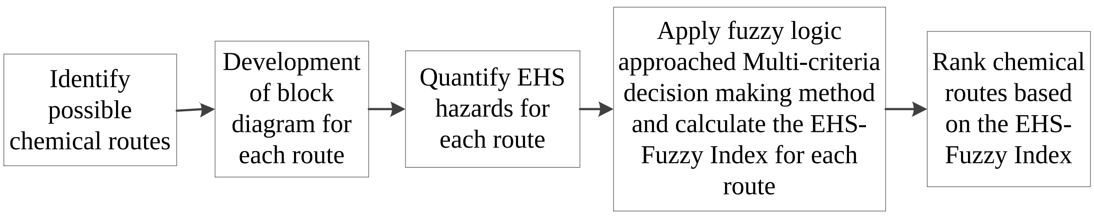

Figure 3.1: Framework for ranking routes based on EHS-Fuzzy Index

Development of the block diagrams for all possible chemical process routes for synthesis of the chemical concerned is the initial effort of this assessment methodology. The reaction and separation stages are the main operations considered in this diagram. The input and output stream should be defined with concentration and composition for all chemicals. Other data such as reaction yield and molar flow rates are estimated using data available during preliminary stage. Chemical material quantities can be estimated with the help of some assumptions.

The inventory is one of the most important parameters considered in this hazard assessment methodology. The estimation of inventory is carried out based on the information available at the preliminary design stage. At this stage it is assumed that reaction route synthesis, reaction conditions and reaction yield data are available. The assumptions made in this work for the estimation of approximate chemical inventories are similar to the assumptions used by Edwards and Lawrence (1993), Cave and Edwards (1997), Gunasekera and Edwards (2003) and Warnasooriya and Gunasekera (2017) in their works of assessing chemical process routes. The assumptions used in this work for inventory estimation are as follows:

- Raw materials and end products storage residence time is 14 days and there are no other intermediate chemical storages.
- Reaction time at the reactor is one hour and it is considered as a separate unit.
- Distillation column is used for separation of binary liquid mixtures and vapor/liquid separation is carried out by flash drum that spends 5 minutes to complete the operation.
- Liquid/liquid azeotropic separation takes 15 minutes to complete its operation.
- The production rate of a particular product is equal for all chemical routes and that is considered as 150,000 te per year; plant operating time is 8,000 hours per year.

3.1.1 Selection of impacts due to EHS hazards

The effects on various elements in the environment due to exposure to chemical substances associated with the process route are considered in identifying impacts on the environment. The main impacts, global warming, toxicity, ozone depletion and acid deposition are considered for assessment of adverse effects on environment.

The health impact of a chemical route is assessed considering the toxic effect on human health within the plant environment. The toxic effect due to accidental airborne quantity and fugitive emission are calculated based on accidental release and continuous release scenarios respectively.

The safety related hazards involved with a chemical process route is important in selecting inherently safer chemical route. In this work the routes assessment based on safety is carried out by considering chemical properties and operating conditions. The parameters, chemical inventory, flammability and explosiveness are selected to assess safety impact related chemical properties. The operation pressure and operation temperature are selected to measure safety impact of the process condition.

In order to represent the above EHS hazards, 13 potential impacts are selected. The impacts or hazard assessment scenarios selected for environmental, health and safety assessment of a chemical process route are shown in the Figure 3.2.in this hazards assessment, both accidental and continuous releases or releases due to daily plant operations are included. In the case of safety, one set of parameters including 5 potential impacts are considered to represent hazards involved with all release scenarios. However, these parameters are grouped in to two, called chemical safety and process safety. Similar classification has been adopted by Edwards and Lawrence (1993) in their work where a methodology was proposed for selecting process routes based on inherent safety. In this assessment methodology the environmental damages due to accidental releases are further categorized into catastrophic or total inventory of chemical release and emissions due to fire.

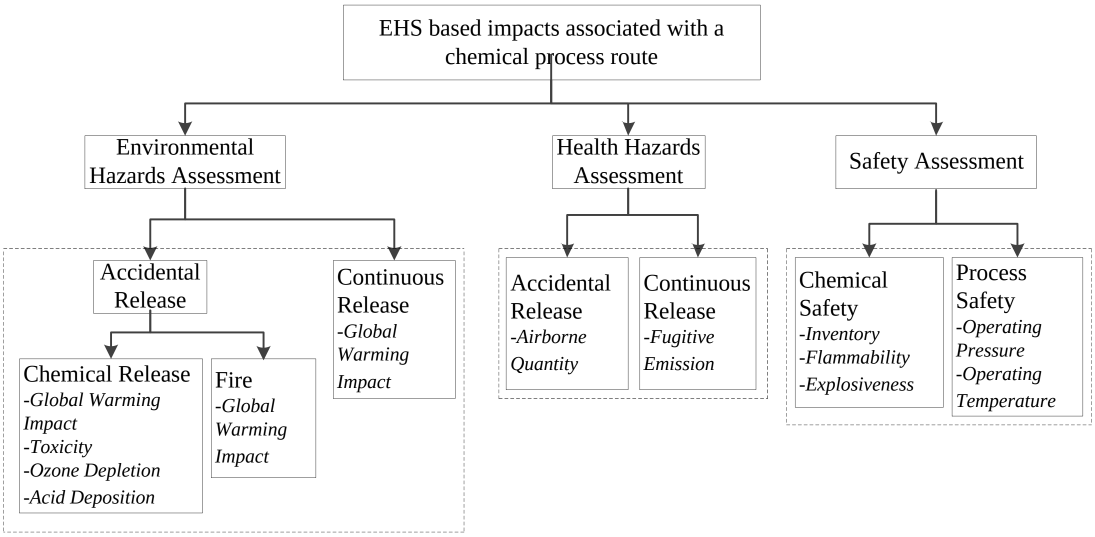

Figure 3.2: EHS based impacts associated with a chemical process route

3.2 Quantification of impacts

3.2.1 Environmental impacts

In this category, seven parameters are used to measure the environmental impacts resulting from chemical process plant releases. The environmental hazard due to accidental release of the total containment of chemicals in the plant is assessed by using four parameters which indicate the impact due to global warming, toxicity, ozone depletion and acid deposition. In addition, the environmental impact of fires resulting due to accidental releases of the total containment is assessed by global warming impact. In this, the evaluation is done based on the assumption that all carbon in chemical inventory is converted to carbon dioxide as a result of the fire. The global warming impact due to daily operational emission from the plant is used as a parameter to assess the environmental hazards due to continuous releases.

In this work, for developing the fuzzy based inherent environment, health and safety assessment (EHS-Fuzzy Index) the "environment" is defined as the ecosystem around the chemical process plant including living organisms.

3.2.1.1 Global warming impact due to greenhouse gas emission of accidental chemical release

It is assumed that global warming is causing the climate change impact. The global warming impact due to greenhouse gas emission (GHG) of accidental chemical releases is estimated using its GHG effect. The global warming of chemical releases is determined using the accidental release of entire GHGs present in the plant inventory. This includes the raw material and end-product stock that has the potential to be released to the atmosphere in case of an accident. The GHGs emitted are expressed in terms of equivalence of carbon dioxide. By using the global warming potential values available in literature (Scheutz et al., 2009), the global warming impact denoted by GWIacc-che is determined quantitatively for n number of GHGs released, using the Equation 1.

$$\mathrm{GWIacc-che} = \sum_{i=1}^{n} f_{\mathrm{GWPi}} \times \frac{Q_i}{M_i} \times 10^3 \qquad (1)$$

Where,

GWIacc-che- the Global Warming Impact due to greenhouse gas emission of accidental chemical releases (Kmol equivalence of CO_2)

M_i- molar mass (g/mol)

f_{GWPi}- global warming potential of chemical i (equivalence of CO_2)

Q_i- total quantity of chemical i released to the environment (te)

n- number of chemicals associated with the chemical process route

3.2.1.2 Toxicity impact on living things

The toxicity parameter is used to measure adverse effects on living organisms in the environment due to chemical exposure to accidental chemical releases. In this assessment, the terrestrial animals are considered to represent the living things in environment. The 'unit world' model environment described in Mackay and Paterson's (1981) work is used in estimating the released chemical concentration in the environment. An affected environment is defined as one square kilometer area circling around the chemical processing plant. The volumes of each compartment are given in Figure 3.3 (Mackay and Paterson, 1981).

The percentage of animals killed by exposing to the released chemical is considered in quantifying the toxicity impact of a chemical associated with a route. The percentage animal kill is estimated using the probit equation given in equation (2). The $Dose_i$ in this equation is the concentration of substance i and $Probit_i$ is the probit variable of substance i that gives a x% animal kill when $Dose_i$ is exposed to same animal species. The constants k1 and k2 are probit constants for chemical substance i for a respective animal group and can be estimated by considering a value such as the Lethal Concentration (LC) value for which the percentage of animal kill is known. The respective $Probit_i$ value to a percentage of animal killed is given by dose-response curve (Crowl and Louvar, 2001).

$$\mathrm{Probit_i} = \mathrm{k1_i} + \mathrm{k2_i}\ln(\mathrm{Dose_i}) \qquad (2)$$

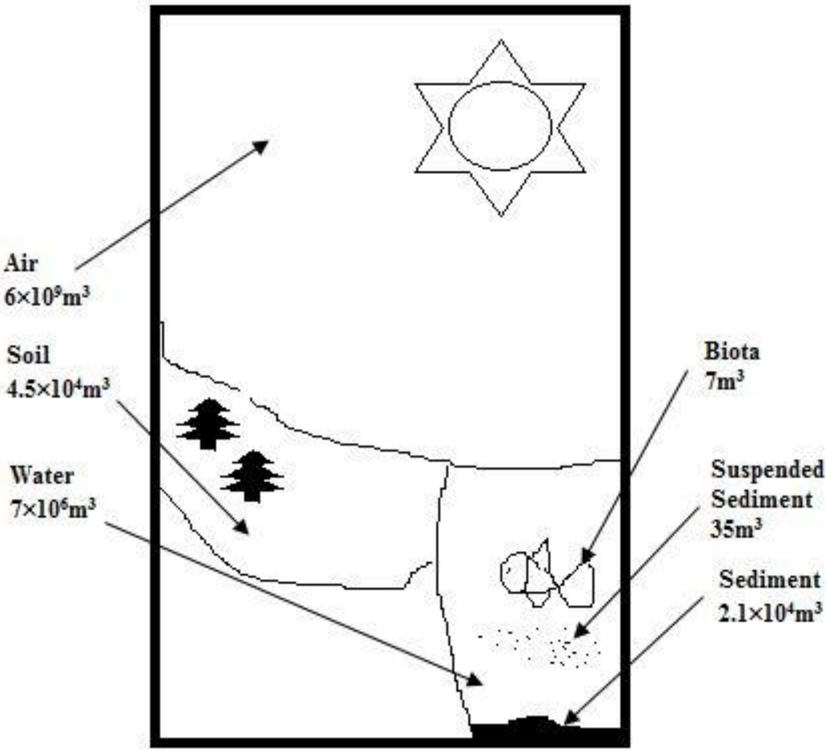

Figure 3.3: The model environment showing compartment volumes

The value of dose in equation (2) is estimated by determining the concentration of the chemical in the environment after the accidental release. This concentration referred to as the Predicted Environmental Concentration (PEC) is estimated by considering accidental release of chemicals under steady state multimedia distribution in the environment. The Fugacity model I is used to estimate the PEC (Mackay, 2001). In this model, air, water, soil, sediment, suspended solid and biota compartments are considered. The concentration of a chemical i in the air compartment (C_i) is determined considering the release of one tone of chemical into the environment. The chemical concentration in air compartment is considered because the major route of accidental chemical exposure is inhalation.

The C_i value should be estimated for all available chemicals associated with the route. The PEC_i for each chemical i is estimated considering the total quantity of chemical i (Q_i) in tons as showing in equation (3) in mol/m^3.

$$\mathrm{PEC_i} = \mathrm{Q_i} \times \mathrm{C_i} \qquad (3)$$

The toxicity due to chemical release is evaluated by the percentage of animal that can be killed due to the PEC_i. The Probit value for PEC_i can be calculated from Equation 2 when k1 and k2 values are known. Corresponding to this probit value, the percentage of animal killed (xi%) can be determined using the dose- response curve (Crowl and Louvar, 2001). The total toxicity impact of all chemicals associated with the chemical process route is quantified by TOXacc as shown in Equation (4). It is assumed that the total impact is additive and therefore, for all n number of chemical substances associated with the chemical process route, xi% values are added to obtain the TOXacc.

$$\mathrm{TOXacc} = \sum_{i=1}^{n} \mathrm{xi}\,\% \qquad (4)$$

In order to determine the constants k1 and k2 the LC inhalation values in mol/m^3 are considered. In the absence of such LC data, alternative data such as the threshold limit value (TLV) can also be considered. The sources of these data include TOXNET (https://toxnet.nlm.nih.gov) and OSHA data banks (https://www.osha.gov).

3.2.1.3 Ozone depletion

The stratospheric ozone layer is earth's sunscreen that protects living organisms from too much ultraviolet radiation. The emission of chemicals from process plants can damage the ozone layer.

The impact on the stratospheric ozone layer is assessed by ozone depletion (OD) that is caused by Cl and Br atoms contained in the emitted chemical molecules and their atmospheric lifetime (Ullmann, 1996). The ozone depletion of accidental chemical releases associated with the chemical process route (ODacc) is estimated by summing the values of individual ozone depletion of each chemical i. The ozone depletion of a chemical route is given by the expression shown in Equation (5).

$$\mathrm{ODacc} = \sum_{i=1}^{n} \tau_i \times \left(N_{i(Cl)} + 30 \times N_{i(Br)}\right) \times \frac{Q_i}{M_i} \times 10^6 \qquad (5)$$

Where

ODacc- ozone depletion impact of a chemical route (years)

τ_i- atmospheric life (years) of chemical i

$N_{i(Cl)}$ and $N_{i(Br)}$- the number of Cl and Br atoms respectively, per molecule

n- number of chemicals associated with the chemical process route

3.2.1.4 Acid deposition

The impact on vegetation due to any form of precipitation with acidic components as a result of accidental emissions of chemicals in the plant is considered in estimating this impact. The substances in the atmosphere deposit on vegetation by wet form or dry form.

The acid deposition of chemicals released is estimated based on the available acidic components in the chemicals associated with the chemical process route. This includes the raw material and end-product stock that will be released to the atmosphere in case of a catastrophic accident. The acidic components emitted are expressed in terms of the amount equivalence of Sulfur dioxide (SO_2). By using the characterization factor for acidification (CF_{AD}) values (Norris, 2003), the acid deposition impact due to accidental chemical release (ADacc) is determined for all acidic chemicals released, using the equation (6).

$$\mathrm{ADacc} = \sum_{i=1}^{n} \mathrm{CF_{AD}} \times \frac{Q_i}{M_i} \times 10^3 \qquad (6)$$

Where,

ADacc- the acid deposition impact due to accidental chemical release (Kmol equivalence of SO_2)

M_i- molar mass (g/mol)

Q_i- total quantity of chemical i released to the environment (te)

n- number of chemicals associated with the chemical process route

$CF_{AD\mathit{i}}$- characterization factor for acidification of chemical i

3.2.1.5 Global warming impact due to greenhouse gas emission of accidental fire

The global warming impact due to greenhouse gas emission of accidental fires is assessed by GHG effect resulting from emissions of the fire. The impact assessment is based on the assumption that all available carbon in chemical substances in the plant chemical inventory are converted into carbon dioxide during the fire associated with the accidental release of the total inventory. The conversion of carbon into carbon dioxide is shown in following balanced equation (7).

$$C_xH_y + (x + \frac{y}{2})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \qquad (7)$$

In this scenario, it is assumed that carbon dioxide is the only GHG that is emitted due to fire. Therefore, the climate change due to global warming impact is considered as proportional to the available carbon moles in the total inventory of the chemical plant. The global warming impact due to GHG emission of accidental fire (GWIacc-fire) is estimated as shown in equation (8).

$$\mathrm{GWIacc-fire} = \sum_{i=1}^{n} N_{i(C)} \times \frac{Q_i}{M_i} \times 10^3 \qquad (8)$$

GWIacc-fire- the global warming impact due to GHG emission of accidental fire (Kmol equivalence of CO_2)

$N_{i(C)}$- the number of C atoms of substance i, per molecule

3.2.1.6 Global warming impact due to greenhouse gas emission of continuous operation

The global warming impact due to GHG emissions from daily operation condition of the process route is estimated by considering the amount of carbon dioxide emitted from continuous operation of the plant. The determination of GHG emission or CO2 emission is based on the cumulative energy demand (CED). The CEDi represents the rate of energy required to heat the reactant i from atmospheric condition to its reaction condition. Similar method has been adopted in the ‘complete green metrics evaluation’ methodology of various chemical routes presented by Andraos (2015).

The energy demand of a chemical process plant is provided by an internal or external energy source. In this study, the CED rate of all reactants are added and divided by heat of reaction energy of carbon combustion (Equation (9)) to estimate the global warming impact due to GHG emission of continuous operation (GWIcon) (Equation (11)).

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad \Delta\mathrm{H_{CO_2}} \qquad (9)$$

The CED calculation method is given in Equation (10). This expresses the energy requirement for conversion of a solid phase chemical substance to a gas phase chemical substance. The energy required to heat a chemical substance depends on the phase of reactant and the phase of reaction that is whether it is a liquid or a gas phase reaction (Andraos, 2015). If the reactant is in liquid phase, the heat capacity for solid and the heat of fusion are neglected. The melting point temperature (T_m) is substituted with atmospheric temperature (298K). On the other hand, if the chemical substances are in gas phase, the heat capacity of solid, the heat capacity of liquid, heat of fusion (ΔH_{fus}) and heat of vaporization (ΔH_{vap}) are neglected and the boiling point temperature (T_b) is substituted with the atmospheric temperature. The temperature dependent heat capacity functions at the constant pressure are used to calculate heat capacities of input substances. The enthalpy changes due to pressure are neglected.

$$\mathrm{CED_i} = \int_{298}^{T_m} C_{p,sol}(T)\, dT + \int_{T_m}^{T_b} C_{p,liq}(T)\, dT + \int_{T_b}^{T_{react}} C_{p,gas}(T)\, dT + \Delta H_{fus} + \Delta H_{vap} \qquad (10)$$

The global warming impact due to GHG emission of continuous operation of a chemical process route (GWIcon) is estimated by Equation 11, where q_i is molar feed rate of chemical substance i in a chemical reaction and CED_i is energy requirement for a chemical substance i to get to the reaction condition from atmospheric condition.

$$\mathrm{GWIcon} = \sum_{i=1}^{n} \frac{\mathrm{CED_i} \times q_i}{\Delta\mathrm{H_{CO_2}}} \qquad (11)$$

Where

GWIcon- the global warming impact due to GHG emission of continuous operation (kmol equivalents of CO_2/hour)

q_i- molar feed rate of chemical i (kmol/hour)

CED_i- cumulative energy demand of chemical i (kJ/mol)

ΔH_{CO2}- heat of combustion of carbon (kJ/mol)

n- number of chemicals associated with the chemical process route

3.2.2 Health impacts

The occupational health impacts on personnel at plant working environment are considered for this assessment. There are two types of inherent health impacts considered in the development of the methodology. They are impacts due to accidental releases that are confined to the chemical plant working environment and impacts due to continuous releases or operational releases also confined to the chemical plant working environment. The health impact due to accidental releases are assessed by airborne quantity due to accidents where the releases are confined to the plant environment and short-term exposure limit. The health impact due to continuous releases are assessed by fugitive emissions and time weight average values.

3.2.2.1 Occupational health impact from work place accidental release airborne quantity

There are three possible accidental releases producing airborne substances which will have impacts within a chemical process plant. The gas phase operations can result in gaseous releases into plant environment due to various operation conditions. The flash liquid releases are observed in liquid phase operations where operating condition is above the boiling point temperature. The releases from liquid phase operation below boiling point temperature will be mainly by evaporation of materials from the pool surfaces.

The airborne quantity (m_{AQ}) in the plant due to accidental gas releases, flash liquid and evaporation from pool surface are determined according to the method proposed by Dow chemicals (1998) for inherent occupational health hazards assessment.

In order to estimate the chemical concentration due to "work place accidental releases along with the airborne quantity (m_{AQ})" flow rate (VF) is used. The VF is calculated considering a typical wind speed within work place (V), the average height of main unit operations' leak source (h) and the floor area of the process plant (A_{Floor}) (Hassim and Hurme, 2010). The calculation of VF is given by Equation (12).

$$\mathrm{VF} = \mathrm{V} \times \mathrm{h} \times \sqrt{\mathrm{A_{Floor}}} \qquad (12)$$

Where,
V- 4m/s (Hassim and Hurme, 2010)
h- 7m (Hassim and Hurme, 2010)
A_{Floor}- cumulative value of average floor area of each unit operation (Hassim and Hurme, 2010)

The mass fraction of each chemical (xi) in a reactor is used to estimate the mass flow of individual chemicals ($xi \times m_{AQ}$). The individual flow rate can be then converted into concentration by dividing it with VF. The hazards due to airborne materials of any accidental release is determined by cumulative value of the ratio between individual concentration of a chemical i and its short-term exposure limit (STELi) as shown in equation (13). The impact due to work place accidental release airborne quantity (AQacc) is calculated for all possible accidental releases using Equation (13). The AQacc values determined for each accident are denoted by AQaccM, where M varies from 1 to the maximum number of possible accidents M. The maximum AQacc value out of all AQacc values for possible accidental releases is selected to represent the health impact of the chemical process route (HAQacc) as shown in Equation (14).

$$\mathrm{AQaccM} = \sum_{i=1}^{M} \frac{x_i \times m_{AQ}}{\mathrm{VF} \times \mathrm{STEL_i}} \qquad (13)$$

$$\mathrm{HAQacc} = \mathrm{Max}\,\{\,\mathrm{AQacc1}, \mathrm{AQacc2}, \mathrm{AQacc3}, \ldots\ldots\} \qquad (14)$$

Where

AQacc1, AQacc2, etc. - the health impact value of each work place accidental release scenario

HAQacc- health impact of work place accidental release airborne quantity of a chemical route

m_{AQ}- airborne quantity (kg/s)

x_i- mass faction of chemical i in the stream

VF- volumetric flow rate (m^3/s) of air in the work place

$STEL_i$- short-term exposer limit of chemical i (kg/m^3)

n- number of chemicals in the stream

3.2.2.2 Occupational health impact due to fugitive emissions

The impact on human health due to emissions from continuous operation at the chemical process plant is assessed by considering fugitive emissions. The fugitive emission rate is determined by following the procedure proposed by Hassim and Hurme (2010) in their work on inherent occupational health assessment.

In this estimation methodology, the main unit operations such as reactors, separators and compressors in the process block diagram of a chemical process route are considered. The number of piping components associated with each unit is determined according to the method presented in the health quotient index development by Hassim and Hurme (2010).

The number of piping components and their pre-calculated emission data give the total fugitive emissions associated with the unit (Hassim et al., 2012). The pre-calculated emissions data are defined by U.S. Environmental Protection Agency (EPA, 1995). The mass fractions of individual chemicals in any fugitive emission are assumed equal to the mass fractions of individual chemical components in the relevant chemical process stream from which the emission took place.

The fugitive emission rate of a chemical ($m_{i,FE}$) can be converted into concentration by dividing it with the volumetric flow rate (VF). The health impact due to fugitive emission of any chemical i released is determined by dividing the fugitive emission concentration with the Time Weighted Average value (TWAi). By assuming that the total effect due to release of chemicals is additive, the impact from all chemicals (FEcont) is determined using Equation (15).

$$\mathrm{FEcont} = \sum_{i=1}^{n} \frac{m_{i,FE}}{VF \times TWA_i} \qquad (15)$$

Where

FEcont- health impact due to fugitive emission of a chemical route

$m_{i,FE}$- fugitive emission rate of chemical substance i (kg/s)

TWAi- time weighted average value of substance i (kg/m^3)

VF- volumetric flow rate (m^3/s)

n- number of chemicals associated with the chemical process route

3.2.3 Safety

For inherent safety assessment, chemical safety and process safety aspects involved in a chemical process plant are considered separately. The inventory, flammability and explosiveness are considered under chemical safety and heat of reaction, operating pressure and operating temperature are considered to assess the process safety. The associated hazards in each of these six parameters and their quantification methods are discussed in the following section.

3.2.3.1 Inventory

Large amount of substances present in the chemical process plant is hazardous compared to small quantities, under the same conditions. The hazard due to inventory of chemical i involved in a route is considered proportional to its quantity present in the plant (Qi). The total hazard posed is assumed additive and is determined using (INVche) Equation (16).

$$\mathrm{INVche} = \sum_{i=1}^{n} Q_i \qquad (16)$$

Where

INVche- chemical safety impact of a chemical route (te)

n- number of chemicals associated with the chemical process route

3.2.3.2 Flammability

The flammability measures the tendency of a chemical to burn. The chemical safety from accidental fire of a flammable substance could be measured by flammability values. A higher hazard is posed by large quantity of more flammable substance than a small quantity. Therefore, the mass fraction of each chemical is used to assess the hazard due to flammability. Assuming additive property of effects from each chemical, the flammability hazard posed by all the chemicals for a chemical route (FLAche) is derived from Equation (17).

$$\mathrm{FLAche} = \sum_{i=1}^{n} Y_i \times F_i \qquad (17)$$

Where

FLAche- flammability hazard of a chemical route

Yi- mass fraction of chemical i

Fi- flammability of chemical i (NFPA fire rating)

n- number of chemicals associated with the chemical process route

The flammability Fi of each chemical involved in the route is taken from National Fire and Protection Agency (NFPA) fire rating. The NFPA ratings have values ranging from 0 (minimum impact) to 4 (extreme impact) as shown in Table 3.1, which is developed by relating flash point (T_f) and boiling point (T_b) values.

Table 3.1: NFPA fire ratings

	Flammability
Non- combustible	0
$T_f > 60\ ^{O}C$	1
$37.78\ ^{O}C < T_f < 60\ ^{O}C$	2
$37.78\ ^{O}C > T_f$ & $37.78\ ^{O}C < T_b$	3
$37.78^{O}C > T_f$ & $37.78\ ^{O}C > T_b$	4

3.2.3.3 Explosiveness

The explosiveness measures the tendency of chemicals to form an explosive mixture in the air. In the assessment of safety impact due to explosiveness for a chemical route (EXPche) is defined as shown in Equation (18). Here, the explosiveness for a chemical i, Ei is determined by the difference between the low explosiveness limit (LEL) and the upper explosiveness limit (UEL). The total explosive hazard posed by all the chemicals associated with the route is estimated by assuming additive effects. The mass fraction Yi and Ei of each chemical i are used in estimating the hazards as shown in Equation (18).

$$\mathrm{EXPche} = \sum_{i=1}^{n} \mathrm{Y_i} \times \mathrm{E_i} \qquad (18)$$

Where

n- number of chemicals associated with the chemical process route

3.2.3.4 Operating pressure

Pressure is the measurement of energy available to cause a chemical release. Therefore, the processes operating under high pressures are generally considered as hazardous. The maximum gauge pressure value associated with the production process of one route is considered to measure the process safety impact due to operating pressure (Ppro) as showing in Equation (19).

$$\mathrm{Ppro} = \mathrm{Max}\{P_1, P_2, \ldots P_j \ldots\} \qquad (19)$$

Where

Ppro- process safety impact due to operating pressure of a chemical route (atm)

P_j- gauge pressure of reaction step j (atm)

3.2.3.5 Operating temperature

The process operating temperature is also a direct measurement of hazard that represents heat energy available for release. Therefore, the hazard due to operating temperature is assessed by considering temperature difference of operating temperature and atmospheric temperature (25^{o}C). The maximum operating temperature value associated with the production process of one route is considered to measure the process safety impact due to operating temperature (Tpro) as showing in Equation (20).

$$\mathrm{Tpro} = \mathrm{Max}\{\mathrm{T}_1, \mathrm{T}_2, \dots \mathrm{T}_j \dots\} \qquad (20)$$

Where

Tpro- process safety impact due to operating temperature of chemical route (K)

T_j- difference between operating temperature and ambient temperature of reaction step j (K)

3.3 Multi criteria decision- making methodology

In this methodology as described in the previous section, there are 13 parameters selected to represent the hazard posed by a chemical process route. In order to select the route that has the least hazard, one must consider all above parameters as criteria for minimizing hazard in the decision making process. The multi criteria decision making theories are important when more than one criteria are present in making a decision. Various approaches are available in making a multicriteria decision such as weighted sum method (WSM), weighted product model (WPM), fuzzy based method and analytical hierarchy mode (AHM) method (Triantaphyllou, 2000). The fuzzy based method is a well established multicriteria decision making method that can be used to integrate number of parameters, with expert knowledge input, avoiding subjective judgments.

Fuzzy logic determines a set of mathematical principles for knowledge representation based on degree of membership rather than crisp membership of classical binary logic.

Unlike two- value Boolean logic, fuzzy logic is multi valued. It deals with degrees of membership and degree of truth. Fuzzy logic uses the continuum of logical values between 0 (false) and 1 (true) instead of just true and false.

3.3.1 Proposed Fuzzy logic- based assessment method

The fuzzy logic approach is one of the important methods used in multicriteria assessments of variety of scientific applications. Its one of the first applications on process control has been during 1980s by E.H. Mamdani (Gentile et al., 2003). Since then, the fuzzy logic approach has been applied in variety of multicriteria risk assessment methodologies (Christen et al., 1994; Khan and Amyotte, 2004; Topuz et al., 2010).

In line with the Gentile et al. (2003) development, fuzzy logic Mamdani's method is incorporated in the parameters combining of the EHS-Fuzzy Index determination methodology. For this, initially a Fuzzy Inference System (FIS) was developed. A FIS is a nonlinear mapping that derives its output based on fuzzy reasoning and a set of fuzzy if-then rules (Gentile et al., 2003). The Mamdani's model is mainly based on groups of 'IF-THEN' rules. These groups of rules must be able to identify the expected behavior of the physical system when values of the inputs are defined for the input fuzzy sets. In the rules, the connector used can be AND or OR that depends on the requirements of the physical model.

The most important aspect of FIS is input and output membership functions. The membership function is a mathematical illustration of fuzzy set and there are few criteria to define them. The criteria used in the methodology proposed in this work are based on those used in the works done by Lootsma (1997) on fuzzy logic for planning and decision making, and by Gentile et al. (2003) on hierarchical fuzzy model for the evaluation of inherent safety. They are as follows:

- Linguistic variable should be defined with fuzzy sets.

- The position of the zero: there is a point of natural zero for the physical system. For example: hazard can be zero when the environmental or health or safety impact is zero for a chemical process route.
- Universe of discourse: total of fuzzy sets that should be defined to cover the whole range
- Development of universe of discourse for output membership function: universe of discourse representing the whole range of the membership is brought to a range from zero to one.
- Distinct semantic meaning: each fuzzy set must be assigned a specific meaning to distinguish from any other set of same linguistic variable.

The fuzzy logic multicriteria decision making approach follows four basic steps. These steps applicable for any fuzzy application are shown in Figure 3.4. The EHS-Fuzzy Index approach consists of 19 FISs. Out of these nineteen, 13 FISs are used for obtaining hazard potential (HP) values corresponding to each 13 EHS impacts identified and quantified in the previous section. In this section, these 13 impacts are also referred to as primary parameters. The other 6 FISs are used for aggregation operations of the 13 HP values obtained above.

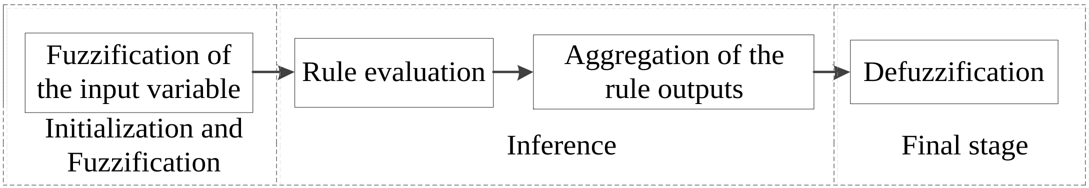

Figure 3.4: Fuzzy based multi criteria decision making approach for EHS- Fuzzy Index

The methodology for the application of FISs in primary parameters and obtaining of respective HP values for the 13 EHS impacts are discussed separately in sections 3.3.2 and 3.3.3. Following this discussion, the development of the methodology on application of FISs in aggregating the 13 hazard potential values and the determination of the EHS-Fuzzy Index are described in section 3.3.4 and section 3.3.5 respectively.

3.3.2 Fuzzy inference system for primary parameters

3.3.2.1 Initialization for primary parameters

In this section, definition of linguistic variables and terms for all primary parameters are presented. The development of the membership functions and respective IF-THEN rules for the primary parameters are presented separately.

The fuzzification starts with input of data (crisp inputs) to the system. The crisp inputs are converted to fuzzy input sets using linguistic variable, membership functions and rule base.

Definition of linguistic variables

Linguistic variables are the input and output variables of the fuzzy inference system (FIS). Linguistic variables are words or sentences in natural language, instead of numerical values. The list of notations used for the linguistic variables in this work for the 13 parameters selected to represent the hazards posed or EHS impacts by a chemical process route also referred to as 13 primary parameters are given in Table 3.2.

Table 3.2: List of input and output notations to the FISs used for the primary parameters

	Primary parameters	**Notation for inputs**	**Units of input**	**Notation for outputs**	**Units of output**
Environmental hazard assessing	Global warming impact due to greenhouse gas emission of accidental chemical release of total inventory	GWIacc-che	Kmol	GWIACC-CHE	HP
	Toxicity of accidental chemical releases	TOXacc	%	TOXACC	HP

	Ozone depletion of accidental chemical releases	ODacc	Years	ODACC	HP
	Acid deposition impact of accidental chemical releases	ADacc	-	ADACC	HP
	Global warming impact due to greenhouse gas emission of accidental fire	GWIacc-fire	Kmol	GWIACC-FIRE	HP
	Global warming impact due to greenhouse gas emission of daily continuous operation in the plant	GWIcon	Kmol/hour	GWICON	HP
Health hazards assessing	Occupational health impact from work place accidental release airborne quantity	HAQacc	-	HAQACC	HP
	Occupational health effect due to fugitive emission	FEcont	-	FECONT	HP
Safety assessing parameters	Inventory	INVche	te	INVCHE	HP
	Flammability	FLAche	-	FLACHE	HP
	Explosiveness	EXPche	%	EXPCHE	HP
	Operating temperature	Tpro	ºC	TPRO	HP
	Operating pressure	Ppro	atm	PPRO	HP

3.3.2.2 Fuzzification and Defuzzification of primary parameters

The most important part of the fuzzy inference system is the IF-THEN rule that describes the relationship between linguistic variables and membership functions. A membership function is defined for the 13 parameters representing the EHS hazards. The list of notations is given in Table 3.2 for primary parameters.

As the parameters representing EHS hazards are numerical values of different units, the membership function is used to convert them to a universal format. In the development of the membership function a Universe of Discourse (U) is defined for each parameter. The universe of discourse is the universal format that can be used to represent the primary parameter.

The primary parameters are converted into hazard potential (HP) value using FIS. The HP of each parameter represents the hazard level from zero to one scale. The FIS proposed in this methodology for conversion of primary parameter value to HP uses the Mamdani model. The steps followed in this methodology are shown below:

- The first step of fuzzy inference requires to identify input membership function corresponding to the impact quantity calculated.
- Using the input membership function, determine the membership value from 0 to 1 corresponding to the impact quantity.
- Identify the relevant output membership function according to the IF-THEN rules.
- Fuzzy inference is completed with highlighting the area of output membership functions according to the membership values.
- The defuzzification is the last step in determination of the hazard potential (HP). There are many types of defuzzification methodologies such as centroid, center of area and maxima. In this methodology, the centroid methodology is used in defuzzification because it is the most widely used method in the Mamdani model. The center of gravity (COG) of the area determined by the output membership function gives the output in terms of Hazard Potential (HP)s.

In order to carry out the above procedure to determine HP values, membership functions are defined. For this, six linguistic terms are defined for each primary parameter or impact. The linguistic variables of the parameter or the impact are defined as very low, low, medium, high, very high and extremely high impact. These six terms were then characterized by fuzzy numbers defined within the universe of discourse. Each of these fuzzy sets characterizing the linguistic variable is represented by a membership function. The membership functions (μ) are defined in triangular shapes. The membership is described by values $0 \leq \mu \leq 1$ (Gentile et al., 2003).

The output membership is also defined from 0 to 1, where 0 indicates absolute absence of hazard and 1 indicates extreme hazard. Where, universe of discourse of all the HP values are defined from zero hazards to extreme high hazard.

The Hazard Potential is defined using six hazard level terms which are in the range from 0 to 1, where 0 indicates absolute absence of hazard and 1 indicates extreme hazard. The universe of discourse of HP is also defined from zero hazard to extreme high hazard. The six hazard levels used in this work are namely, very low hazard, low hazard, medium hazard, high hazard, very high hazard and extremely high hazard.

Criteria for the construction of membership function

The height of the membership function indicates the maximum possible value produced by the fuzzy inference rules. Usually the height of the membership is considered as one.

The membership functions for primary parameters in this work were developed to meet following criteria:

- Height of each membership (μ) is defined as a one
- Range of output membership function is given [0 1]
- Crossover points of each memberships at μ= 0.5
- Range of initial and final fuzzy sets of output functions are stretched according to fuzzy numbers defined in each section. This is done because the centroid defuzzification method is based on the calculation of the clipped output set.

3.3.3 Definition of membership function and IF-THEN rules for primary parameters

3.3.3.1 Membership functions and IF-THEN rules for global warming impact due to greenhouse gas emission of accidental chemical releases

The universe of discourse of the global warming caused by GHG due to accidental chemical release of total inventory (GWIacc-che) is defined from 0 Kmol of CO_2 equivalents to an emission amount of 227 300 Kmol of CO_2 equivalents. The latter is the GHG emissions from Kilauea volcano within one day. This quantity of emission is assumed as the case where an extreme hazard or maximum possible impact on global warming due to GHG emissions can occur. The fuzzy number defining input and output memberships GWIacc-che are shown in Table 3.3. The membership functions drawn according to this definition are shown in Figure 3.5 and Figure 3.6.

Table 3.3: Fuzzy sets of GWIacc-che and the shape of the input and output membership functions

Inputs	**Linguistic description**	**Abbreviation**	**Shape**	**Fuzzy number**
GWIacc-che (GHG Emission Kmol of CO_2 equivalence)	Very Low Global Warming Impact	VLGWI	Triangular	[0, 0, 22730]
	Low Global Warming Impact	LGWI	Triangular	[0, 22730, 45460]
	Medium Global Warming Impact	MGWI	Triangular	[22730, 45460, 90920]
	High Global Warming Impact	HGWI	Triangular	[45460, 90920, 136380]
	Very high Global Warming Impact	VHGWI	Triangular	[90920, 136380, 227300]
	Extremely high Global Warming Impact	EHGWI	Triangular	[136380, 227300, 227300]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
GWIACC-CHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]

	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

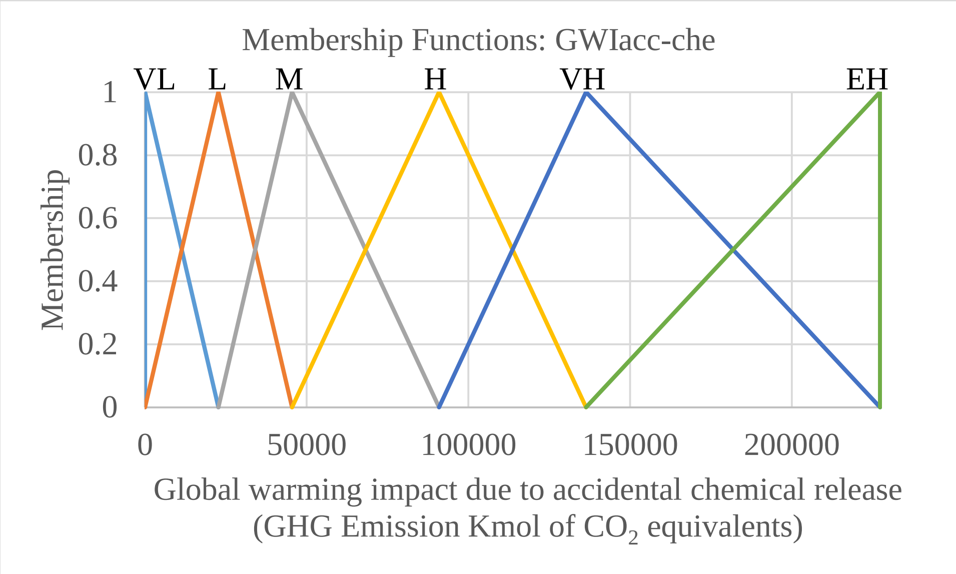

Figure 3.5: Input membership functions of GWIacc-che

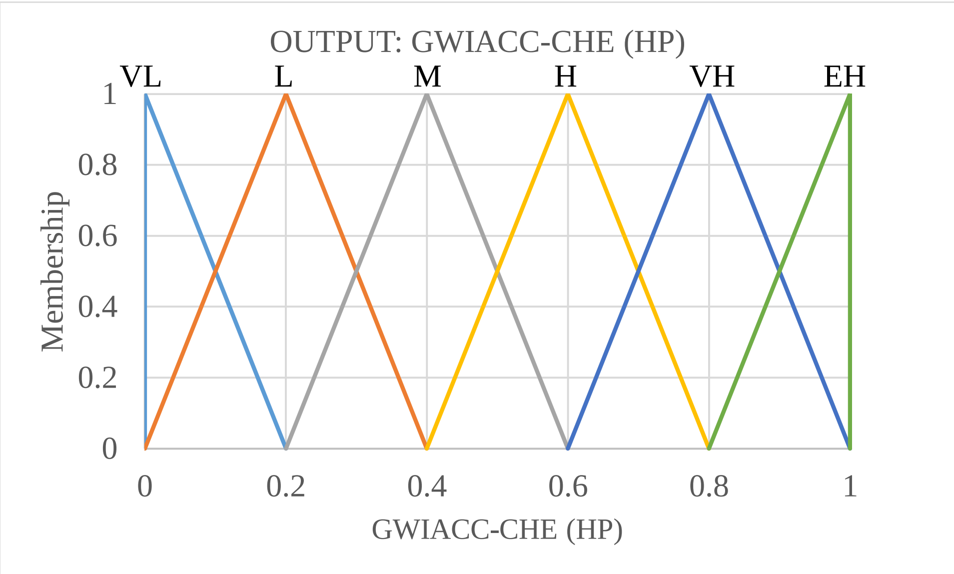

Figure 3.6: Output membership functions of GWIACC-CHE

IF-THEN rules

The IF-THEN rules for global warming impact due to greenhouse gas emission of accidental chemical release of the total inventory were developed by relating the GHG emissions with global warming impact. The global warming impact is low, if the greenhouse gas emissions of accidental chemical release are low. Further, the impact increases with the increase in the amount of greenhouse gas emissions from accidental chemical release. Based on this, the Fuzzy IF-THEN rules developed for GWIacc-che are shown in Table 3.4.

The general rule is:
IF ("Greenhouse gas emission of accidental chemical releases" is ___) THEN ("Global warming impact" is ___).
All possible rules for this impact are shown in Table 3.4.
One example for an operation is:
IF ("Greenhouse gas emission of accidental chemical releases" is very low (VLGWI)) THEN ("Global warming impact" is very low (VLH)).

Table 3.4: Fuzzy IF-THEN rules for GWIacc-che

	IF (GWIacc-che)					
	VLGWI	LGWI	MGWI	HGWI	VHGWI	EHGWI
THEN (GWIACC-CHE (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.2 Membership functions and IF-THEN rules for toxicity due to accidental chemical releases

The percentage of animal killed due to chemical inhalation is considered for toxicity measurement. The universe of discourse of the TOXacc is defined from 0 to 100%. This range is define considering maximum and minimum percentage of animal that can be killed. The fuzzy sets defining TOXacc of input and output memberships are shown in Table 3.5. The membership functions drawn according to this definition are shown in Figure 3.7 and Figure 3.8.

Table 3.5: Fuzzy sets of TOXacc and the shape of the input and output membership functions

Inputs	Linguistic Description	Abbreviation	Shape	Fuzzy number
TOXacc (Percentage of animal killed %)	Very Low Toxicity	VLTOX	Triangular	[0, 0, 10]
	Low Toxicity	LTOX	Triangular	[0, 10, 20]
	Medium Toxicity	MTOX	Triangular	[10, 20, 40]
	High Toxicity	HTOX	Triangular	[20, 40, 60]
	Very High Toxicity	VHTOX	Triangular	[40, 60, 100]
	Extremely High Toxicity	EHTOX	Triangular	[60, 100, 100]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
TOXACC (HP)	Very Low Hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low Hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard	EHH	Triangular	[0.8, 1, 1.2]

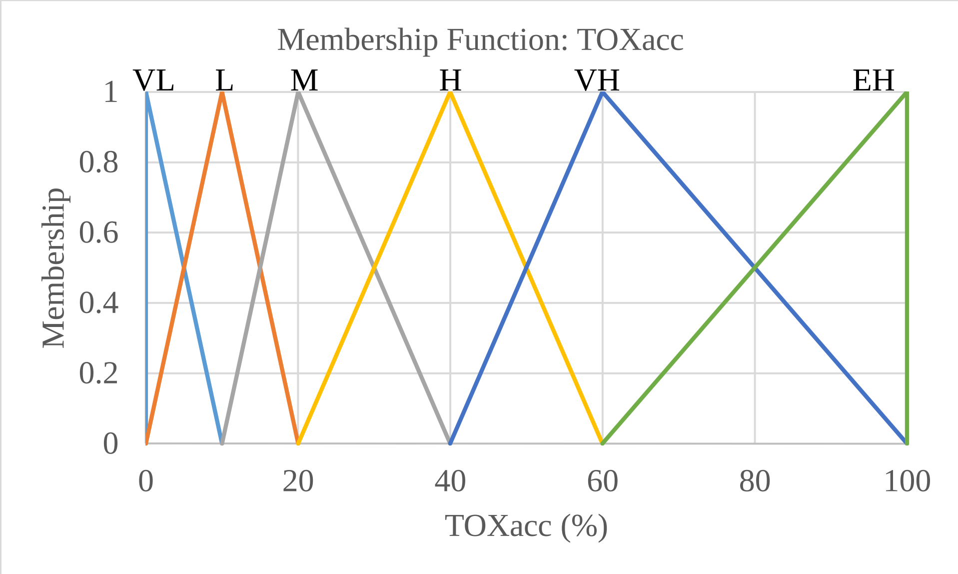

Figure 3.7: Input membership functions of TOXacc

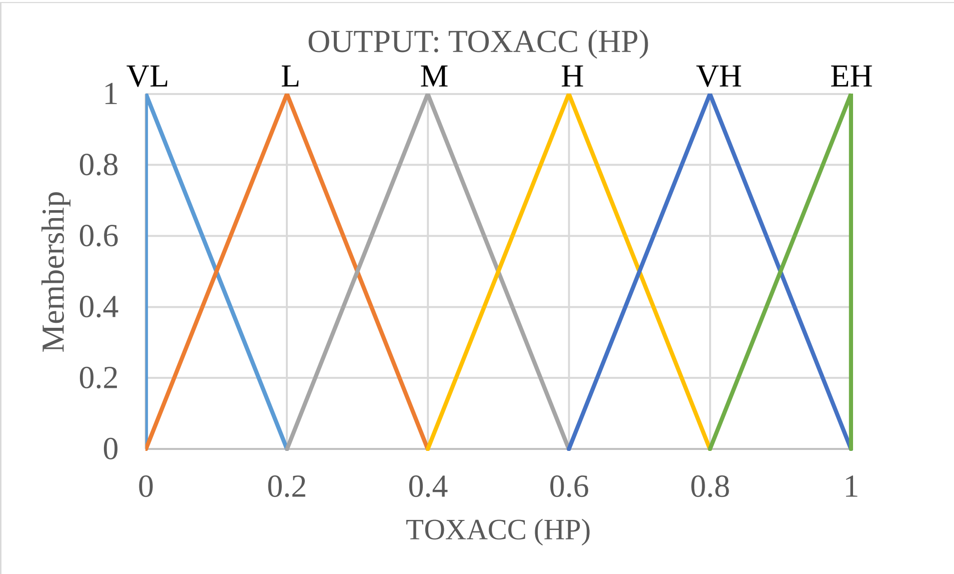

Figure 3.8: Output membership functions of TOXacc

IF-THEN rules

The IF-THEN rules for toxicity due to accidental chemical releases represent the relationship between toxicity and hazard. The hazard due to toxicity is low if the toxicity of accidentally released chemicals is low. Further, the hazard increases with the increase in toxicity. Based on this, the Fuzzy IF-THEN rules developed for TOXacc are shown in Table 3.6.

The general rule is:

IF ("Toxicity due to accidental chemical releases" is ___) THEN ("Hazard due to toxicity" is ___).

One example for this rule is:

IF ("Toxicity due to accidental chemical release" is very low) THEN ("Hazard due to toxicity" is very low).

Table 3.6: Fuzzy IF-THEN rules for TOXacc

	IF (TOXacc)					
	VLTOX	LTOX	MTOX	HTOX	VHTOX	EHTOX
THEN (TOXACC (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.3 Membership functions and IF-THEN rules for ozone depletion due to accidental chemical release

The universe of discourse of the ozone depletion is defined considering ozone depletion impact due to gases emitted from Kilauea volcano. The ozone depletion impact caused by the gases released from eruption of Kilauea volcano during a 3.29×10^9 years period (Gunasekera & Edwards, 2003) is considered as the situation where an extremely high ozone depletion impact can occur. The fuzzy numbers defining ODacc of input and output membership functions are shown in Table 3.7. The membership function drawn according to this definition are shown in Figure 3.9 and 3.10.

Table 3.7: Fuzzy sets of ODacc and shape of input and output membership functions

Inputs	**Linguistic description**	**Abbreviation**	**Shape**	**Fuzzy Number**
ODacc (years)	Very Low Ozone Depletion	VLOD	Triangular	$[0, 0, 3.29 \times 10^8]$
	Low Ozone Depletion	LOD	Triangular	$[0, 3.29 \times 10^8, 6.58\times 10^8]$

	Medium Ozone Depletion	MOD	Triangular	[3.29×10^8, 6.58×10^8, 1.32×10^9]
	High Ozone Depletion	HOD	Triangular	[6.58×10^8, 1.32×10^9, 1.97×10^9]
	Very High Ozone Depletion	VHOD	Triangular	[1.32×10^9, 1.97×10^9, 3.29×10^9]
	Extremely High Ozone Depletion	EHOD	Triangular	[1.97×10^9, 3.29×10^9, 3.29×10^9]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
ODACC-CHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

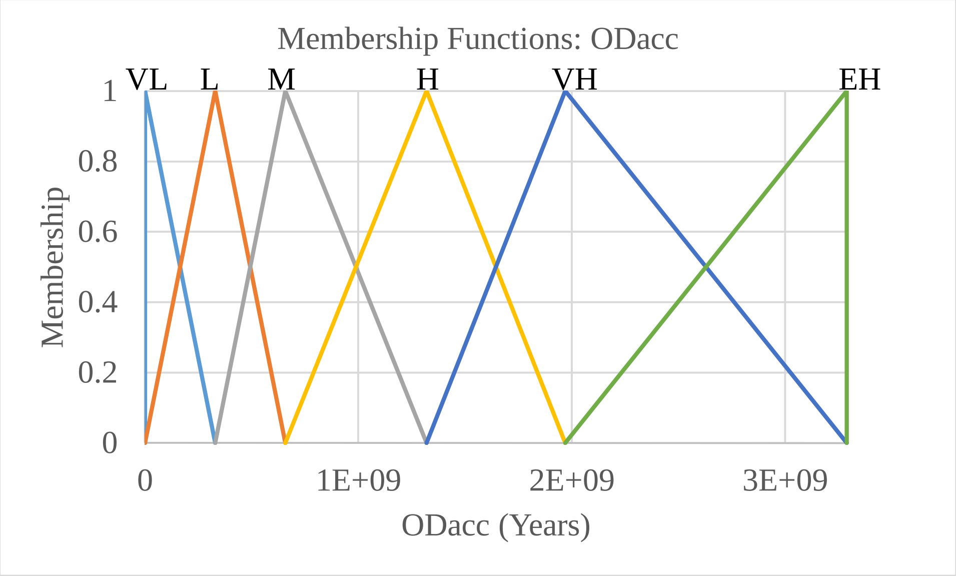

Figure 3.9: Input membership functions of ODacc

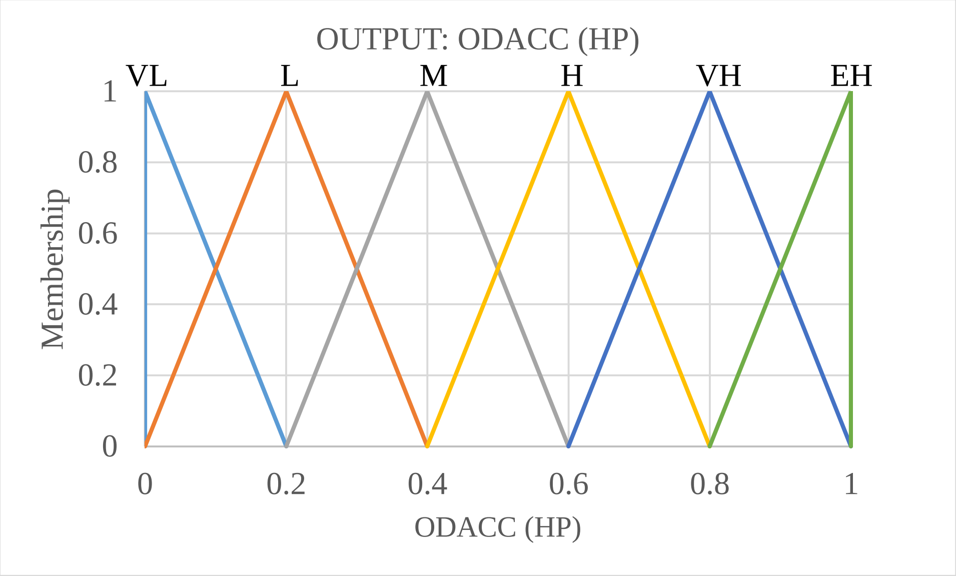

Figure 3.10: Output membership functions for ODacc

IF-THEN rules

The IF-THEN rules for ozone depletion impact due to accidental chemical release of the total inventory represent the relationship between ozone depletion and hazard potential. The hazard potential due to ozone depletion is low if the ozone depletion impact value of chemical accidentally released is low. Further, the hazard potential increases as the ozone depletion value increases. Therefore, the Fuzzy IF-THEN rules developed based on this for ODacc are shown in Table 3.8.

The general rule is:

IF ("Ozone depletion of accidental chemical releases" is ___) THEN ("Hazard potential" is ___).

One example for this rule is:

IF ("Ozone depletion of accidental chemical releases" is very low) THEN ("Hazard potential" is very low).

Table 3.8: Fuzzy IF-THEN rules for ODacc

	IF (ODacc)					
	VLODI	LODI	MODI	HODI	VHODI	EHODI
THEN (ODACC-CHE (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.4 Membership functions and IF-THEN rules for acid deposition due to accidental chemical release

The universe of discourse of the acid deposition caused by accidental chemical release (ADacc) is defined from 0 Kmol of SO_2 equivalents to an emission amount of 260 420 Kmol of SO_2 equivalents (Gerlach & McGee, 2002). The latter quantity is the SO_2 emission from Kilauea volcano within one day. This quantity of emission is assumed as the quantity that can pose an extreme hazard or maximum possible acid deposition impact due to SO_2 emissions. The fuzzy sets defining ADacc input and output membership functions are shown in Table 3.9. The membership functions drawn according to this definition are shown in Figure 3.11 and Figure 3.12.

Table 3.9: Fuzzy sets of ADacc and the shape of input and output memberships

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
ADacc (SO_2 emission Kmol of SO_2 equivalent)	Very Low Acid Deposition	VLAD	Triangular	[0, 0, 26042]
	Low Acid Deposition	LAD	Triangular	[0, 26042, 52084]

	Medium Acid Deposition	MAD	Triangular	[26042, 52084, 104168]
	High Acid Deposition	HAD	Triangular	[52084, 104168, 156252]
	Very High Acid Deposition	VHAD	Triangular	[104168, 156252, 260420]
	Extremely High Acid Deposition	EHAD	Triangular	[156252, 260420, 260420]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
ADACC (HP)	Very Low Hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low Hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard	EHH	Triangular	[0.8, 1, 1.2]

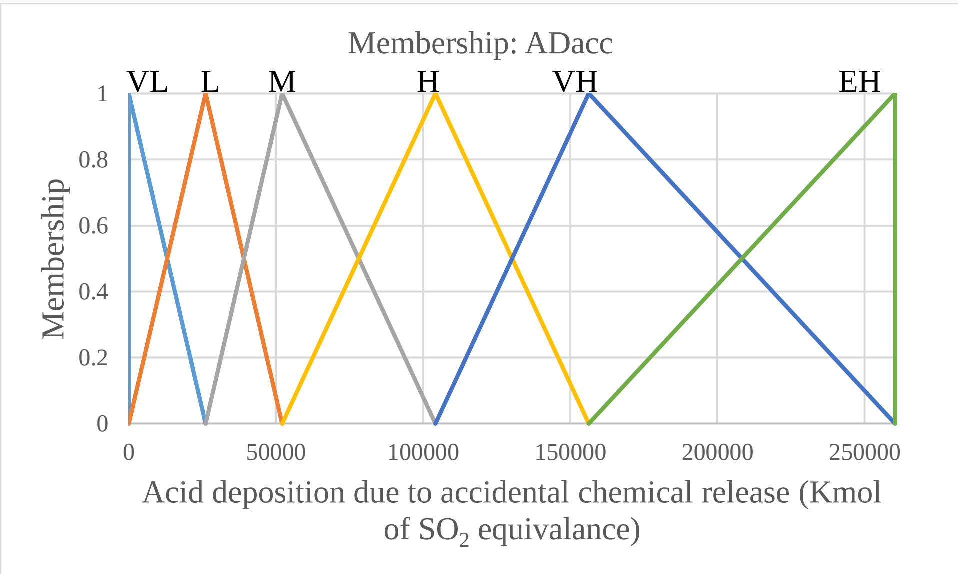

Figure 3.11: Input membership functions of ADacc

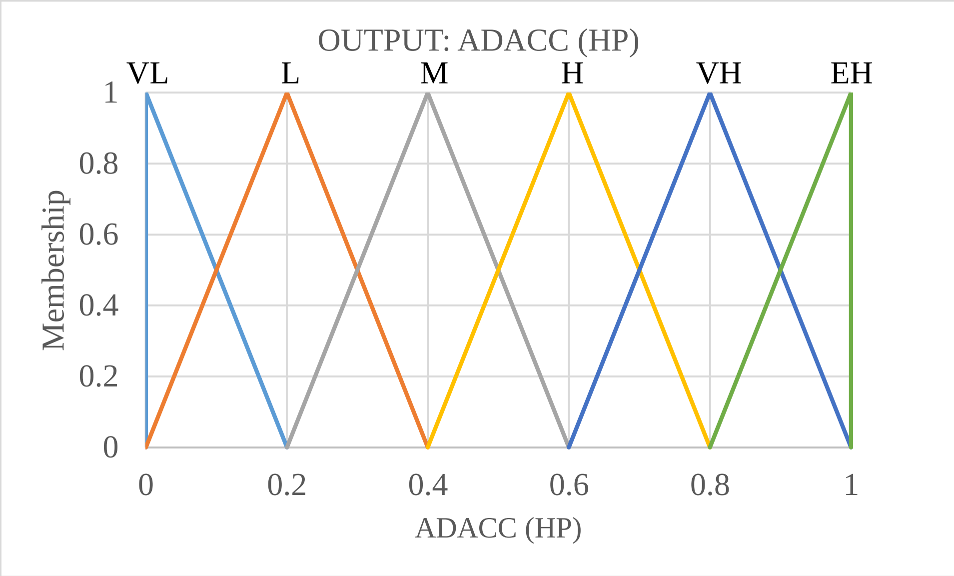

Figure 3.12: Output membership functions for ADacc

IF-THEN rules

The IF-THEN rules for acid deposition due to accidental chemical releases represent the relationship between acid deposition and hazard potential. The hazard potential of acid deposition is low if the acid deposition impact is low. Further, the hazard potential increases as the acid deposition impact of chemical accidentally released increases. Based on this, the Fuzzy IF-THEN rules developed for ADacc are shown in Table 3.10.

The general rule is:

IF ("Acid deposition due to accidental chemical release" is ___) THEN ("Hazard potential" is ___).

One example for this rule is: IF ("Acid deposition due to accidental chemical release" is very low) THEN ("Hazard potential" is very low).

Table 3.10: Fuzzy IF-THEN rules for ADacc

	IF (ADacc)					
	VLAD	LAD	MAD	HAD	VHAD	EHAD
THEN (ADACC (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.5 Membership functions and IF-THEN rules for global warming impact due to greenhouse gas emission of accidental fire

The universe of discourse of the global warming caused by GHG emission due to accidental fire (GWIacc-fire) is defined from 0 Kmol of CO_2 equivalents to an emission amount of 1, 591, 100 Kmol of CO_2 equivalents. The latter value is the GHG emission from Kilauea volcano within seven days (Gerlach & McGee, 2002; Tilling et al., 2010). This quantity of emission is considered as the quantity that can result in an extreme hazard or maximum possible global warming impact due to GHG emissions. The fuzzy sets defining GWIacc-fire input and output memberships are shown in Table 3.11. The membership function drawn according to this definition are shown in Figure 3.13 and Figure 3.14.

Table 3.11: Fuzzy sets of GWIacc-fire and shape of input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
GWIacc-fire (GHG Emission Kmol of CO_2 equivalent)	Very Low Global Warming Impact	VLGWI	Triangular	[0, 0, 159110]
	Low Global Warming Impact	LGWI	Triangular	[0, 159110, 318220]
	Medium Global Warming Impact	MGWI	Triangular	[159110, 318220, 636440]
	High Global Warming Impact	HGWI	Triangular	[318220, 636440, 954660]
	Very high Global Warming Impact	VHGWI	Triangular	[636440, 954660, 1591100]
	Extremely high Global Warming Impact	EHGWI	Triangular	[954660, 1591100, 1591100]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**

GWIACC-CHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

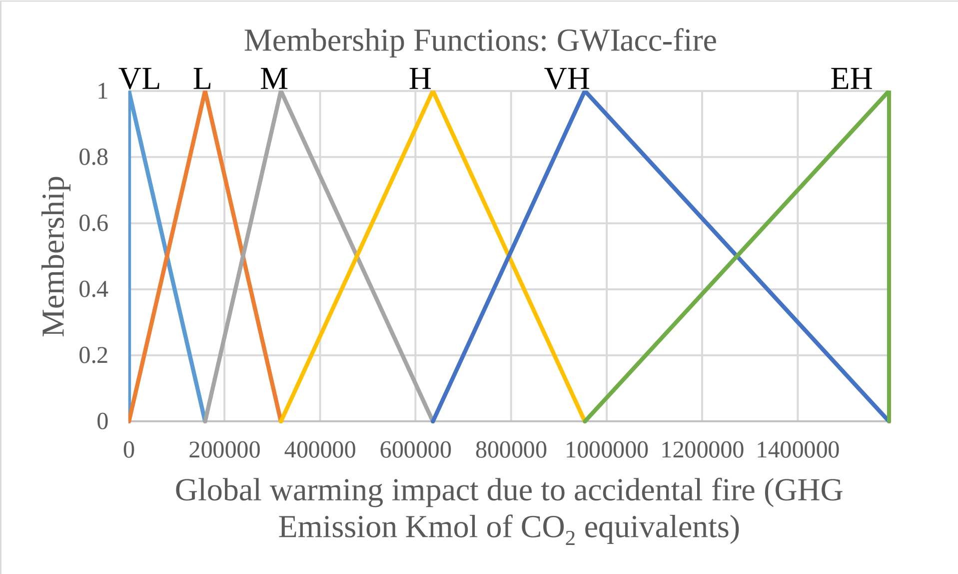

Figure 3.13: Input membership funtions of GWIacc-fire

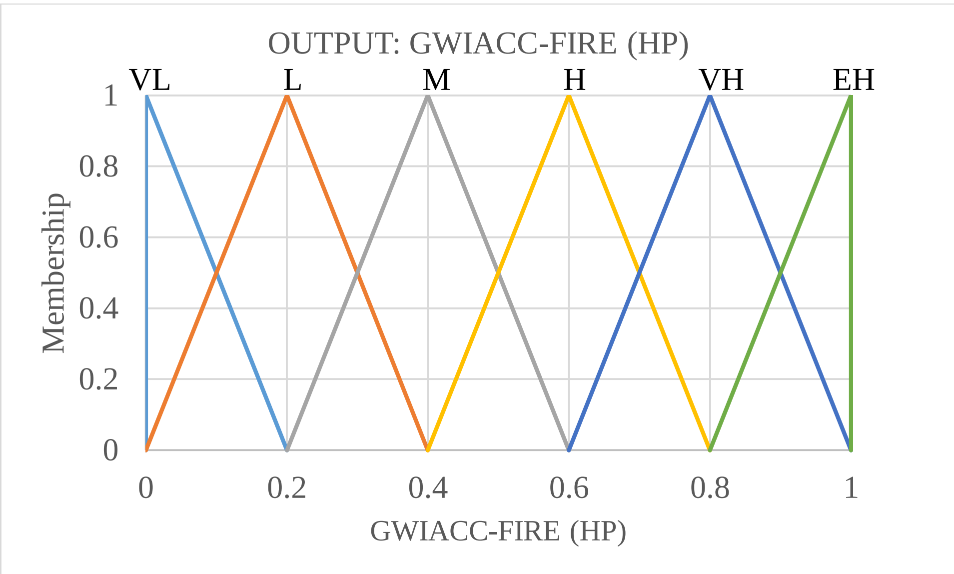

Figure 3.14: Output membership functions for GWIacc-fire

IF-THEN rules

The IF-THEN rules for global warming impact due to greenhouse gas emission of accidental fire represent the relationship between GHG emission (global warming impact) and hazard potential. The global warming impact is low, if the Greenhouse gas emission of accidental fire is low. Further, the impact increases s the amount of the greenhouse gas emissions of accidental fire increases. Based on this, the Fuzzy IF-THEN rules developed for GWIacc-fire are shown in Table 3.12.

The general rule is:

IF ("Global warming impact" is ___) THEN ("Hazard potential" is ___).

One example for this rule is:

IF ("Global warming impact" is very low) THEN ("Hazard potential" is very low).

Table 3.12: Fuzzy IF-THEN rules for GWIacc-fire

	IF (GWIacc-fire)					
	VLGWI	LGWI	MGWI	HGWI	VHGWI	EHGWI
THEN (GWIACC-FIRE (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.6 Membership functions and IF-THEN rules for global warming impact due to greenhouse gas emission of continuous operation

The universe of discourse of the global warming caused by GHG emissions due to continuous daily operational releases (GWIcon) is defined from 0 Kmol of CO_2 equivalents/hour to an emission amount of 9471 Kmol of CO_2 equivalents per hour. The latter amount is the quantity of the GHG emission from Kilauea volcano per hour (Gerlach & McGee, 2002). This quantity of emission is considered as quantity of GHG that can pose an extreme hazard or maximum possible global warming impact due to GHG emissions. The fuzzy sets defining the input and output memberships of GWIcon are shown in Table 3.13. The membership function drawn according to this definition are shown in Figure 3.6.

Table 3.13: Fuzzy sets of GWIcon and shape of input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
GWIcon (GHG Emission Kmol of CO_2 equivalence)	Very Low Global Warming Impact	VLGWI	Triangular	[0, 0, 947]
	Low Global Warming Impact	LGWI	Triangular	[0, 947, 1894]
	Medium Global Warming Impact	MGWI	Triangular	[947, 1894, 3788]
	High Global Warming Impact	HGWI	Triangular	[1894, 3788, 5683]
	Very high Global Warming Impact	VHGWI	Triangular	[3788, 5683, 9471]
	Extremely high Global Warming Impact	EHGWI	Triangular	[5683, 9471, 9471]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
GWICON (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

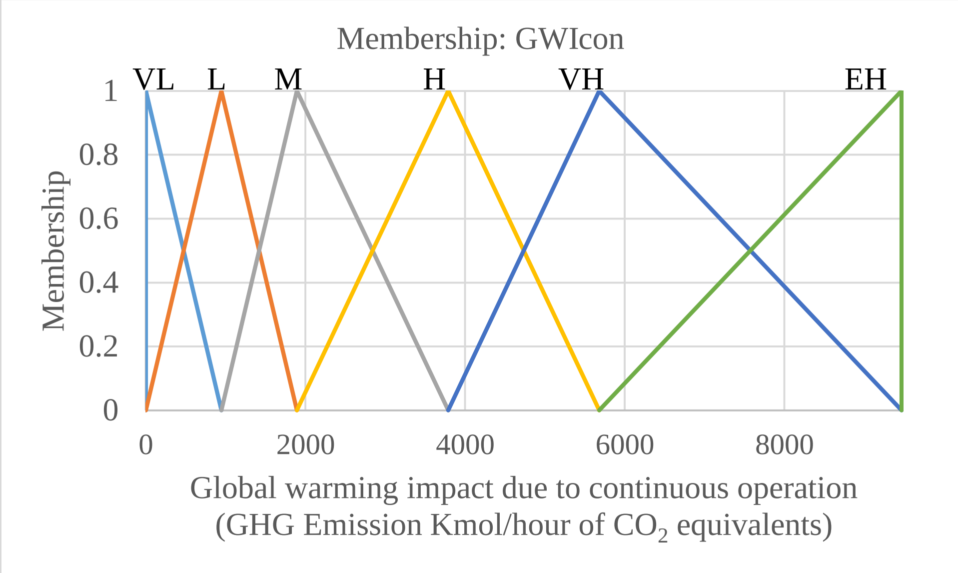

Figure 3.15: Input membership funtions of GWIcon

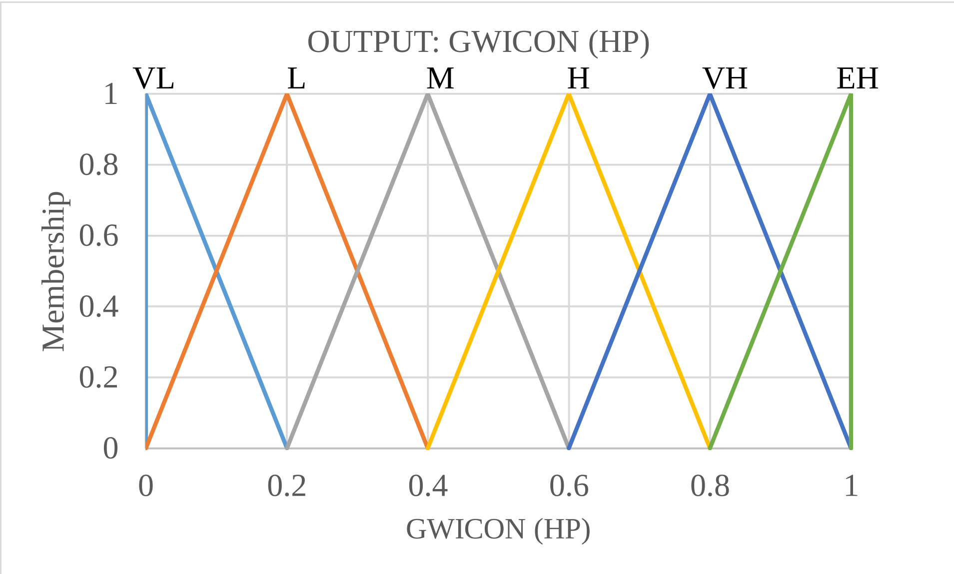

Figure 3.16: Output membership functions of GWIcon

IF-THEN rules

The IF-THEN rules for global warming impact due to greenhouse gas emission of continuous operational releases represent the relationship between GHG emission and hazard potential. The global warming impact is low, if the greenhouse gases in chemicals released continuously is low. Further, the global warming impact increases with the increase in amount of the greenhouse gas emissions in the chemicals released continuous. Based on this, the Fuzzy IF-THEN rules developed for GWIcon are shown in Table 3.14.

The general rule is:

IF ("Greenhouse gas emission of continuous releases" is ___) THEN ("Hazard potential" is ___).

One example for this rule is:

IF ("Greenhouse gas emission of accidental chemical releases" is very low) THEN ("hazard potential" is very low).

Table 3.14: Fuzzy IF-THEN rules for GWIcon

	GWIcon					
	VLGWI	LGWI	MGWI	HGWI	VHGWI	EHGWI
GWIACC (HP)	VLH	LH	MH	HH	VHH	EHH

3.3.3.7 Membership functions and IF-THEN rules for health impact due to continuous emission in the plant

The health impact due to continuous operation of the chemical processing plant is measured by considering fugitive emissions (FEcon). The universe of discourse of the health impact due to continuous operation FEcon is defined from 0 to 1. The universe of discourse is considered as 0 for the least health impact and extreme health impact as 1. The fuzzy sets defining FEcon input and output memberships are shown in Table 3.15. The membership function drawn according to this definition are shown in Figure 3.17 and Figure 3.18.

Table 3.15: Fuzzy sets of FEcon and shape of for input and output memberships

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
FEcon	Very Low occupational health impact due to Fugitive Emission	VLFE	Triangular	[0, 0, 0.1]
	Low occupational health impact due to Fugitive Emission	LFE	Triangular	[0, 0.1, 0.2]

	Medium occupational health impact due to Fugitive Emission	MFE	Triangular	[0.1, 0.2, 0.4]
	High occupational health impact due to Fugitive Emission	HFE	Triangular	[0.2, 0.4, 0.6]
	Very High occupational health impact due to Fugitive Emission	VHFE	Triangular	[0.4, 0.6, 1]
	Extremely High occupational health impact due to Fugitive Emission	EHFE	Triangular	[0.6, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
FECON (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

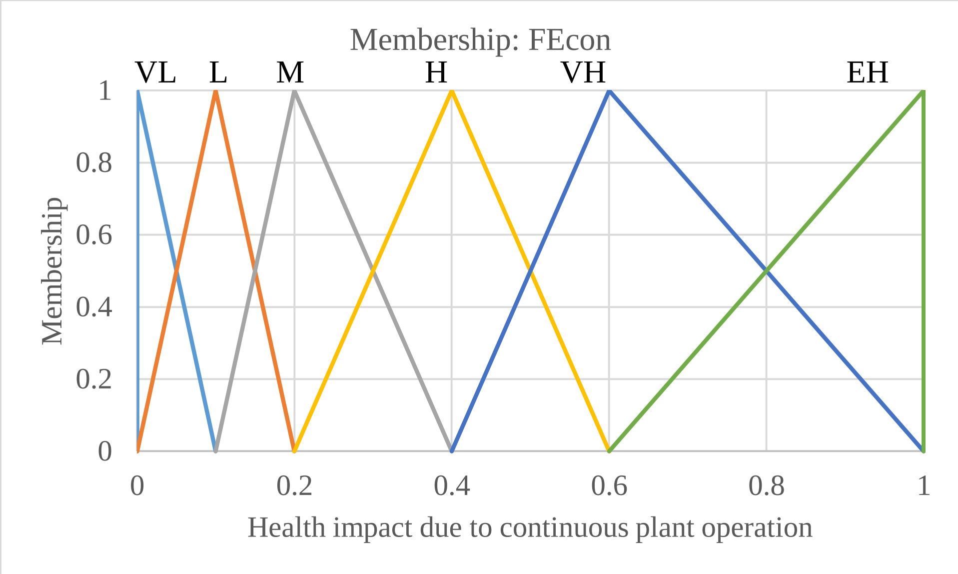

Figure 3.17: Input membership functions of FEcon

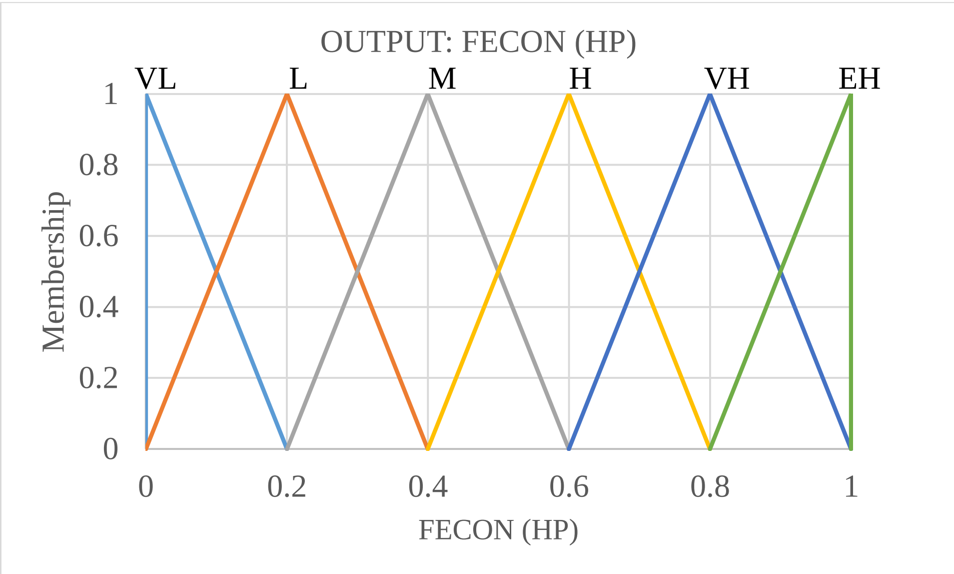

Figure 3.18: Output membership functions for FEcon

IF-THEN rules

The IF-THEN rules for occupational health impact due to fugitive emission of continuous emission from the chemical plant represent the relationship between health impact due to fugitive emission and hazard potential. The occupational health impact is low if the fugitive emission from continuous plant operation is low. Further, the hazard potential increases with the increase in fugitive emissions from continuous plant operation. Based on this, the Fuzzy IF-THEN rules developed for FEcon are shown in Table 3.16.

The general rule is:

IF ("Occupational health impact due to fugitive emission of continuous plant operation" is ___) THEN ("hazard potential" is ___).

The example for an operation is:

IF ("Occupational health impact due to fugitive emission of continuous plant operation" is very low) THEN ("Hazard potential" is very low).

Table 3.16: Fuzzy IF-THEN rules for FEcon

	IF (FEcon)					
	VLFE	LFE	MFE	HFE	VHFE	EHFE
THEN (FECON (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.8 Membership functions and IF-THEN rules for occupational health impact from work place accidental release airborne quantity at the plant premises

The universe of discourse of the AQacc is defined from 0 to 1. The upper limit is defined considering highest impact on occupational health where AQacc is 1. The fuzzy sets defining AQacc of input and output memberships are shown in Table 3.17. The membership function drawn according to this definition are shown in Figure 3.19 and Figure 3.20.

Table 3.17: Fuzzy sets of AQacc and the shape of input and output memberships

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
HAQacc	Very Low occupational health impact due to Airborne Quantity	VLHAQ	Triangular	[0, 0, 0.1]
	Low occupational health impact due to Airborne Quantity	LHAQ	Triangular	[0, 0.1, 0.2]

	Medium occupational health impact due to Airborne Quantity	MHAQ	Triangular	[0.1, 0.2, 0.4]
	High occupational health impact due to Airborne Quantity	HHAQ	Triangular	[0.2, 0.4, 0.6]
	Very High occupational health impact due to Airborne Quantity	VHHAQ	Triangular	[0.4, 0.6, 1]
	Extremely High occupational health impact due to Airborne Quantity	EHHAQ	Triangular	[0.6, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
HAQACC (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

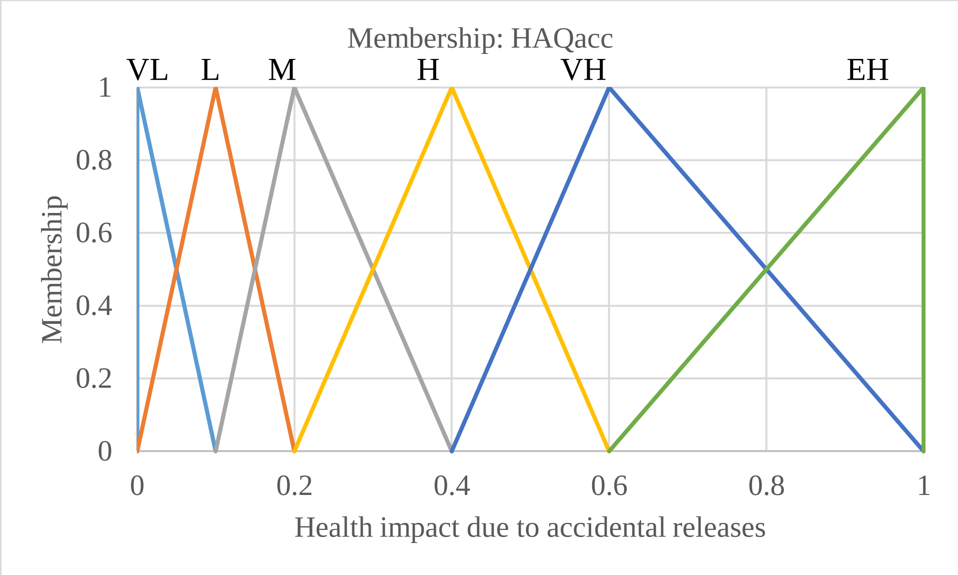

Figure 3.19: Input membership functions of HAQacc

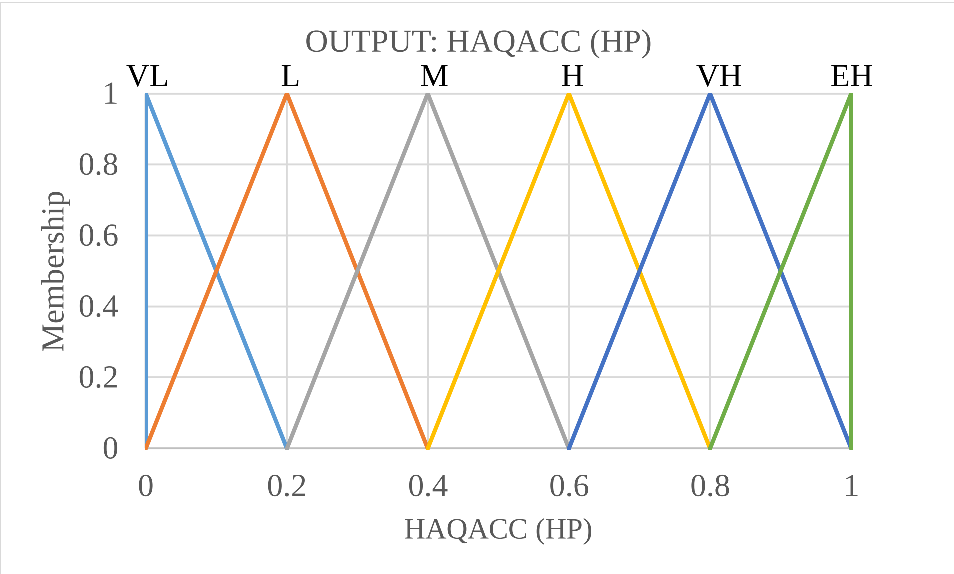

Figure 3.20: Output membership functions for HAQacc

IF-THEN rules

The IF-THEN rules for occupational health impact due to work place accidental release airborne quantity represent the relationship between occupational health impact and hazard potential. The occupational health impact is low if the airborne quantity of accidental releases within the plant is low. Further, the hazard potential will increase with the increase in airborne accidental releases. Based on this, the Fuzzy IF-THEN rules developed for HAQacc are shown in Table 3.18.

The general rule is:

IF (“Occupational health impact due to work place accidental release airborne quantity” is ___) THEN (“Hazard potential” is ___).

The example for an operation is: IF (“Occupational health impact due to work place accidental release airborne quantity” is very low) THEN (“Hazard potential” is very low).

Table 3.18: Fuzzy IF-THEN rules for HAQacc

	IF (HAQacc)					
	VLHAQ	LHAQ	MHAQ	HHAQ	VHHAQ	EHHAQ
THEN (HAQACC (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.9 Membership function and IF-THEN rules for explosiveness of chemical substances

The explosiveness of chemical substances is measured by explosive limits. The input for fuzzification is explosiveness of chemical substance (EXPche) and output after defuzzification is hazard potential (HP).

The universe of discourse of the EXPche is defined from 0 to 100. The lower limit of universe of discourse for EXPche is defined as zero where explosive hazard is absent. The upper limit is defined considering the highest explosive hazard. The input and output parameter ranges are divided into fuzzy sets as shown in Table 3.19. The membership functions drawn according to this definition are shown in Figure 3.21 and Figure 3.22.

Table 3.19: Fuzzy sets of EXPche and shape of input and output memberships

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
EXPche (%)	Very Low Explosiveness	VLAD	Triangular	[0, 0, 10]

	Low Explosiveness	LAD	Triangular	[0, 10, 20]
	Medium Explosiveness	MAD	Triangular	[10, 20, 40]
	High Explosiveness	HAD	Triangular	[20, 40, 60]
	Very High Explosiveness	VHAD	Triangular	[40, 60, 100]
	Extremely High Explosiveness	EHAD	Triangular	[60, 100, 100]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
EXPCHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

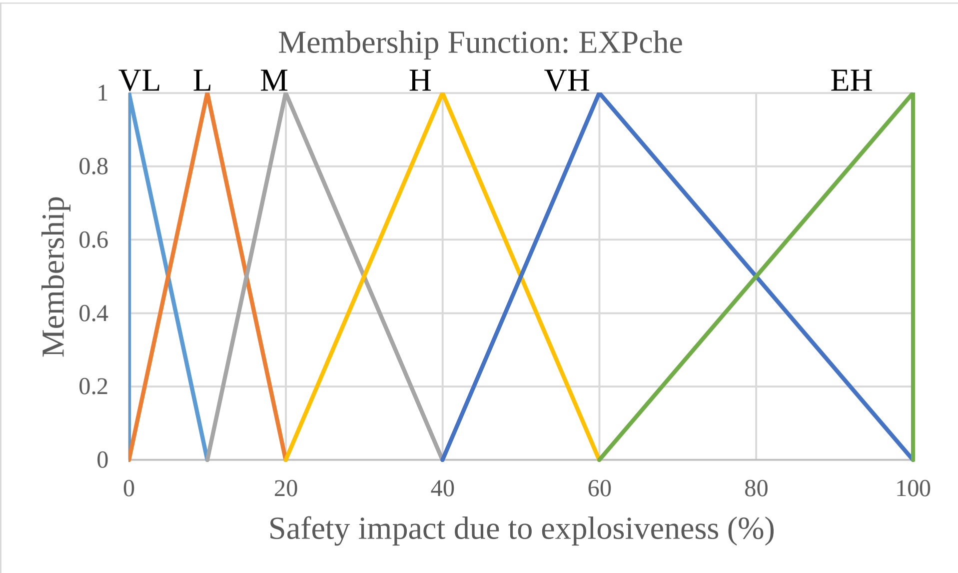

Figure 3.21: Input membership funtions of EXPche

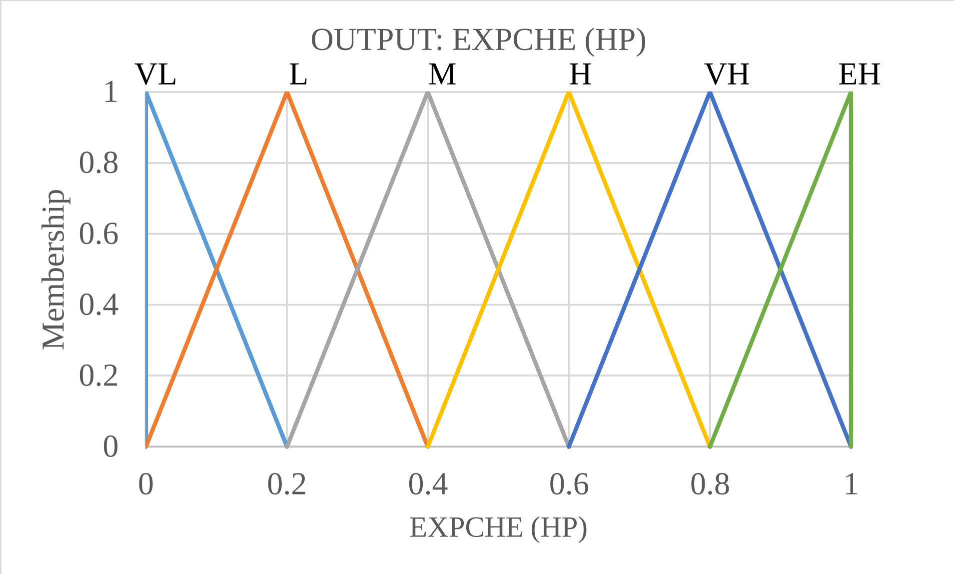

Figure 3.22: Output membership functions for EXPche

IF-THEN rules

The IF-THEN rules for explosiveness of chemicals represent the relationship between explosiveness and hazard potential. The hazard potential due to explosiveness is low if the explosiveness associated with the chemical is low. Further, the hazard potential will increase with the increase in explosiveness of chemical represent. Based on this, the Fuzzy IF-THEN rules developed for EXPche are shown in Table 3.20.

The general rule is:

IF (“Explosiveness of chemical substance” is ___) THEN (“Hazard potential” is ___).

The example for an operation is:

IF (“Explosiveness of chemical substance” is very low) THEN (“Hazard potential” is very low)

Table 3.20: Fuzzy IF-THEN rules for EXPche

	IF (EXPche)					
	VLGWI	LGWI	MGWI	HGWI	VHGWI	EHGWI
THEN (EXPCHE (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.10 Membership functions and IF-THEN rules for flammability of chemical substance

The flammability of chemical substance is measured by NFPA fire rating. The input for fuzzification is flammability of chemical substance (FLAche) and output after defuzzification is hazard potential (HP).

The universe of discourse of the FLAche is defined from 0 to 4. The lower limit of universe of discourse for FLAche is defined as zero when fire hazard is least. The upper limit is defined considering the highest fire hazard. The input and output parameter ranges are divided into fuzzy sets as shown in Table 3.21. The membership functions drawn according to this definition are shown in Figure 3.23 and Figure 3.24.

Table 3.21: Fuzzy sets of FLAche and shapes of input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
FLAche	Very Low Flammability	VLFLA	Triangular	[0, 0, 0.4]
	Low Flammability	LFLA	Triangular	[0, 0.4, 0.8]
	Medium Flammability	MFLA	Triangular	[0.4, 0.8, 1.6]
	High Flammability	HFLA	Triangular	[0.8, 1.6, 2.4]
	Very High Flammability	VHFLA	Triangular	[1.6, 2.4, 4]
	Extremely High Flammability	EHFLA	Triangular	[2.4, 4, 4]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
FLACHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]

	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

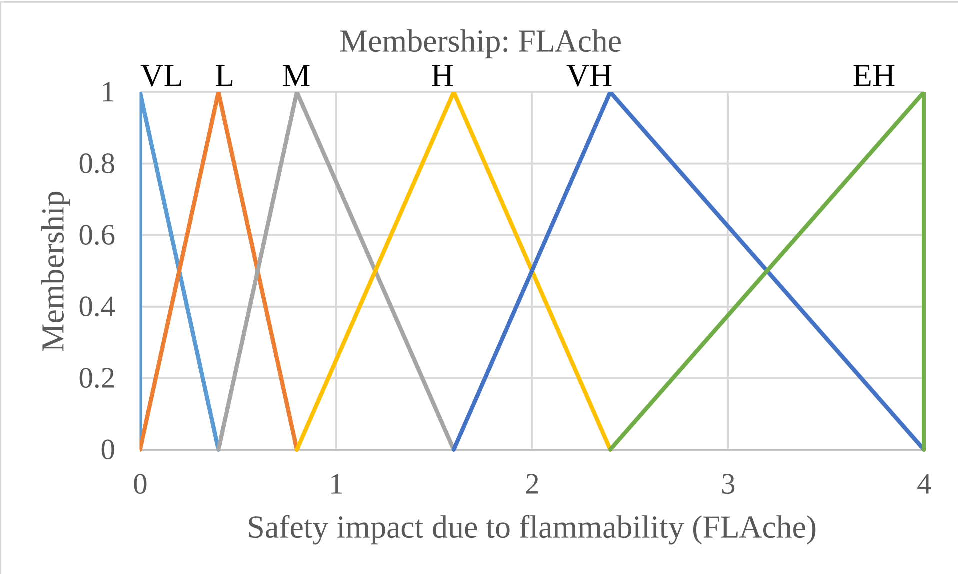

Figure 3.23: Input membership functions for FLAche

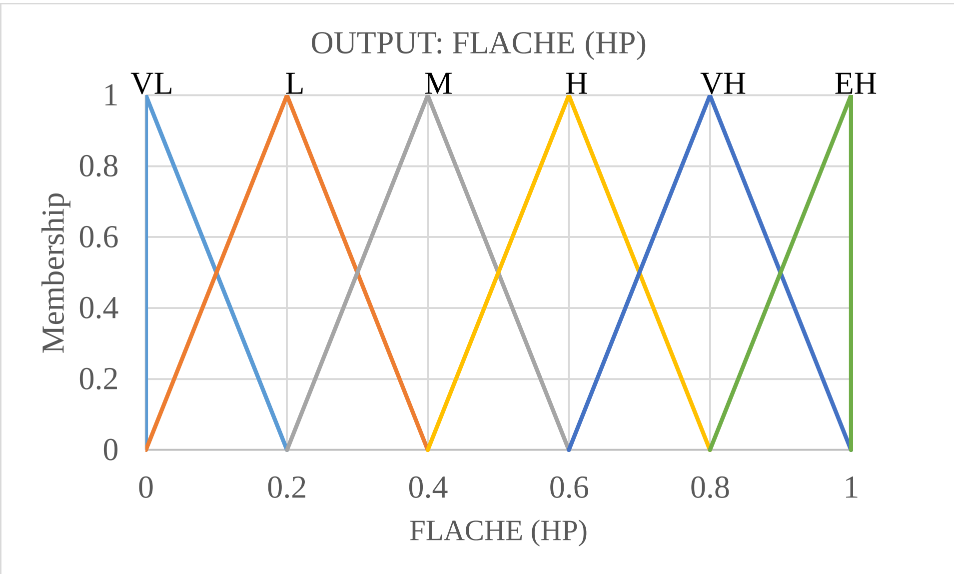

Figure 3.24: Output membership function for FLAche

IF-THEN rules

The IF-THEN rules for flammability of chemicals represent the relationship between flammability and hazard potential. The hazard potential due to flammability is low if the flammability associated with the chemical is low. Further, the hazard potential will increase with the increase in flammability of chemical represent. Based on this, the Fuzzy IF-THEN rules developed for FLAche are shown in Table 3.22.

The general rule is: IF ("Flammability of chemical substance" is ___) THEN ("Hazard potential" is ___).

The example for an operation is: IF ("Flammability of chemical substance" is very low) THEN ("Hazard potential" is very low).

Table 3.22: Fuzzy IF-THEN rules for FLAche

	IF (FLAche)					
	VLFLA	LFLA	MFLA	HFLA	VHFLA	EHFLA
THEN (FLACHE (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.11 Membership functions and IF-THEN rules for to inventory of chemical substance

The hazard due to inventory of chemical substance is measured by quantity of inventory present in the plant. The input for fuzzification is the quantity of inventory of chemical substance (INVche) and output after defuzzification is hazard potential (HP).

The universe of discourse of the INVche is defined from 0 to 100, 000 Tonnes. The lower limit is defined as a zero where least hazard is posed by the inventory. The upper limit is defined according to theamount proposed by Edwards and Lawrance (1993). The universe of discourse range is divided into fuzzy sets as shown in Table 3.23. The membership functions drawn according to this definition are shown in Figure 3.25 and Figure 3.26.

Table 3.23: Fuzzy sets of INVche and shapes of the input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
INVche (Tonnes)	Very Low Inventory	VLINV	Triangular	[0, 0, 10000]
	Low Inventory	LINV	Triangular	[0, 10000, 20000]
	Medium Inventory	MINV	Triangular	[10000, 20000, 40000]
	High Inventory	HINV	Triangular	[20000, 40000, 60000]
	Very High Inventory	VHINV	Triangular	[40000, 60000, 100000]
	Extremely High Inventory	EHINV	Triangular	[60000, 100000, 100000]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
INVCHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

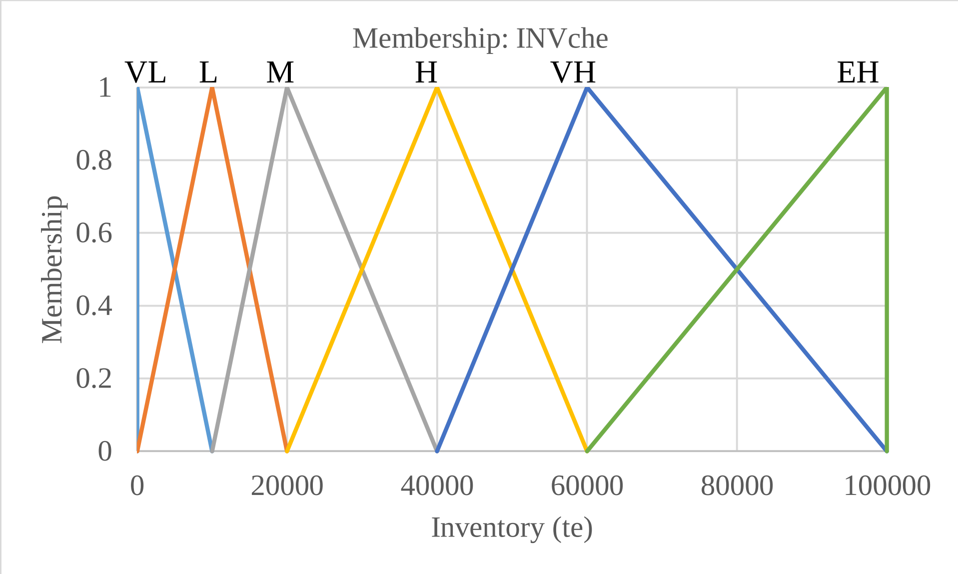

Figure 3.25: Input membership functions for INVche

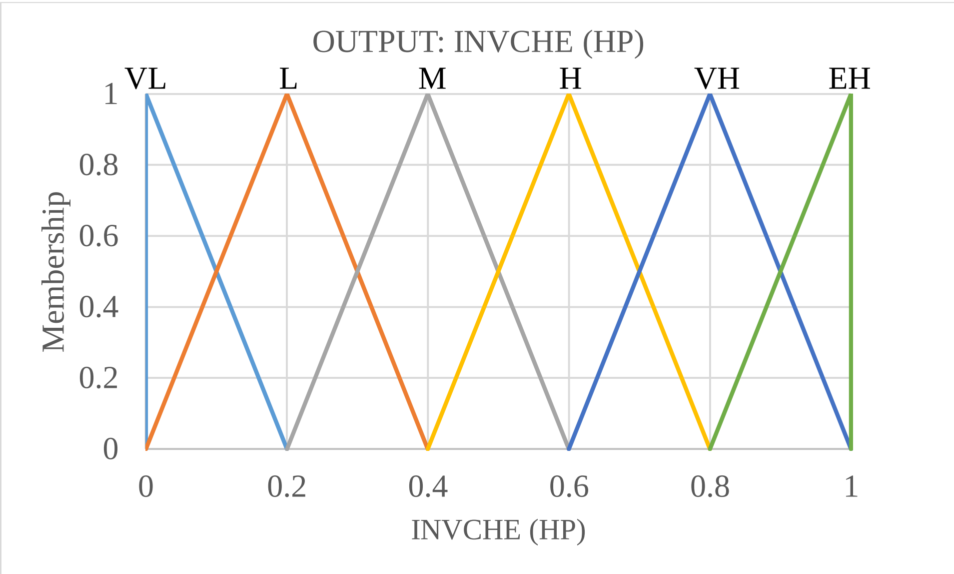

Figure 3.26: Output membership functions for INVche

IF-THEN rules

The IF-THEN rules for the quantity of chemical substances represent the relationship between inventory and hazard potential. The hazard potential due to inventory is low if the inventory is low. Further, the hazard potential will increase with the increase in the inventory of chemicals present in the plant. Based on this, the Fuzzy IF-THEN rules developed for INVche are shown in Table 3.24.

The general rule is:

IF (“Inventory of chemical substance” is ___) THEN (“Hazard potential” is ___).

The example for an operation is:

IF (“Inventory of chemical substance” is very low) THEN (“Hazard potential” is very low).

Table 3.24: Fuzzy IF-THEN rules for INVche

	IF (INVche)					
	VLINV	LINV	MINV	HINV	VHINV	EHINV
THEN (INVCHE (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.12 Membership function and IF-THEN rules for operating temperature of chemical reaction

The hazard due to operating temperature of reaction is measured by the maximum operating temperature. The input for fuzzification is operating temperature of chemical reaction (Tpro) and output after defuzzification is hazard potential (HP).

The universe of discourse of the Tpro is defined from 0 ^{O}C to 900 ^{O}C. The upper limit is defined considering the limit proposed by Edwards and Lawrance (1993) in their chemical routes selection methodology. The input and output fuzzy sets as shown in Table 3.25. The membership functions drawn according to this definition are shown in Figure 3.27 and Figure 3.28.

Table 3.25: Fuzzy sets of Tpro and shape of the input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
Tpro (^{O}C)	Very Low Operating Temperature	VLT	Triangular	[0, 0, 90]
	Low Operating Temperature	LT	Triangular	[0, 90, 180]

	Medium Operating Temperature	MT	Triangular	[90, 180, 360]
	High Operating Temperature	HT	Triangular	[180, 360, 540]
	Very High Operating Temperature	VHT	Triangular	[360, 540, 900]
	Extremely High Operating Temperature	EHT	Triangular	[540, 900, 900]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
TPRO (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

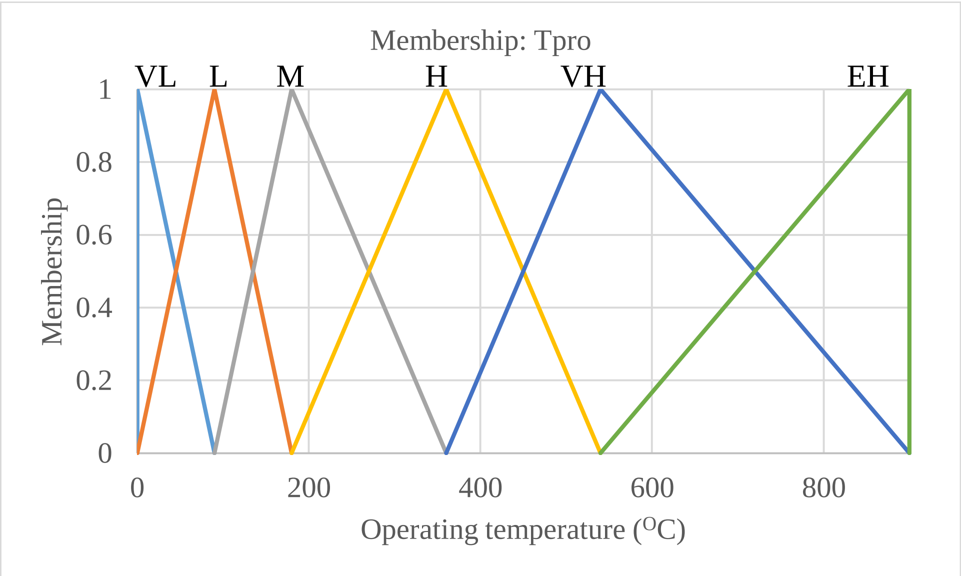

Figure 3.27: Input membership functions for Tpro

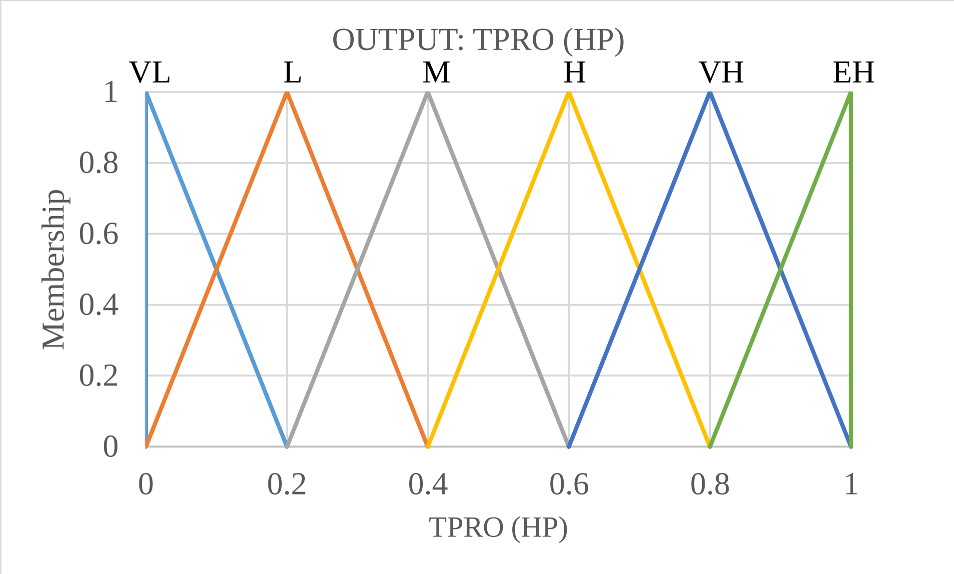

Figure 3.28: Output membership functions for Tpro

IF-THEN rules

The IF-THEN rules for operating temperature of chemical reactions represent the relationship between temperature and hazard potential. The hazard potential due to operating temperature is low if the operating temperature is low. Further, the hazard potential will increase with the increase in operating temperature of chemical reaction. Based on this, the Fuzzy IF-THEN rules developed for Tpro are shown in Table 3.26.

The general rule is:

IF (“Temperature of chemical substance” is ___) THEN (“Hazard potential” is ___).

The example for an operation is: IF (“Temperature of chemical substance” is very low) THEN (“Hazard potential” is very low).

Table 3.26: Fuzzy IF-THEN rules for Tpro

	IF (Tpro)					
	VLT	LT	MT	HT	VHT	EHT
THEN (TPRO (HP))	VLH	LH	MH	HH	VHH	EHH

3.3.3.13 Membership functions and IF-THEN rules for operating pressure of chemical reaction

The impact due to operating pressure of reaction is measured by maximum operating pressure used in the chemical reaction. The input for fuzzification is operating pressure of chemical reaction (Ppro) and output after defuzzification is hazard potential (HP). The universe of discourse of Ppro is defined from 0 atm to 550 atm. These limits are defined based on limits proposed in the methodology developed for routes selection by Edwards and Lawrance (1993). The input and output fuzzy sets for Ppro are shown in Table 3.27. The membership functions drawn according to this definition are shown in Figure 3.29 and Figure 3.30.

Table 3.27: Fuzzy sets of Ppro and shapes of input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
Ppro (^{O}C)	Very Low Operating Pressure	VLP	Triangular	[0, 0, 55]
	Low Operating Pressure	LP	Triangular	[0, 55, 110]
	Medium Operating Pressure	MP	Triangular	[55, 110, 220]
	High Operating Pressure	HP	Triangular	[110, 220, 330]
	Very High Operating Pressure	VHP	Triangular	[314, 393, 550]
	Extremely High Operating Pressure	EHP	Triangular	[330, 550, 550]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Number**
PPRO (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]

	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

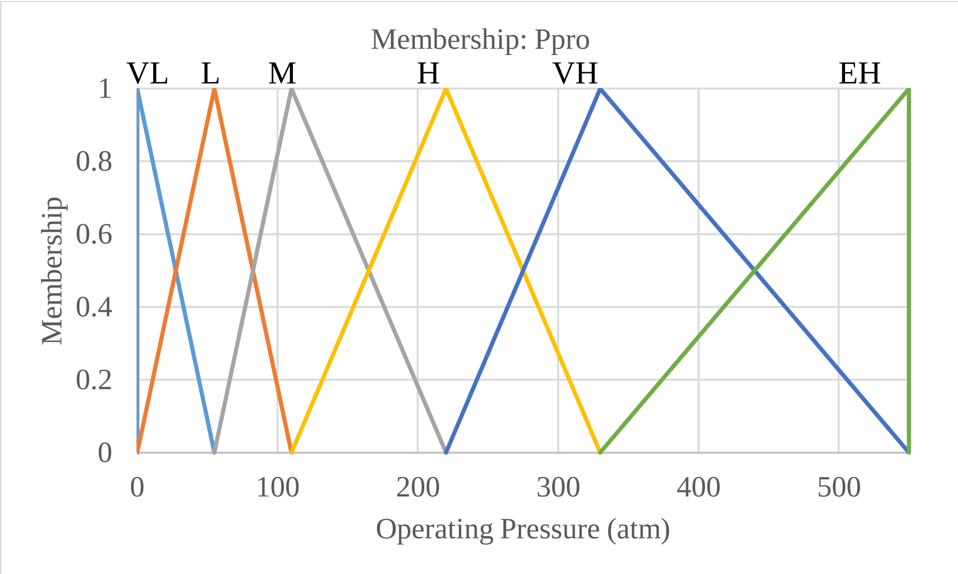

Figure 3.29: Input membership functions for Ppro

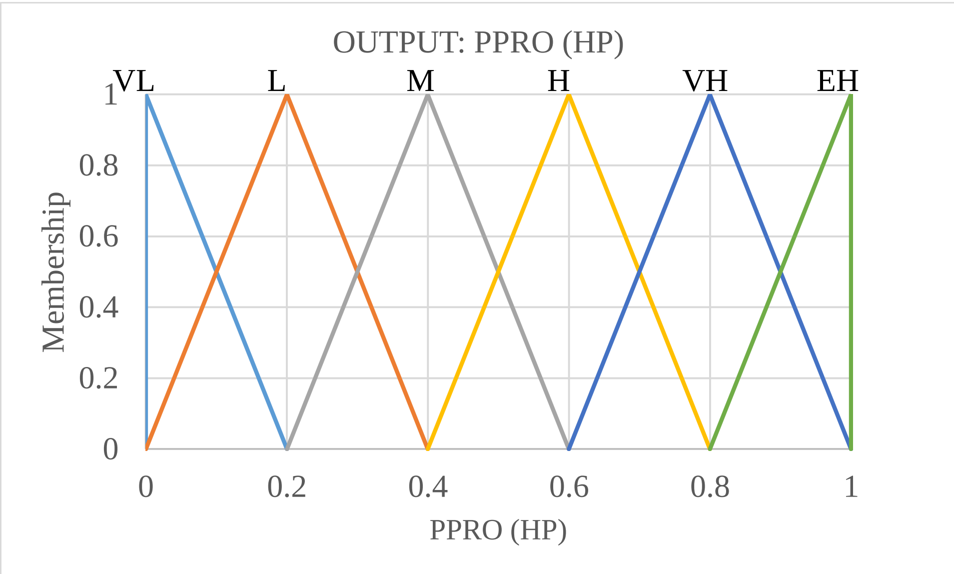

Figure 3.30: Output membership functions for Ppro

IF-THEN rules

The IF-THEN rules for impact due to operating pressure of chemicals reaction represent the relationship between temperature and hazard potential. The hazard potential due to pressure is low if the operating pressure involved is low. Further, the hazard potential will increase with the increase in operating pressure of chemical reaction. Based on this, the Fuzzy IF-THEN rules developed for Ppro are shown in Table 3.28.

The general rule is:

IF ("Pressure of chemical substance" is ___) THEN ("Hazard potential" is ___).

The example for an operation is: IF ("Pressure of chemical substance" is very low) THEN ("Hazard potential" is very low).

Table 3.28: Fuzzy IF-THEN rules for Ppro

	IF (Ppro)					
	VLP	LP	MP	HP	VHP	EHP
THEN (PPRO)	VLH	LH	MH	HH	VHH	EHH

3.3.4 Fuzzy inference system for intermediate parameters

3.3.4.1 Definition of linguistic variables for intermediate parameters

The fuzzy logic application derives different types of intermediate variables when primary parameters are aggregated. The notation used for these intermediate parameters in determining EHS-Fuzzy Index are listed in Table 3.29. The primary inputs along with intermediate variable are shown in figure 3.31 and are described in section 3.3.4.2.

Table 3.29: Notation of intermediate parameters and final index

Intermediate parameters	**Units**	**Notation**
Fuzzy based environmental, health and safety hazard index	HP	EHS-Fuzzy Index
Environmental impact due to accidental and continuous releases	HP	ENV2REL

Employee health and safety impact	HP	HANDS
Environmental impact due to accidental releases	HP	ENVACC
Environmental impact due to continuous releases	HP	ENVCON
Health impact on human at the plant environment	HP	HEAL2REL
Safety impact of a chemical process route	HP	SAF2CHPR
Environmental impact due to accidental chemical release	HP	ENVCHE
Environmental impact due to accidental fire	HP	ENVFIRE
Safety impact due to chemical properties	HP	SAFCHE
Safety impact due to process condition	HP	SAFPRO

HP= hazard potential

3.3.4.2 Fuzzy hierarchical model for EHS-Fuzzy Index

The hazards assessment of EHS is carried out using fuzzy hierarchical model. In this work a model tree is proposed for the aggregation of parameters as shown in Figure 3.31.

The EHS-fuzzy hierarchy describes the way in which environmental, health and safety hazards of a chemical process route are combined. The main levels of the hierarchy are also shown in Figure 3.31. The comparison and aggregation method used in this hierarchy are summarized in Table 3.30.

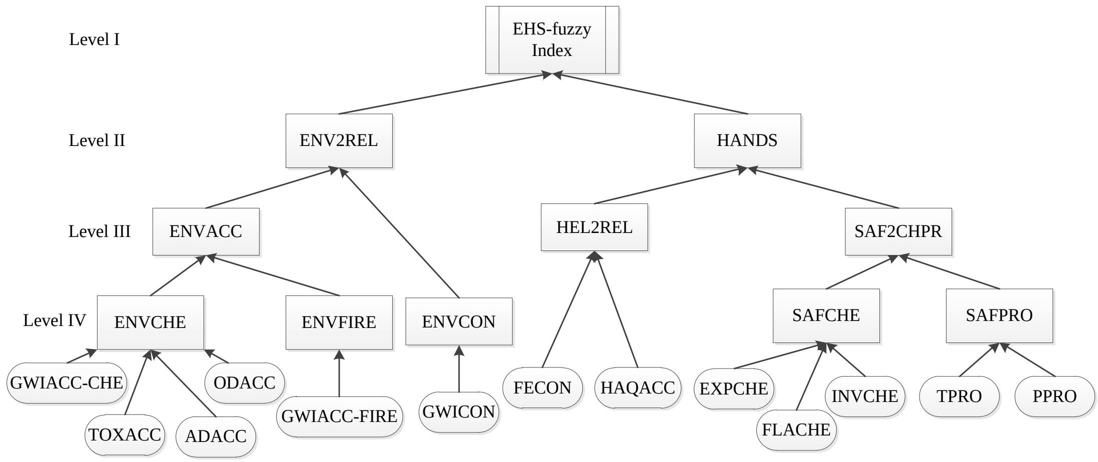

Figure 3.31: The fuzzy hierarchical model for EHS hazard assessment of a chemical process route

Table 3.30: Summary of aggregation method used in EHS-Fuzzy Index hierarchy

HP Parameters aggregated*	Resultant Parameter	Aggregation Method
Primary Parameters (Level IV)		
GWIACC-CHE, TOXACC, ODACC and ADACC	ENVCHE	Fuzzy Addition
GWIACC-FIRE	ENVFIRE	Not aggregated at this level
GWICON	ENVCON	Not aggregated at this level
EXPCHE, FLACHE and INVCHE	SAFCHE	Fuzzy Addition
TPRO and PPRO	SAFPRO	Fuzzy Addition
Intermediate parameters (Level III)		
ENVCHE and ENVFIRE	ENVACC	Pairwise
FECON and HAQACC	HEL2REL	Pairwise
SAFCHE and SAFPRO	SAF2CHPR	Pairwise
Intermediate parameters (Level II)		
ENVACC and ENVCON	ENV2REL	Pairwise
HEL2REL and SAF2CHPR	HANDS	Pairwise
Intermediate parameters (Level I)		
ENV2REL and HANDS	EHS-Fuzzy Index	Pairwise

3.3.4.2.1 Aggregation of de-fuzzified primary parameters (Level IV) by addition

The level IV is obtained by fuzzy addition of HP of primary parameters giving intermediate parameters. The ENVCHE is a result of combination of hazard potential of four primary parameters. These four include global warming impact due to greenhouse gas emission of accidental chemical release (GWIacc-che), toxicity due to accidental chemical release (TOXacc), ozone depletion due to accidental chemical release (ODacc) and acid deposition due to accidental chemical release (ADacc). The fuzzy addition is applied for hazard potential values of above four parameters that is (GWIACC-CHE + TOXACC + ODACC + ADACC) to determine the ENVCHE value.

The hazard potential value of global warming impact due to greenhouse gas emission of accidental fire (GWIacc-fire) is GWIACC-FIRE. The hazard potential value ENVFIRE is derived using only one parameter that is GWIACC-FIRE. Therefore, the value of ENVFIRE remains the same as GWIACC-FIRE.

The ENVCON intermediate parameter is also derived using one parameter that is the global warming impact due to greenhouse gas emissions of continuous daily operations (GWIcon). Therefore, the value of ENVCON is equal to the hazard potential value of GWIcon that is GWICON.

The SAFCHE is derived by adding three parameters that measure safety aspects. The hazard potential of impact due to explosiveness (EXPche), impact due to flammability (FLAche) and impact due to inventory (INVche) are denoted by EXPCHE, FLACHE and INVCHE respectively. These three HPs are used for fuzzy addition to obtain SAFCHE.

The SAFPRO is the resultant of combination of two main process conditions, namely temperature and pressure of a chemical reaction involved in the chemical process route. The hazard potential of operating temperature (Tpro) and operating pressure (Ppro) denoted by TPRO and PPRO respectively are used in deriving SAFPRO by fuzzy addition.

3.3.4.2.2 Aggregation of intermediate parameters (Level III, II and I) by pair wise comparison

The level III is determined by aggregating parameters pair wise producing three intermediate parameters namely, ENVACC, HEL2REL and SAF2CHPR. The ENVACC is the resultant of fuzzy aggregation of ENVCHE and ENVFIRE.

The HEL2REL is determined considering the two scenarios of release, impact due to workplace accidental releases and continuous releases (fugitive emission). The pair wise fuzzy aggregation of parameters is applied for HP values of primary parameters of occupational health impact due to fugitive emission within the plant (FEcon) and occupational health impact from work place accidental release airborne quantity (AQacc).

The safety related hazards of a chemical process route, SAF2CHPR is derived by aggregating the hazards due to properties of chemical substances used with the respective chemical process route (SAFCHE) and the hazards due to process condition that should be maintained for chemical reactions (SAFPRO).

The level II is represented with two intermediate parameters namely, ENV2REL and HANDS. The HANDS is the combined effect of individual effects of occupational on health aspect (HEL2REL) and safety hazard aspect (SAF2CHPR). The combined impact of occupational health due to work place accidental release and due to continuous release is given by HEL2REL. The aggregation of hazard potential values of environmental impacts due to accidental releases, ENVACC and that of continuous releases, ENVCON produces the ENV2REL.

At the level I of the hierarchy, the fuzzy based inherent environmental, health and safety index (EHS- Fuzzy Index) is derived by combining hazard potential values of environmental impacts (due to accidental and continuous releases) (ENV2REL) and occupational health and safety impacts (HANDS).

3.3.4.3 Definition of Universe of Discourse for intermediate parameters in level IV

The ENVCHE is the resultant of fuzzy addition of four hazard potential values GWIACC-CHE, TOXACC, ODACC and ADACC. The universe of discourse of ENVCHE is defined from 0 to 4 because universe of discourse of each hazard potentials of the four aggregated primary parameters are ranged from 0 to 1.

The SAFCHE is determined by fuzzy addition of three hazard potential values (EXPCHE, FLACHE and INVCHE). The Universe of Discourse of SAFCHE is defined from 0 to 3.

The SAFPRO is the resultant of addition of two hazard potential values (TPRO and PPRO). Universe of Discourse of the SAFEPRO is defined from 0 to 2 because only two HP are added.

3.3.5 Fuzzy aggregation of intermediate parameters according to the hieratical model

According to the hazard assessment hierarchy of a chemical process route described in section 3.3.4 the primary parameters are converted into hazard potential (HP) values and aggregated first. The intermediate parameters in level iv of the hierarchy are the resultants of the aggregation.

Most of the intermediate parameters in the EHS fuzzy hierarchy and the final index value are resultant of pair wise fuzzy aggregation. The ENVACC, ENV2REL, HEL2REL, SAF2CHPR and HANDS are intermediate parameters resulting from defuzzification of pair wise comparison.

The defuzzification of all pair wise comparison operations is carried out using the centroid method. The center of gravity (COG) of the area determined by the output membership functions of the aggregating parameters gives the aggregated output in terms of a Hazard Potential (HP) value. The defuzzification of pair wise comparison of HEL2REL and HANDS gives the final EHS-Fuzzy Index of the chemical process route. The pairwise aggregation of intermediate parameters are discussed separately in the following section.

3.3.5.1 The pair wise aggregation for intermediate parameters of ENVACC

The ENVACC is the resultant of fuzzy aggregation of ENVCHE and ENVFIRE inputs. The ENVCHE is determined by four primary parameters (GWIacc-che, TOXacc, ODacc and ADacc). The HP values of these four parameters are added using fuzzy simple addition with assumption of each one contributes independently to the overall hazard. The universe of discourse of the aggregated parameter, ENVCHE is defined from 0 to 4 and that of ENVFIRE is 0 to 1.

The fuzzy sets defining input and output memberships of ENVACC are shown in Table 3.31. The membership functions drawn according to this definition are shown in Figure 3.32, Figure 3.33 and Figure 3.34.

Table 3.31: Fuzzy sets and shapes of input and output memberships for ENVACC

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
ENVCHE (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.8]
	Low Hazard Potential	LH	Triangular	[0, 0.8, 1.6]
	Medium Hazard Potential	MH	Triangular	[0.8, 1.6, 2.4]
	High Hazard Potential	HH	Triangular	[1.6, 2.4, 3.2]
	Very High Hazard Potential	VHH	Triangular	[2.4, 3.2, 4]
	Extremely High Hazard Potential	EHH	Triangular	[3.2, 4, 4]

ENVFIRE (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
ENVACC (HP)	Very Low Hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low Hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard	EHH	Triangular	[0.8, 1, 1.2]

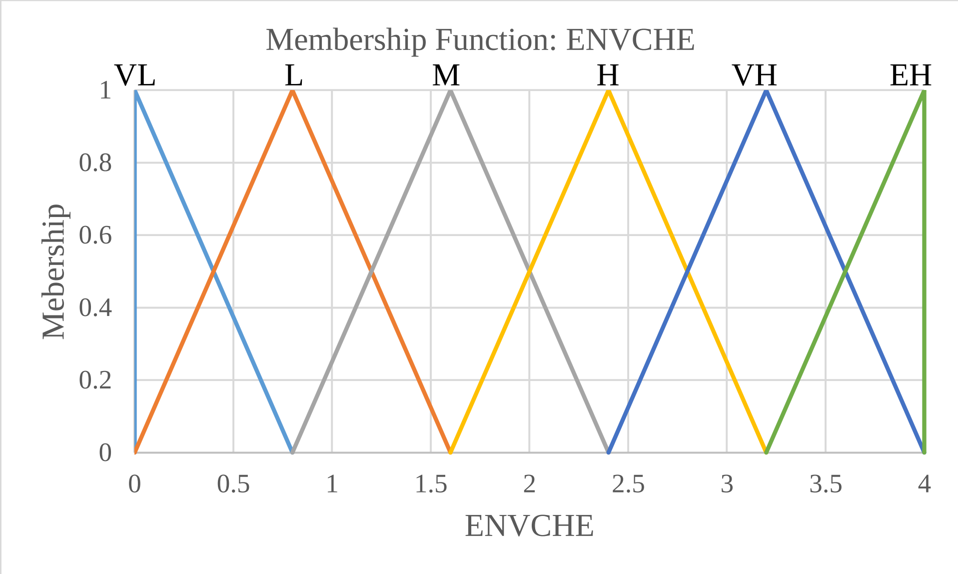

Figure 3.32: Input membership functions for ENVCHE

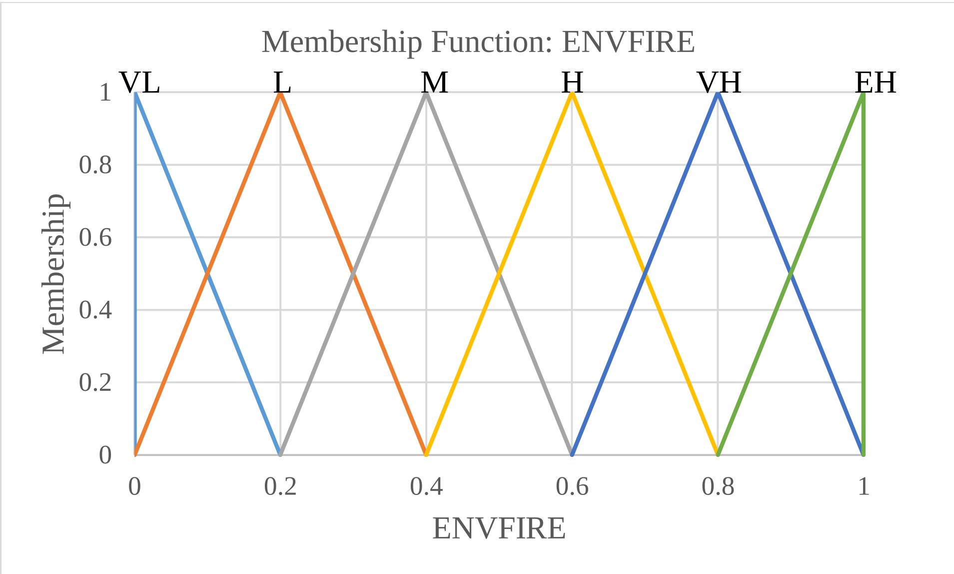

Figure 3.33: Input membership functions for ENVFIRE

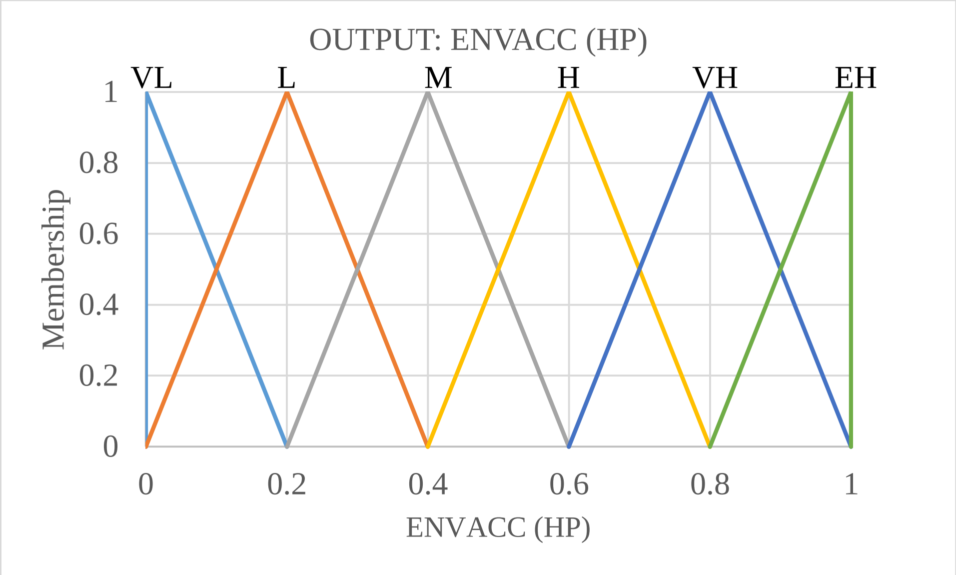

Figure 3.34: Output membership functions for ENVACC

IF-THEN rules

The IF-THEN rules for environment impact due to accidental release (ENVACC) represent the relationship between ENVCHE, ENVFIRE and ENVACC.

The general rule is: IF ("ENVCHE" is ___) AND ("ENVFIRE" is ___) THEN ("Hazard due to ENVACC" is ___).

The rules constructed for this aggregation are given in Table 3.32.

An example for one operation is: IF ("ENVCHE" is very low) AND ("ENVFIRE" is very low) THEN ("Hazard due to ENVACC" is very low).

Table 3.32: Fuzzy IF-THEN rules for ENVACC

THEN (ENVACC)		IF (ENVFIRE)					
		VLH	LH	MH	HH	VHH	EHH
AND (ENVCHE)	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

3.3.5.2 The pair wise aggregation for intermediate parameters of ENV2REL

The ENV2REL is the resultant of aggregation of ENVACC and ENVCON inputs. The determination of ENVACC is presented in the section of 3.3.5.1 and ENVCON is given by GWICON. The universe of discourse of ENVACC and ENVCON is defined from 0 to 1. The fuzzy sets defining ENVACC and the shapes of input and output memberships are shown in Table 3.33. The membership function drawn according to this definition are showing in Figure 3.35, Figure 3.36 and Figure 3.37.

Table 3.33: Fuzzy sets and shapes of input and output memberships for ENV2REL

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
ENVACC (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
ENVCON (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]

	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
ENV2REL (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

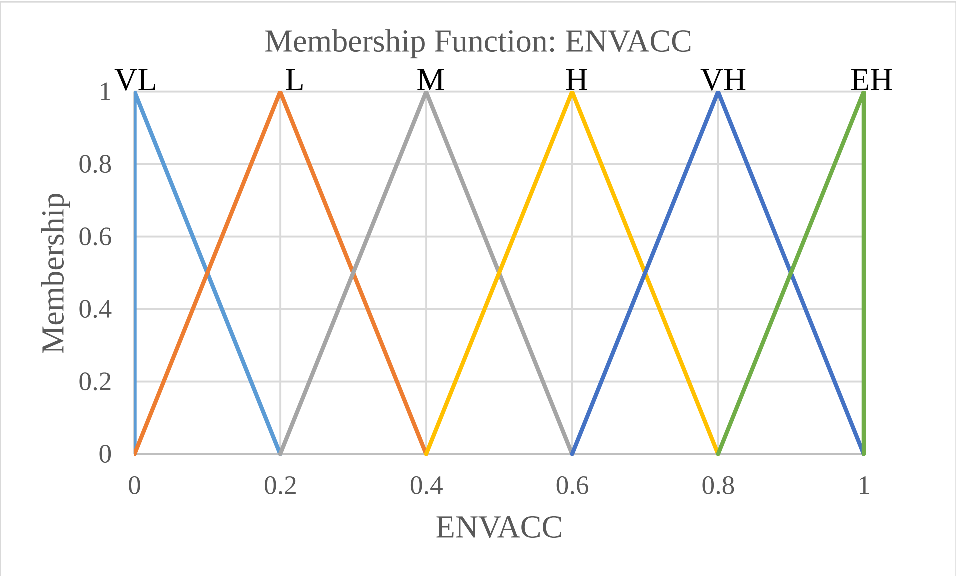

Figure 3.35: Input membership functions for ENVACC

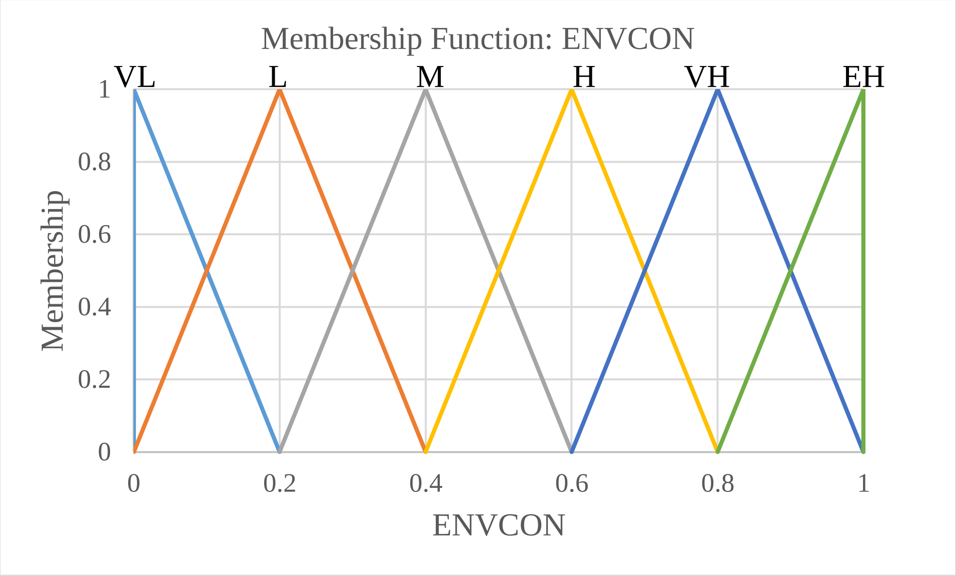

Figure 3.36: Input membership functions for ENVCON

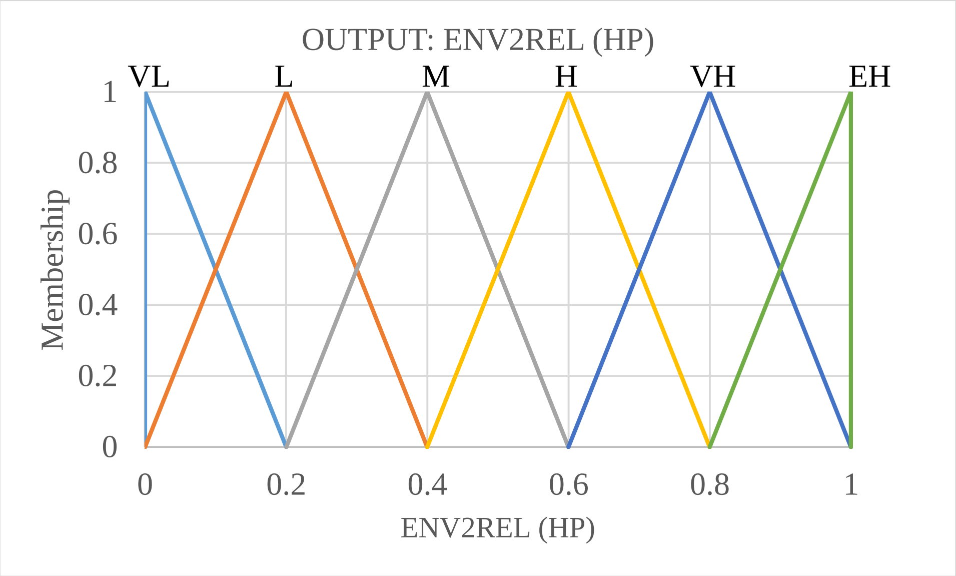

Figure 3.37: Output membership functions for ENV2REL

IF-THEN rules

The IF-THEN rules for environment impact due to continuous and accidental releases (ENV2REL) represent the relationship between ENVACC, ENVCON and ENV2REL. The general rule is:

IF ("ENVACC" is ___) AND ("ENVCON" is ___) THEN ("Hazard due to ENV2REL" is ___).

The rules for this aggregation are given in Table 3.34.

An example for one operation is:

IF (“ENVACC” is very low) AND (“ENVCON” is very low) THEN (“Hazard due to ENV2REL” is very low).

Table 3.34: Fuzzy IF-THEN rules for ENV2REL

THEN (ENV2REL)		IF (ENVACC)					
		VLH	LH	MH	HH	VHH	EHH
AND (ENVCON)	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

3.3.5.3 The pair wise aggregation for intermediate parameters of HEL2REL

The HEL2REL is the resultant of aggregation of FECON and HAQACC inputs. The universe of discourse of each input parameters is in the range [0 1]. The, fuzzy sets defining HEL2REL and the shapes of input and output memberships are shown in Table 3.35. The membership functions drawn according to this definition are shown in Figure 3.38, Figure 3.39 and Figure 3.40.

Table 3.35: Fuzzy number and shapes of input and output memberships for HEL2REL

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
FECON (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]

	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
HAQACC (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
HEL2REL (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

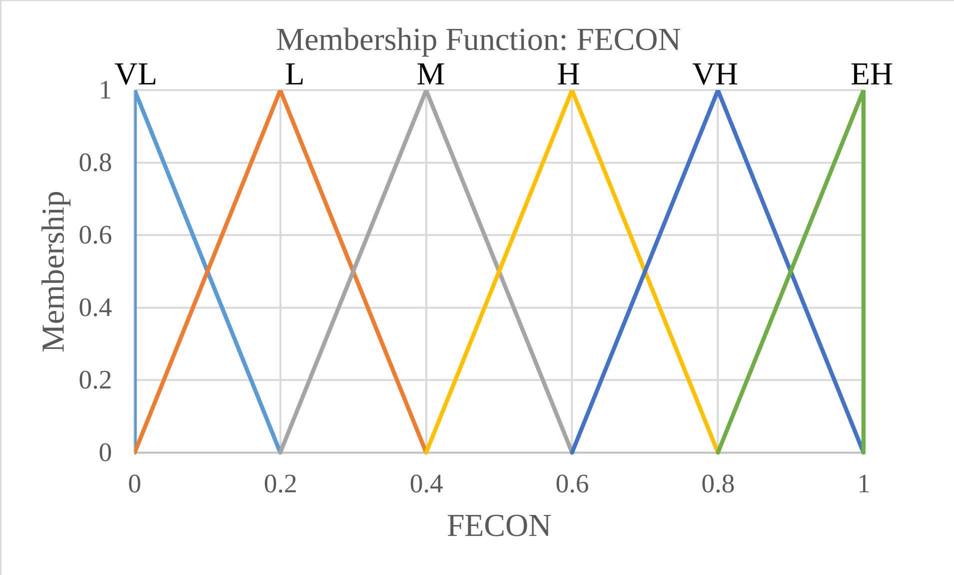

Figure 3.38: Input membership functions for FECON

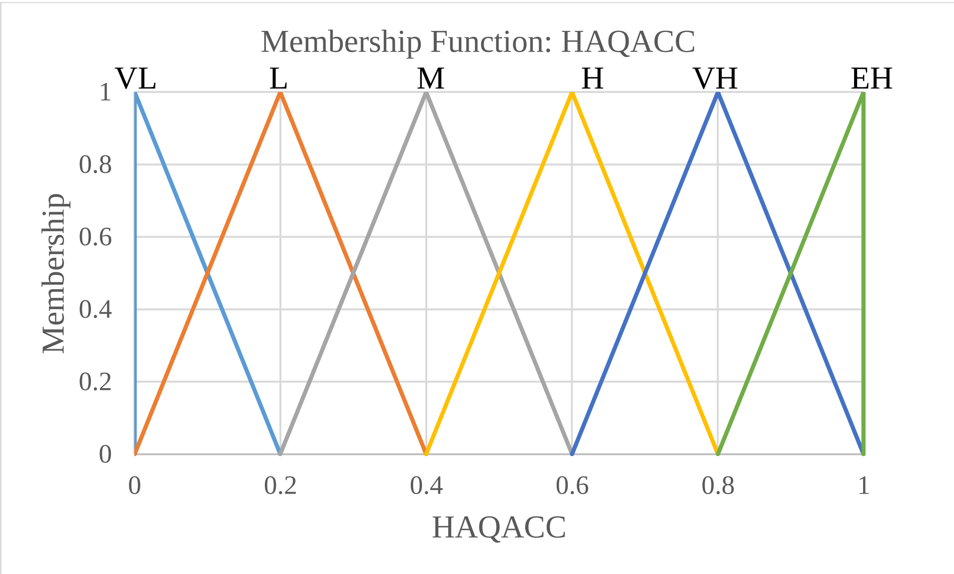

Figure 3.39: Input membership functions for HAQACC

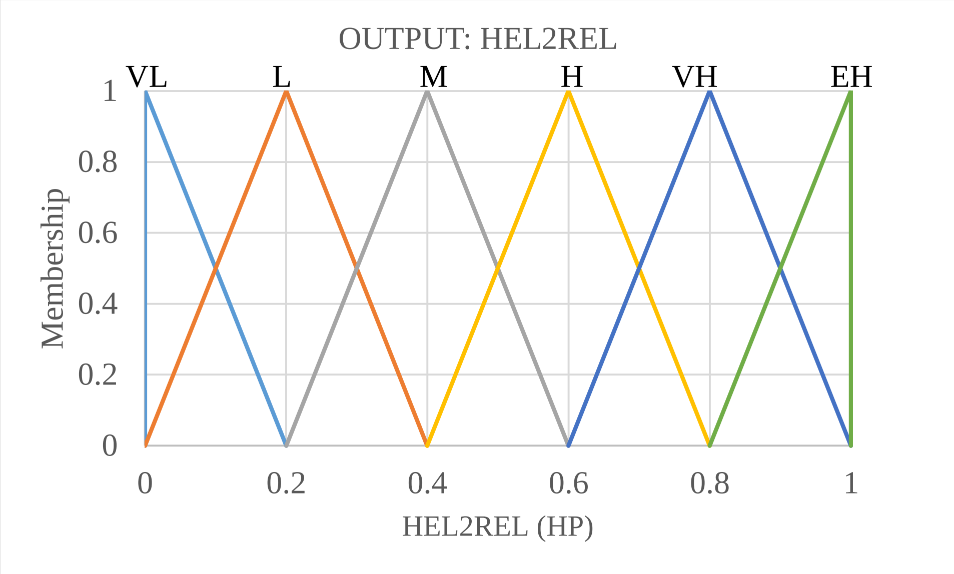

Figure 3.40: Output membership functions for HEL2REL

IF-THEN rules

The IF-THEN rules for environmental impact due to continuous and accidental releases (ENV2REL) represent the relationship between FECON, HAQACC and the HEL2REL.

The general rule is:

IF ("FECON" is ___) AND ("HAQACC" is ___) THEN ("HEL2REL" is ___).

The rules for this aggregation are given in Table 3.36.

An example for one operation is:

IF ("FECON" is very low) AND ("HAQACC" is very low) THEN ("HEL2REL" is very low).

Table 3.36: Fuzzy IF-THEN rules for HEL2REL

THEN (HEL2REL)		IF (FECON)					
		VLH	LH	MH	HH	VHH	EHH
AND (HAQACC (HP))	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

3.3.5.4 The pair wise aggregation for intermediate parameters of SAF2CHPR

The SAF2CHPR is the resultant of aggregation of SAFCHE and SAFPRO inputs. The SAFCHE is derived by three primary parameters, EXPche, FLAche and INVche. The hazard potentials of these three parameters are added using fuzzy addition with the assumption of each one contributing independently to the overall hazard. The universe of discourse of aggregated parameter of SAFCHE is [0 3].

The SAFPRO is determined by addition of hazard potentials of two primary parameters, Tpro and Ppro. The universe of discourse of SAFPRO is [0 2]. The fuzzy sets defining SAF2CHPR and the shapes of input and output membership functions are shown in Table 3.37. The membership functions drawn according to this definition are shown in Figure 3.41, Figure 3.42 and Figure 3.43.

Table 3.37: Fuzzy sets and shapes of input and output memberships for SAF2CHPR

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
SAFCHE (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.6]
	Low Hazard Potential	LH	Triangular	[0, 0.6, 1.2]
	Medium Hazard Potential	MH	Triangular	[0.6, 1.2, 1.8]
	High Hazard Potential	HH	Triangular	[1.2, 1.8, 2.4]
	Very High Hazard Potential	VHH	Triangular	[1.8, 2.4, 3]
	Extremely High Hazard Potential	EHH	Triangular	[2.4, 3, 3]
SAFPRO (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.4]
	Low Hazard Potential	LH	Triangular	[0, 0.4, 0.8]
	Medium Hazard Potential	MH	Triangular	[0.4, 0.8, 1.2]

	High Hazard Potential	HH	Triangular	[0.8, 1.2, 1.6]
	Very High Hazard Potential	VHH	Triangular	[1.2, 1.6, 2]
	Extremely High Hazard Potential	EHH	Triangular	[1.6, 2, 2]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
SAF2CHPR (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

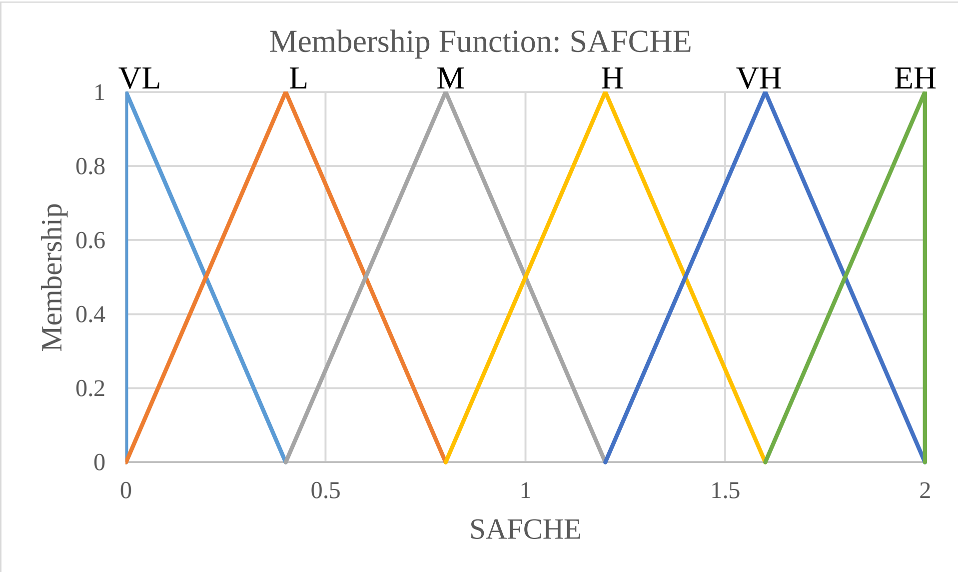

Figure 3.41: Input membership functions for SAFCHE

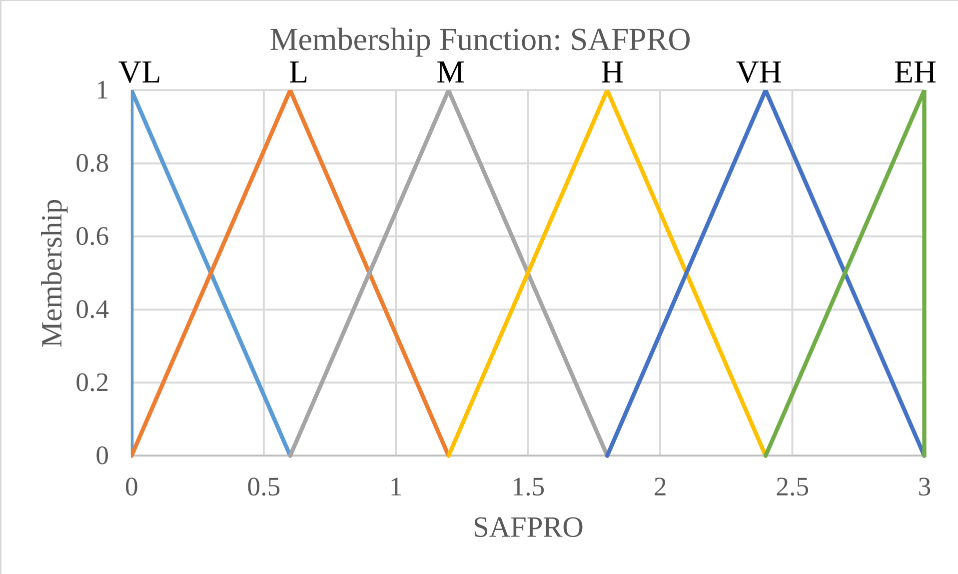

Figure 3.42: Input membership functions for SAFPRO

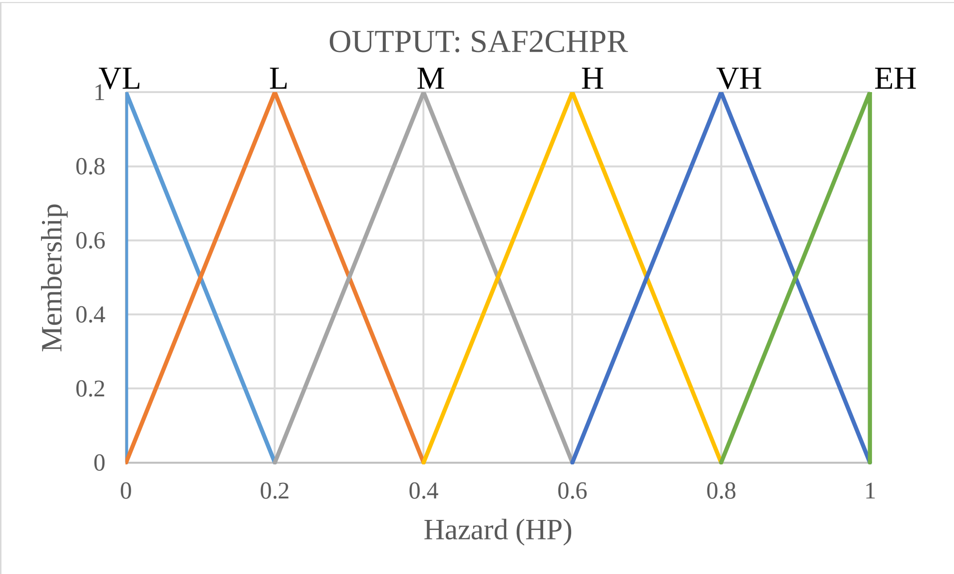

Figure 3.43: Output membership functions for SAF2CHPR

IF-THEN rules

The IF-THEN rules for SAF2CHPR represent the relationship between SAFCHE and SAFPRO.

The general rule is:

IF (“SAFCHE” is ___) AND (“SAFPRO” is ___) THEN (“SAF2CHPR” is ___).

The rules for this aggregation are given in Table 3.38.

An example for one operation is:

IF ("SAFCHE" is very low) AND ("SAFPRO" is very low) THEN ("SAF2CHPR" is very low).

Table 3.38: Fuzzy IF-THEN rules for SAF2CHPR

THEN (SAF2CHPR)		IF (SAFPRO)					
		VLH	LH	MH	HH	VHH	EHH
AND (SAFCHE)	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

3.3.5.5 The pair wise aggregation for intermediate parameters of HANDS

The HANDS is the resultant of HEL2REL and SAF2CHPR inputs. The determination of HEL2REL and SAF2CHPR are presented in the above section. The fuzzy sets defining HANDS and its input and output memberships are shown in Table 3.39. The membership function drawn according to this definition are shown in Figure 3.44, Figure 3.45 and Figure 3.46.

Table 3.39: Fuzzy sets and shapes of input and output memberships for HANDS

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
HEL2REL (HP)	Very Low Hazard Potential	VLH	Triangular	[-0.2, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]

	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1.2]
SAF2CHPR (HP)	Very Low Hazard Potential	VLH	Triangular	[-0.2, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy number**
HANDS (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

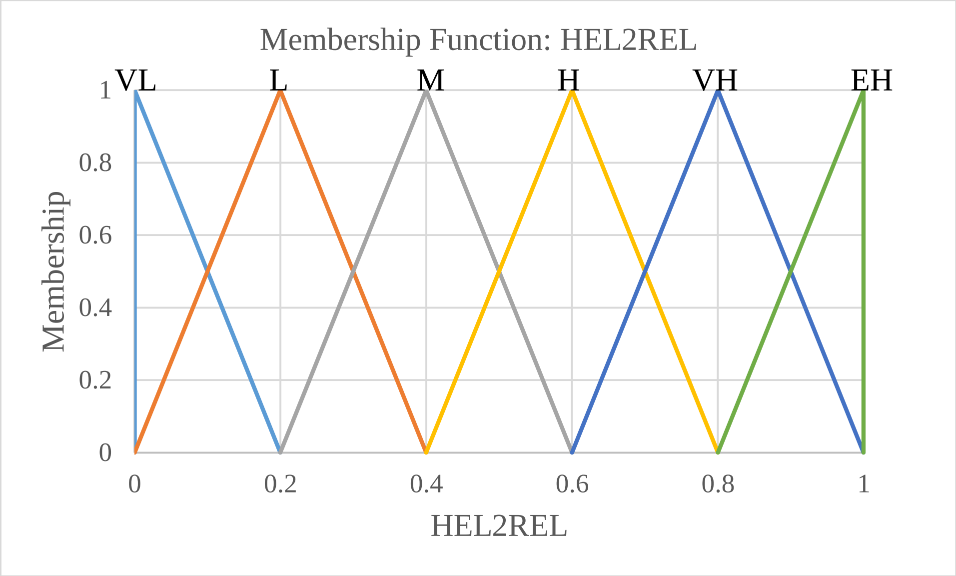

Figure 3.44: Input membership functions for HEL2REL

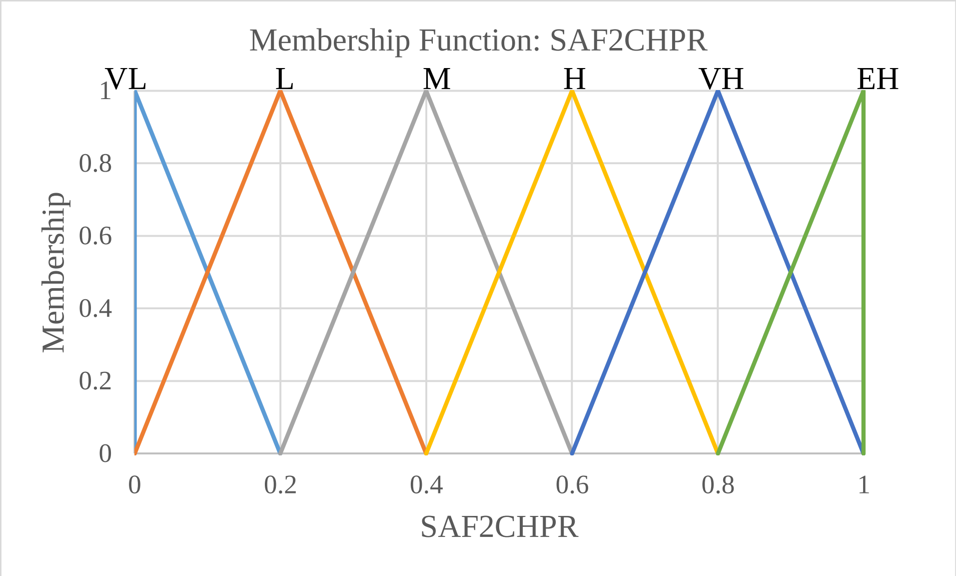

Figure 3.45: Input membership functions for SAF2CHPR

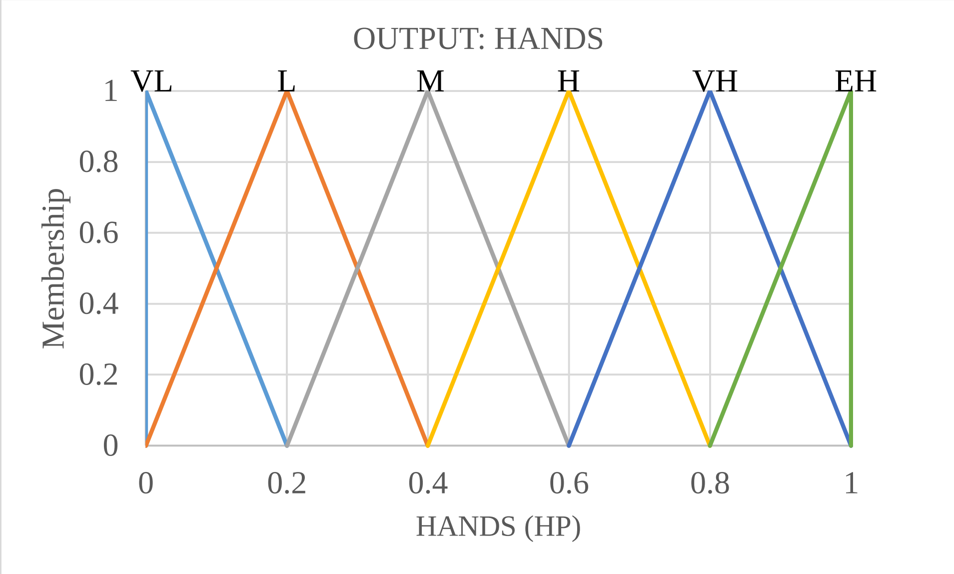

Figure 3.46: Output membership functions for HANDS

IF-THEN rules

The IF-THEN rules for HANDS represent the relationship between SAF2CHPR and HEL2REL.

The general rule is:

IF (“SAF2CHPR” is ___) AND (“HEL2REL” is ___) THEN (“HANDS” is ___).

The rules constructed for this aggregation are given in Table 3.40.

An example for one operation is:

IF (“SAF2CHPR” is very low) AND (“HEL2REL” is very low) THEN (“HANDS” is very low).

Table 3.40: Fuzzy IF-THEN rules for HANDS

THEN (HANDS)		IF (SAF2CHPR)					
		VLH	LH	MH	HH	VHH	EHH
AND (HEL2REL)	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

3.3.5.6 The pair wise aggregation for determination of EHS-Fuzzy Index

The final result of the hierarchical model, EHS-Fuzzy Index is given by aggregation of ENV2REL and HANDS inputs. The determination of ENV2REL and HANDS are presented in the previous section.

Table 3.41: Fuzzy number and shapes of input and output membership functions for EHS-Fuzzy Index

Inputs	Linguistic Description	Abbreviation	Shape	Fuzzy number
ENV2REL (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
HANDS (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]

Outputs	Linguistic Description	Abbreviation	Shape	Fuzzy number
EHS-Fuzzy Index (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]
	Medium hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

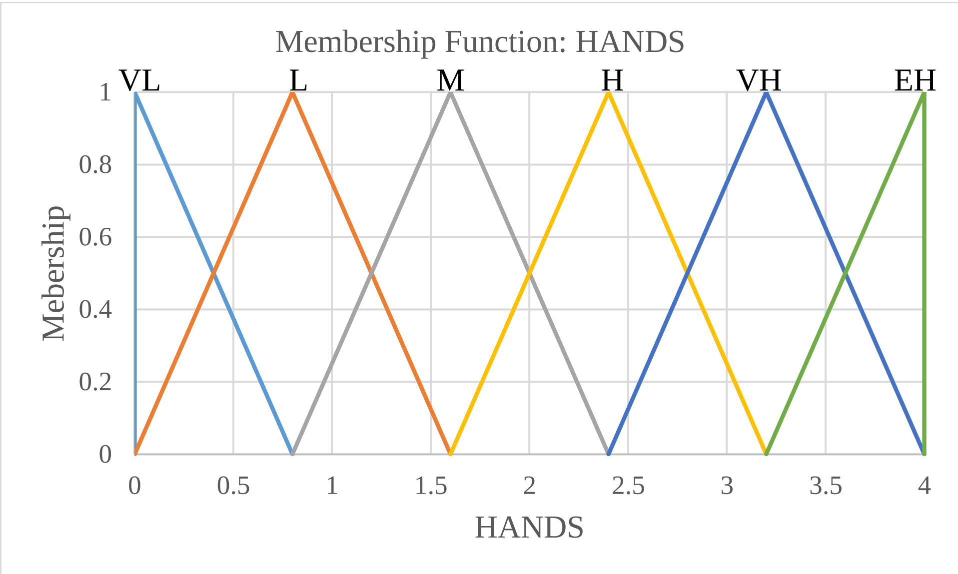

Figure 3.47: Input membership functions for HANDS

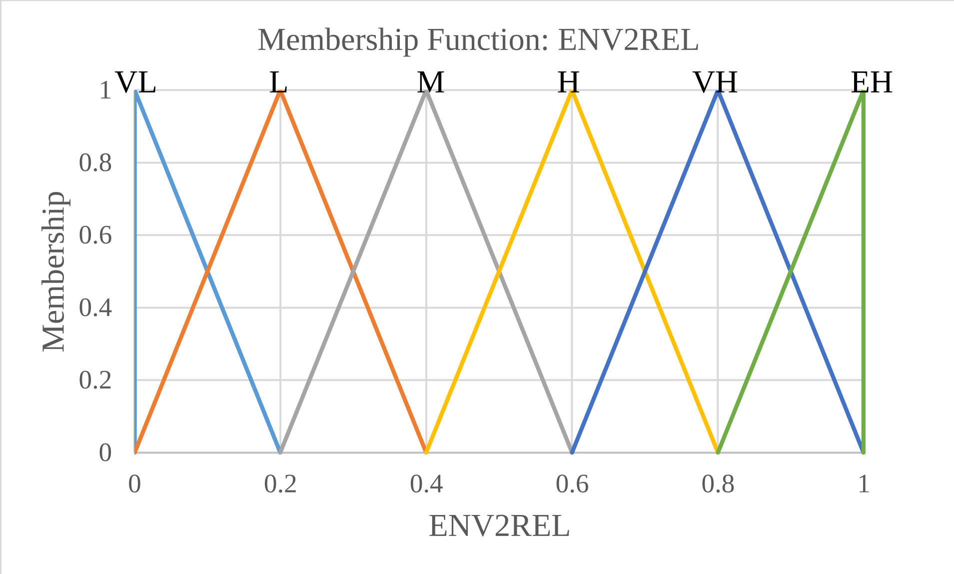

Figure 3.48: Input membership functions for EHV2REL

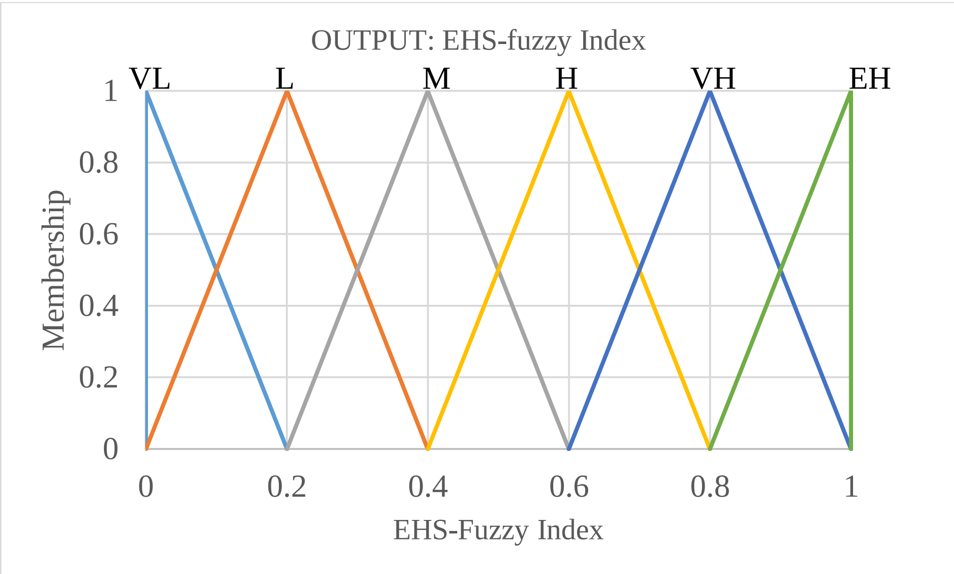

Figure 3.49: Output membership functions for EHS-Fuzzy Index

IF-THEN rules

The IF-THEN rules for the EHS-Fuzzy Index represent the relationship between ENV2REL and HANDS.

The general rule is:

IF ("ENV2REL" is ___) AND ("HANDS" is ___) THEN ("EHS-Fuzzy Index" is ___).

The rules constructed for this aggregation are given in Table 3.31.

An example for one operation is:

IF (“ENV2REL” is very low) AND (“HANDS” is very low) THEN (“EHS-Fuzzy Index” is very low).

Table 3.42: Fuzzy IF-THEN rules for EHS-Fuzzy Index

THEN (EHS-Fuzzy Index)		IF (ENV2REL)					
		VLH	LH	MH	HH	VHH	EHH
AND (HANDS)	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

The EHS-Fuzzy Index derived after aggregating HNDS and ENV2REL is in hazard potential units and it takes the values in the range from 0 to 1. An index value closer to 0 indicates a chemical process routes with lower hazards and 1 with highest hazard.

3.6 Comparison of EHS–Fuzzy Index methodology with EHS assessment using radial polygon diagram method

In order to verify the EHS assessment results of the EHS-Fuzzy Index methodology proposed in this work, the radial polygon diagrams methodology is used. The radial polygon diagram is a simple visual diagram, which has several sides. Each side of the polygon has two vertices. The vertices of each side are located at a distance of radius from the center of the polygon.

A polygon diagram with 13 sides representing the 13 EHS assessment parameters is considered to visualize the hazard involved with the chemical process route. Universe of discourse of each parameter is represented by the radius of polygon diagram. The values of the 13 parameters related to the chemical route are normalized on to a scale from 0 to 1 using the universe of discourse defined for each parameter in the previous section. The normalization is done by dividing the quantified impact parameter value with the maximum hazard value in the universe of discourse. The area covered by the

13 normalized parameter values on the polygon diagram is used to determine the percentage of covered area.

An example of a polygon diagram showing the 13 vertices represented by the 13 EHS parameters is given figure 3.50. The center of polygon is defined as zero and each vertex is given the value 1 which represents the maximum hazard of each parameter.

The area of the diagram is equal to the EHS impact of a chemical process route and its maximum value is equal to the area of the whole radial polygon diagram. The area percentage of the diagram represents the hazard potential of the any chemical process route.

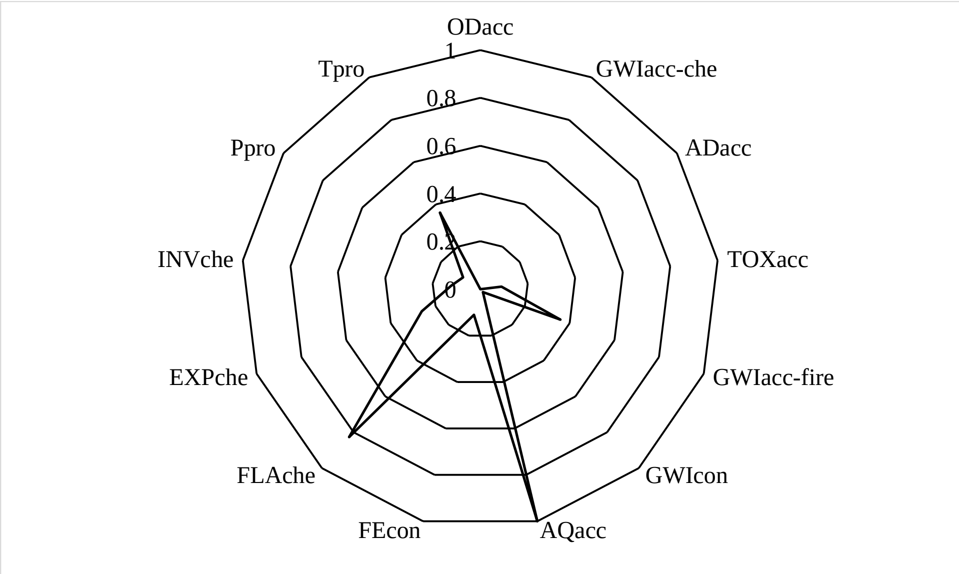

Figure 3.50: Radial polygon diagram showing the 13 EHS parameters in vertices for a chemical process route

3.7 Case Study Application

The fuzzy based environmental, health and safety assessment methodology (EHS-Fuzzy Index) proposed in this work was applied in the case study Methyl Methacrylate. The EHS- Fuzzy Index values of six chemical routes to manufacture methyl methacrylate (MMA) were estimated. These six routes are described below.

3.7.1 MMA Chemical process routes description

The details of Methyl methacrylate (MMA) manufacturing routes were obtained from literature (Lawrence, 1996). The notations used for MMA manufacturing routes are given in Table 3.43. The process block diagrams of all routes were developed using data from Lawrence (1996).

Table 3.43: Notations for MMA manufacturing process routes

MMA manufacturing route	**Notation**
Acetone Cyanohydrin based route	ACH
Ethylene via Propionaldehyde based route	C2/PA
Ethylene via Methyl Propionate based route	C2/MP
Propylene based route	C3
Tertiary Butyl Alcohol based Route	TBA
Isobutylene based Route	i-C4

3.7.1.1 Acetone Cyanohydrin based route (ACH)

The MMA manufacturing starts with producing hydrogen cyanide. This is next reacted with acetone to produce acetone cyanohydrin (ACH). The ACH is treated with sulphuric acid in the heated reaction condition to give methacrylamide. Finally, the methacrylamide react with methanol to produce MMA and sulphuric acid. Sulphuric acid is recovered as a by-product.

3.7.1.2 Ethylene via Propionaldehyde based route (C2/PA)

As a first step, ethylene is reacted with carbon monoxide and hydrogen to produce propionaldehyde. In the second step, propionaldehyde is condensed with formaldehyde to give methacrolein. Then methacrolein is oxidized to methacrylic acid in the third step. Finally, the methacrylic acid is reacted with methanol to give MMA.

3.7.1.3 Ethylene via Methyl Propionate based route (C2/MP)

The first step of this route is to react ethylene with carbon monoxide in the presence of methanol to yield methyl propionate. Methylal (dimethyl formal or modified formaldehyde) is used to condense the methyl propionate to MMA.

3.7.1.4 Propylene based route (C3)

Initially, propylene is reacted with carbon monoxide in the presence of hydrogen fluoride to give isobutyryl fluoride. This is followed by hydrolysis to produce isobutyric acid. Hydrogen fluoride is recovered for recycling. The isobutyric acid is oxydehydrogenated to methacrylic acid. The methacrylic acid is reacted with methanol to yield MMA.

3.7.1.5 Tertiary Butyl Alcohol based route (TBA)

Tertiary butyl alcohol (TBA) is oxidized first to methacrolein and then to methacrylic acid in two stages. The methacrylic acid is reacted with methanol to yield MMA.

3.7.1.6 Isobutylene based Route (i-C4)

Isobutylene (i-C4) is oxidized first to methacrolein and then to methacrylic acid in two stages. The methacrylic acid is reacted with methanol to yield MMA.

Chapter 4

RESULTS AND DISCUSSION

This section presents the results of application and verification of the developed EHS-Fuzzy Index methodology in Methyl Methacrylate (MMA) manufacturing routes. As the first step of application of developed methodology, the inventory of each route was calculated using the assumption given in section 3.1. The quantities of each chemical available for MMA manufacturing route were calculated considering balanced reaction equations and the reaction yield.

The 13 quantified impact values of the primary parameters, representing hazards posed by the six chemical routes to manufacturing MMA are given in the Table 4.1. The equation to derive these values were discussed in the section 3.2. An example calculation of these 13 parameters are shown in Appendix A.1. The STEL, TWA, LC50 and molecular weight values used in this calculation for all chemicals associated with each chemical route is shown in Appendix A.2.

Table 4.1: Quantified impacts representing EHS aspects in the MMA routes assessment

Parameters	Unit	Impact Values					
		TBA	i/C4	C3	C2/MP	C2/PA	ACH
GWIacc-che	Kmol	0	0	0	0	0	76,052
TOXacc	%	1	1	1	9	9	2
ODacc	Years	0	0	0	0	0	0
ADacc	Kmol	0	0	0	0	0	59,467
GWIacc-fire	Kmol	634,367	634,215	766,846	569466	571878	645,527
GWIcon	Kmol	166	192	141	117	151	345
FEcon	-	0.006	0.007	0.57	0.055	0.11	0.37
HAQacc	-	0.23	0.25	6,100,633	7.20	18.70	165

EXPche	%	11.7	12.9	12.3	20.4	26.2	13.2
FLAche	-	1.93	3.28	3.38	3.15	3.31	2.83
INVche	te	13,099	11,977	13,833	12,170	12,213	14,460
Ppro	atm	6.5	6.5	99	99	48	6
Tpro	^{o}C	325	370	330	325	325	1,175

The EHS 13 parameter values shown in table 4.1 were defined as the primary parameters and were used as the crisp inputs to the fuzzy inference system. The crisp outputs from the fuzzy inference system are referred to as the hazard potential values in this work.

4.1 Ranking routes to manufacture Methyl Methacrylate

The Table 4.2 shows the routes to produce MMA ranked based on EHS-Fuzzy Index. The hazard potential values estimated for the environmental, health and safety parameters are given in Tables 4.3, Table 4.4 and Table 4.5 respectively.

The hazard potential calculation for the 13 primary parameters was a single input fuzzy operation. The intermediate parameters; SAF2CHPR, HEL2REL, HANDS, ENVACC and ENV2REL were determined considering pair wise comparison of fuzzy logic application. An example calculation of the HP values for primary parameters and intermediate parameters using fuzzy inference system are shown in Appendix B.1 and Appendix B.2 respectively.

Table 4.2: Routes to produce MMA ranked based on EHS fuzzy Index

Chemical Process Route	**EHS-Fuzzy Index**	**Hazard increases**
TBA	0.25	↓
I/C4	0.27	
C2/PA	0.34	
C2/MP	0.35	
ACH	0.42	
C3	0.46	

The low value of EHS-Fuzzy Index indicates a less EHS impact and less hazard potential. A higher EHS-Fuzzy Index value indicates a high EHS impact and a higher hazard potential. Therefore, according to the results obtained from case study, TBA route shows the least EHS impact and C3 route shows the highest EHS impact.

The environment impact, health impact and safety impact assessment are discussed individually in the following sections.

4.2 Comparison of chemical process routes based on environmental impacts

The environmental impact due to releases (ENV2REL) of a chemical process route is assessed by pair wise comparison of environment impact due to accidental releases (ENVACC) and environment impact due to continuous releases (ENVCON). The ENV2REL is the resultant of environment impact due to catastrophic releases and continuous releases of a chemical process plant. The universe of discourse of input parameters (ENVACC and ENVCON) and output parameter (ENV2REL) is in [0, 1].

The ENVACC is derived from two intermediate parameters, which are environmental impact due to accident chemical release (ENVCHE) and environment impact due to accidental fire (ENVFIRE). The most possible accidents at the chemical process plant are accidental chemical spillage and accidents chemical fire. Both are represented in the ENVACC.

The ENVCHE is derived from four parameters. The universe of discourse of ENVCHE is in [0, 4] because it is derived by simple fuzzy addition of hazard potential vales of four primary parameters, which are GWIACC-CHE, TOXACC, ODACC and ADACC.

The ENVFIRE is derived from one parameter. The universe of discourse of ENVFIRE is [0, 1] because it is equal to the hazard potential value of GWIACC-FIRE.

The ENVCON is equal to the GWICON that is hazard potential value of global warming impact due to continuous releases. The Universe of Discourse of GWICON is [0, 1].

Table 4.3: Hazard potential values for environment impact assessment parameters

Parameter	**TBA**	**I/C4**	**C3**	**C2/MP**	**C2/PA**	**ACH**
ENV2REL	**0.18**	**0.18**	**0.21**	**0.18**	**0.18**	**0.22**
ENVACC	0.3	0.3	0.38	0.3	0.3	0.41
ENVCHE	0.05	0.05	0.05	0.2	0.2	1.01
GWIACC-CHE	0	0	0	0	0	0.53
TOXACC	0.05	0.05	0.05	0.2	0.2	0.05
ODACC	0	0	0	0	0	0
ADACC	0	0	0	0	0	0.43
ENVFIRE	0.6	0.6	0.68	0.55	0.55	0.6
GWIACC-FIRE	0.6	0.6	0.68	0.55	0.55	0.6
ENVCON	0.05	0.05	0.05	0.05	0.05	0.09
GWICON	0.05	0.05	0.05	0.05	0.05	0.09

According the results shown in Table 4.3, the ENV2REL values are shown in bold numbers. The TBA, I/C4, C2/MP and C2/PA routes show the least environmental impact. However, all six chemical routes have approximately the same environmental impact. The environmental impact due to C3 and ACH chemical process routes are slightly higher than the other routes. The highest environmental impact with hazard potential value 0.22 was observed in ACH rout to manufacture MMA.

The highest environmental impact due to accidental releases (ENVACC) is observed in the ACH chemical route with a hazard potential value of 0.41. The least impact value, 0.3 is associated with the TBA, I/C4, C2/MP and C2/PA routes. The highest ENVCON value is shown by ACH route. All other routes have equal environmental impact value.

4.3 Comparison of chemical process routes based on occupational health impacts

The health impact assessment is a result of pair wise comparison of FECON and HAQACC. The FECON value represents the health impact due to continuous emissions of daily plant operations. The HAQACC represents the health impact due to accidental releases within the plant environment. The universe of discourse of

FECON and HAQACC are defined in [0, 1] and output (HEL2REL) is defined in [0, 1]. The hazard potential values of FECON, HAQACC and HEL2REL are shown in Table 4.4.

Table 4.4: Hazard potential values for health impact assessment

Parameter	**TBA**	**I/C4**	**C3**	**C2/MP**	**C2/PA**	**ACH**
HEL2REL	**0.22**	**0.26**	**0.84**	**0.51**	**0.6**	**0.78**
FECON	0	0	0.75	0.12	0.25	0.57
HAQACC	0.43	0.45	1	1	1	1

According to the HEL2REL results, the TBA route is the most occupational healthy chemical route. The C3 chemical route pose a higher occupational health hazard to people working in the plant environment.

The TBA and I/C4 routes pose the least occupational health impact due to continuous releases of chemical process plant while C3 route pose the highest occupational health impact due to continuous releases. The FECON values for TBA and I/C4 are negligible and therefore shown as zero in table 4.4.

The C3, C2/MP, C2/PA and ACH routes show a higher occupational health hazard due to workplace accidental releases. The primary parameter AQacc values of these routes have exceeded the upper limit in the universe of discourse of input AQacc parameter. Therefore, the HAQACC for these routes shown the maximum value 1 after defuzzification.

4.4 Comparison of chemical process routes based on safety

The safety impact of a chemical route (SAF2CHPR) is assessed by pair wise comparison of SAFCHE and SAFPRO. The universe of discourse of SAFCHE is defined in the range [0, 3] because it is a resultant of fuzzy addition of EXPCHE, FLACHE and INVCHE. The universe of discourse of SAFPRO is in the range [0, 2] because it is obtained by simple fuzzy addition of TPRO and PPRO. The universe of discourse of the output intermediate parameter, SAF2CHPR is [0, 1].

Table 4.5: Hazard potential values for safety impact assessment parameters

Parameter	**TBA**	**I/C4**	**C3**	**C2/MP**	**C2/PA**	**ACH**
SAF2CHPR	**0.32**	**0.4**	**0.48**	**0.5**	**0.49**	**0.5**
SAFCHE	1.21	1.39	1.45	1.54	1.61	1.42
EXPCHE	0.25	0.25	0.25	0.4	0.47	0.28
FLACHE	0.68	0.89	0.92	0.89	0.89	0.86
INVCHE	0.28	0.25	0.28	0.25	0.25	0.28
SAFPRO	0.6	0.68	0.9	0.9	0.71	1.05
TPRO	0.55	0.63	0.55	0.55	0.55	1
PPRO	0.05	0.05	0.35	0.35	0.16	0.05

According to the SAF2CHPR results, TBA route is the inherently safest MMA manufacturing route compared to other five MMA routes. The C3, C2/MP, C2/PA and ACH routes have approximately equal hazard potential values higher than the TBA route.

The inherently safer chemical route when chemical properties are considered is TBA while C2/PA route is the most unsafe. Further, the TBA route poses the least process safety impact while ACH has the most unsafe process conditions.

4.5 Ranking chemical process routes based on individual environmental, health and safety aspects

The chemical process routes ranked based on EHS individual hazard potential values are given in the Table 4.6. The rank 1 represents the least hazard potential and ranking increases with the increase of hazard potential value.

Table 4.6: The routes ranked according to individual EHS results

Routes	E-Hazard Potential	Rank	H-Hazard Potential	Rank	S-Hazard Potential	Rank
TBA	0.18	1	0.22	1	0.32	1
I/C4	0.18	1	0.26	2	0.4	2
C3	0.21	5	0.84	6	0.48	3
C2/MP	0.18	1	0.51	3	0.5	6
C2/PA	0.18	1	0.6	4	0.49	4
ACH	0.22	6	0.78	5	0.5	6

The individual EHS ranking shows that the TBA route pose the least environmental hazard, health hazard and safety hazard. The highest hazard ranked route for individual environmental and safety is the ACH route and that for health is the C3 route.

The ACH route has the highest environmental hazard because it has more acidic chemicals and GHG gases in its inventory.

The C3 route has the highest health hazard potential value, as this route has a high occupational health impact due to work place continuous releases of hydrogen fluoride.

4.6 Verification of the results by radial polygon diagram method

The EHS impacts quantified for MMA manufacturing routes were aggregated using the polygon diagram methodology and the results are presented in this section. In order to verify the methodology proposed in this work the final results obtained from EHS-Fuzzy Index methodology are compared with the results determined by combining impacts of EHS using the area covered in the radial polygon diagram.

The radial polygon diagrams are drawn considering normalized EHS parameter values. The universe of discourse defined for the 13 EHS parameters were considered in the normalization process of each parameter. The normalization is done by dividing the quantified impact parameter value with the maximum hazard value in the universe of discourse. Normalized values take the hazard range from 0 to 1. The maximum hazard value in the universe of discourse are shown in the Table 4.7.

Table 4.7: The maximum hazard value in the universe of discourse

Parameters	Values	Units
GWIacc-che	227300	Kmol/day
TOXacc	100	%
ODacc	3.29×10^9	Years
ADacc	260420	Kmol/day
GWIacc-fire	1591100	Kmol
GWIcon	9471	Kmol/hr
FEcon	1	-
AQacc	1	-
EXPche	100	%
FLAche	4	-
INVche	100000	Tonne
Tpro	900	^oC
Ppro	550	atm

The radial polygon diagrams developed for the six chemical routes of MMA showing the area covered under the curve (DA) and percentages of area compared with the total area in the radial polygon diagram (PA) are shown in Figures from 4.1 to 4.6. The RPDA is the radial polygon diagram area.

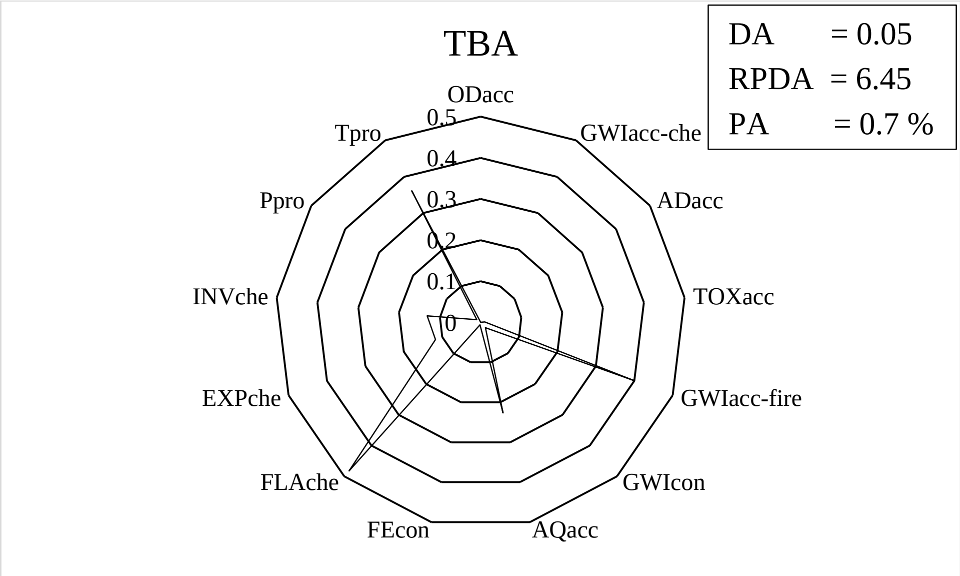

Figure 4.1: Radial polygon diagram for TBA route

(DA- diagram area; RPDA- radial polygon diagram area; PA- percentage of area)

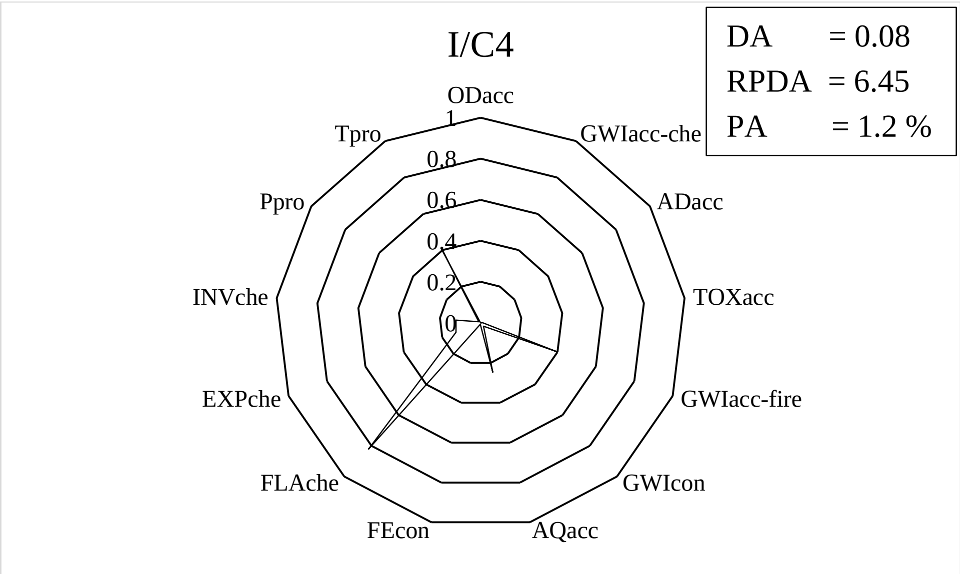

Figure 4.2: Radial polygon diagram for I/C4 route

(DA- diagram area; RPDA- radial polygon diagram area; PA- percentage of area)

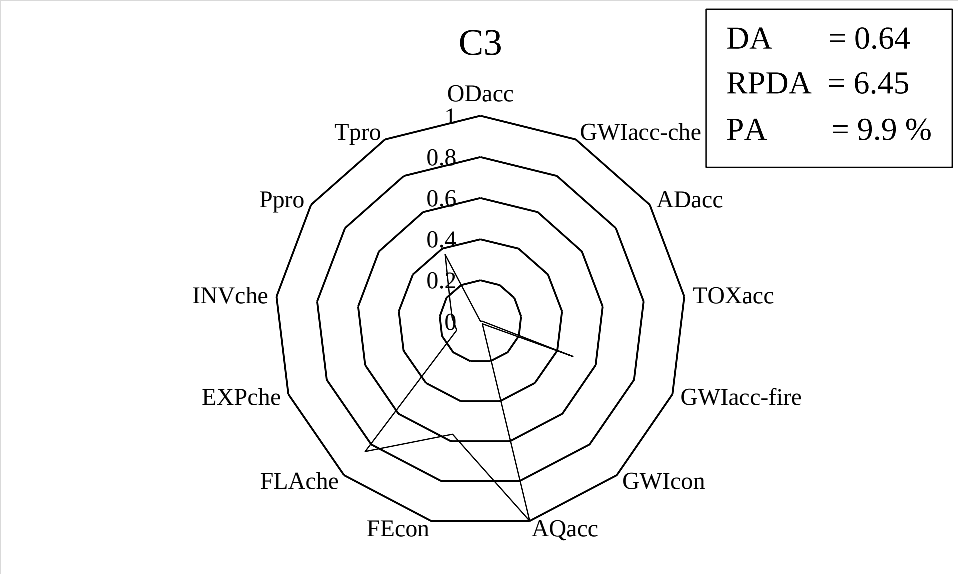

Figure 4.3: Radial polygon diagram for C3 route

(DA- diagram area; RPDA- radial polygon diagram area; PA- percentage of area)

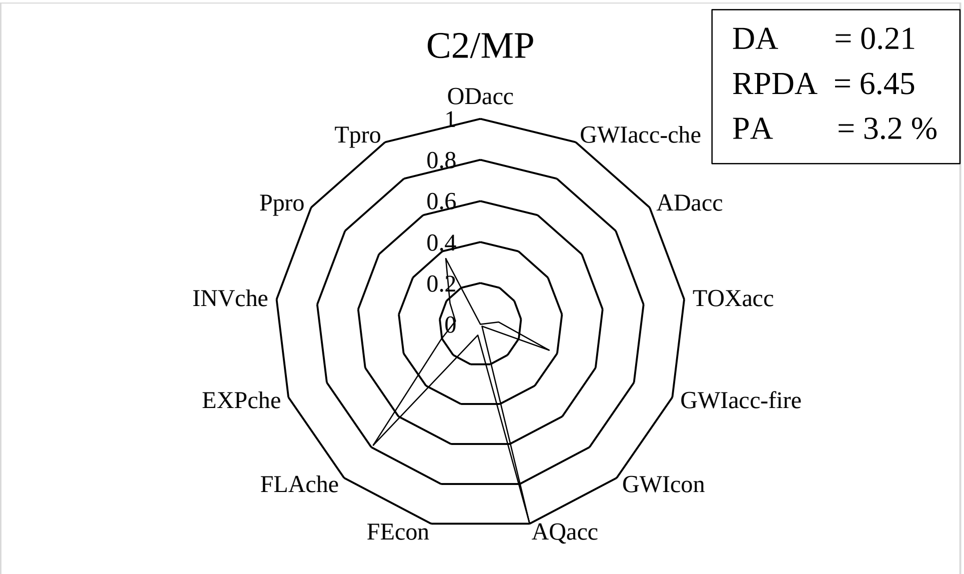

Figure 4.4: Radial polygon diagram for C2/MP route

(DA- diagram area; RPDA- radial polygon diagram area; PA- percentage of area)

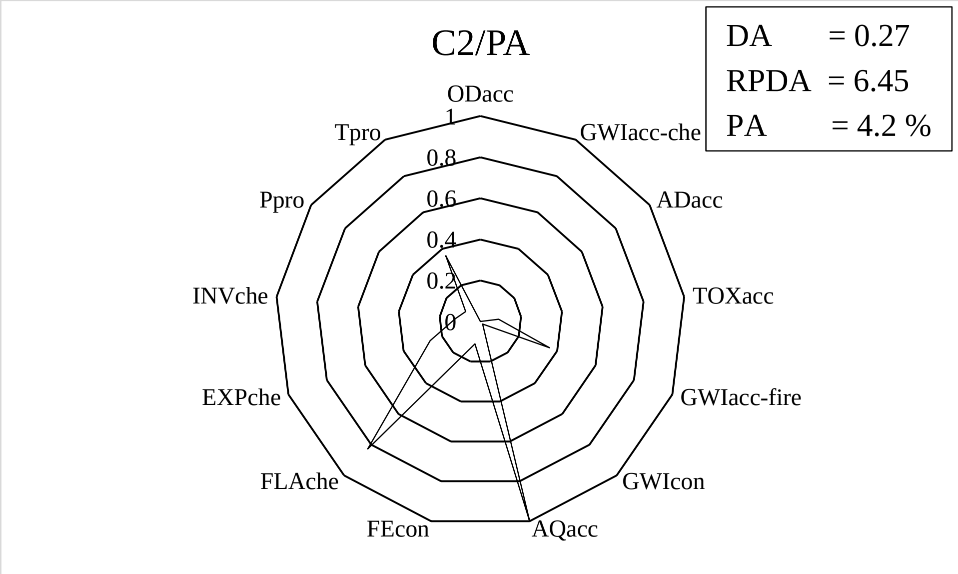

Figure 4.5: Radial polygon diagram for C2/PA route

(DA- diagram area; RPDA- radial polygon diagram area; PA- percentage of area)

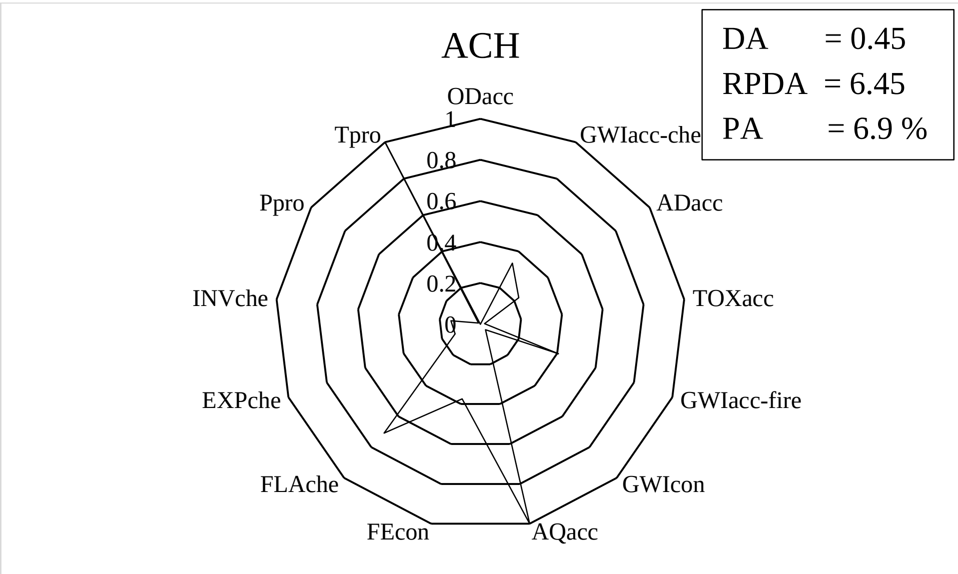

Figure 4.6: Radial polygon diagram for ACH route

(DA- diagram area; RPDA- radial polygon diagram area; PA- percentage of area)

The result obtained by EHS-fuzzy Index can be verified by comparing with the results obtained from the radial polygon diagram (Table 4.8). The MMA routes ranked according to EHS-fuzzy Index and area percentage of each radial polygon diagram are given in Table 4.9.

Table 4.8: Comparison of radial polygon diagram and EHS-Fuzzy Index values for chemical routes to manufacture MMA

Chemical Process Route	**EHS-Fuzzy Index**	**Radial Polygon Diagram (%)**
TBA	0.25	0.7
I/C4	0.27	1.2
C2/PA	0.34	0.27
C2/MP	0.35	3.2
ACH	0.42	6.9
C3	0.46	9.9

Table 4.9: Comparison of chemical routes to manufacture MMA ranked based on radial polygon diagram and EHS-Fuzzy Index

Chemical route	Area in radial polygon diagram ((unit area)^2)	Rank according to the Radial polygon diagram	Rank according to the EHS-fuzzy Index
TBA	0.05	1	1
I/C4	0.08	2	2
C3	0.64	6	6
C2/MP	0.21	3	4
C2/PA	0.27	4	3
ACH	0.45	5	5

According to the above results, both methods show that TBA route is the chemical route with least EHS impact. The C3 route is ranked 6 in both methods indicating that it is the chemical route having the most EHS hazards.

Chapter 5

CONCLUSIONS

This chapter gives the conclusions made in this work, that developed a methodology to compare and select the best chemical route based on inherent environment hazards, occupational health hazards and safety, during early stages of chemical process plant design and development.

The fuzzy logic based inherent environment, health and safety index (EHS-Fuzzy Index) developed in this work ranks chemical process routes based on inherent environmental hazards, inherent health hazards and inherent safety. A lower EHS-Fuzzy Index value indicates a chemical route with lower hazard based on the inherent environmental hazards, occupational health hazards and safety impacts when both types of chemical releases (accidental and daily operational) are considered. The EHS-Fuzzy Index method is simple and considers only the information available during early stages of a chemical plant design and development.

Therefore, the best chemical route to develop a chemical process plant is indicated by the route having the lowest EHS-Fuzzy Index value among alternative routes to manufacture the same chemical. In addition, alternative chemical routes can be compared considering individual inherent environmental hazards or inherent health hazards or inherent safety. This EHS-Fuzzy Index method developed is generic and therefore, it can be applied in possible routes to produce any chemical.

Application of the EHS-Fuzzy Index in routes to produce MMA showed that the TBA route has the lowest EHS hazard when accidental as well as daily operational releases are considered. Therefore, this indicates that TBA route is the potentially best chemical route to manufacture methyl methacrylate compared to other possible five routes.

The validity of the EHS-Fuzzy Index method was tested by applying the same case study to produce MMA in the radial polygon methodology. Both methods showed the similar ranking results for routes to produce MMA.

Chapter 6

RECOMMENDATIONS

The methodology developed compares and ranks chemical routes based on inherent environmental hazards, occupational health hazards and safety, during preliminary design stage of chemical process plant considering both types of chemical releases, accidental as well as daily operational. In this methodology the magnitude of the consequences of accidents or releases were used in the analysis. The incorporation of probability of occurrence of the accident or the chemical release along with the consequence magnitude (risk) is an important aspect that could be studied in a future work.

This methodology could be further developed to apply during other stages of plant design such as basic engineering or detailed engineering for process alternatives selection. As more data are available during these stages compared to the preliminary design stage the assessment methodology would also be different.

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Appendix A.1

Example calculation for Tertiary Butyl Alcohol based Route (TBA)

1. Balance reaction equation and operation condition

Step 1

$$(CH3)3COH + O2 \rightarrow CH2CCH3CHO + 2H2O$$

Tertiary Butyl Alcohol + Oxygen - Methacrolein + Water

Vapour phase

Pressure: 4.8 atm

Temperature: 350 ° C

Yield: 83%

Step 2

$$CH2CCH3CHO + O2 \rightarrow 2CH2CCH3COOH$$

Methacrolein + Oxygen - Methacrylic Acid

Vapour Phase

Pressure: 3.7 atm

Temperature: 350 ° C

Yield: 57.75%

Step 3

$$CH2CCH3COOH + CH3OH \rightarrow CH2 = C(CH3)COOCH3 + H2O$$

Methacrylic Acid + Methanol - Methyl Methacrylate + Water

Liquid Phase

Pressure: 6.8-7.5 atm

Temperature: 70-100 °C

Yield: 75%

2. Process block diagram

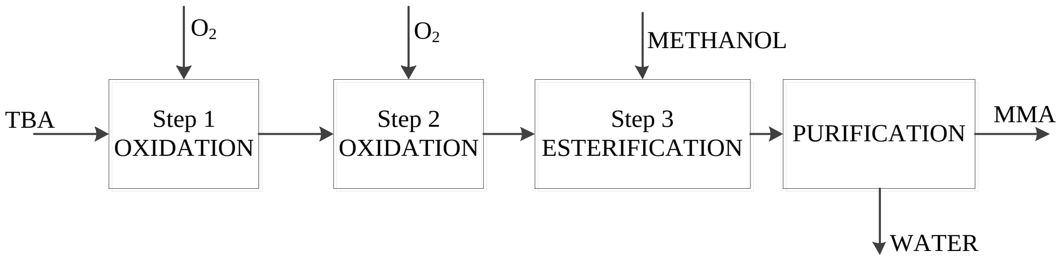

Figure A.1: Process block diagram for TBA route (Lawrence, 1996)

3. Inventory calculation

$$\text{MMA quantity } = \frac{150000}{8000} \times 14 \times 24 \text{ (te)} = 6300 \text{ te}$$

Table A.1: Chemical inventory for TBA route

Chemical	Chemical quantity (te)			
	Separation	Reactor	Storage	Total
Methacrolein	5.3	35.9		41.2
Methacrylic Acid	13.4	21		34.9
Methanol	0.5	8	2016	2024.5
Methyl Methacrylate (MMA)	9.4		6300	6309.4
Oxygen	0.6	6.4		7
Tert But Alcohol	0.7	2.8	469	4672.5
Water	3.2	6.7		9.9

4. Global warming impact due to greenhouse gas emission of accidental chemical release

$$\text{GWIacc} - \text{che} = \sum_{i=1}^{n} f_{\text{GWP}} \times \frac{Q_i}{M_i} \times 10^3 = 0 \text{ kmol}$$

The GWIacc-che is zero because f_{GWP} of all chemical used for TBA route are zero.

5. Toxicity impact on living things

Predicted environment concentration (PEC) for Methanol

Calculation of PEC:

C = Z × f

Cair = Zair × f

f = MT/(Zair×Vair+Zwater×Vwater+Zsoil×Vsoil+Zsediment×Vsediment+Zsuspendent sediment×Vsuspendent sediment +Zbiota×Vbiota)

MT- mol of pollutant in compartment

C- concentration of pollutant in compartment (mol/m3)

V- volume of compartment (m3)

f- prevailing fugacity (Pa)

Z- fugacity capacity of pollutant in compartment (mol/m3-Pa)

Table A.2: Volume and Z of each compartment

Compartment	Volume (m^3)	Z
Air	6.0×10^{9}	0.00041
Water	7.0×10^{6}	2.242152
Soil	4.5×10^{4}	0.007493
Sediment	2.1×10^{4}	0.014985
Suspended Sediment	35	0.046828
Biota	7	0.380717

PEC= 0.0014278 mol/m^3

Calculation of constant for Probit equation

LC50 = 2.615 mol/m^3

STEL = 0.01014 mol/m^3

Probits values from Chemical Process Safety (Crowl & Louvar, 2001).

Probits for LC50 = 5

Probits for STEL = 2

$\mathrm{Probit_i} = \mathrm{k1_i} + \mathrm{k2_i}\ln(\mathrm{Dose_i})$

k1 = 4.4805 for methanol

k2 = 0.5403 for methanol

Probits for PEC = 0.9406

Percentage of animal killed (xi) = 0%

Table A.3: Percentage of animal killed by TBA route

Chemical	xi (%)
Methacrolein	0
Methacrylic Acid	0
Methanol	0
Methyl Methacrylate (MMA)	1
Oxygen	0
Tert But Alcohol	0
Water	0

$$\mathrm{TOXacc} = \sum_{i=1}^{n} \mathrm{xi}\,\% \; = 1\%$$

6. Ozone depletion

The N_{Cl} and N_{Br} are zero for all chemical available TBA route.

$$\mathrm{ODacc} = \sum_{i=1}^{n} \tau_i \times \left(N_{i(Cl)} + 30 \times N_{i(Br)}\right) \times \frac{Q_i}{M_i} \times 10^6 \; = 0$$

7. Acid deposition

The CF_{AD} is zero for all chemical substance of TBA route.

$$\mathrm{ADacc} = \sum_{i=1}^{n} CF_{AD} \times \frac{Q_i}{M_i} \times 10^3 = 0$$

8. Global warming impact due to greenhouse gas emission of accidental fire

$$\text{GWIacc} - \text{fire} = \sum_{i=1}^{n} N_{i(C)} \times \frac{Q_i}{M_i} \times 10^3$$

Table A.4: The GWIacc-fire for TBA route

Chemical	Mi	Qi	Ni	GWIi
Methacrolein	70.1	41.15536	4	2348.72
Methacrylic Acid	86.09	34.934695	4	1623.17
Methanol	32.04	2024.501	1	63186.67
Methyl Methacrylate	100.12	6309.3756	5	315059.2
Oxygen	32	7.00316	0	-
Tert But Alcohol	74.2	4672.5238	4	252149.7
Water	18	9.9457316	0	-
GWIacc-fire				634367.5

9. Global warming impact due to greenhouse gas emission of continuous operation

$$\text{GWIcon} = \sum_{i=1}^{n} \frac{\text{CED}_i \times q_i}{\Delta H_{CO_2}}$$

$$\Delta H_{CO_2} = 393.7 \text{ kJ/mol}$$

Table A.5: The GWIcon for TBA route

Chemical	**qi (kmol/hr)**	**CEDi**	**GWIcon (i)**
Methacrolein	225.65	74.967	42.97
Methacrylic Acid	249.72	54.175	34.36
Methanol	249.72	41.135	26.09
MMA	0	0	0
Oxygen	387.80	9.996	9.85
Tert But Alcohol	225.65	92.152	52.82
Water	0	0	0
GWIcon			**166.08**

10. Occupational health impact from work place accidental release airborne quantity

AQg — mass rate of vapour due to gaseous release (kg/s)

AQf — mass rate of vapour due to flashing (kg/s)

AQp- airborne material evaporation from the surface from pool evaporation (kg/s)

D — diameter of the hole (mm)

Pa — absolute pressure (kPa, Pg + 101.35)

MWavg — avarage molecular weight for materials in each process route

T — operating temperature (^{0}C)

L — liquid leak rate (kg/s)

Pg — guage pressure (kPa)

ρ_1 — liquid density (kg/m^3)

Cp — specific heat at constant pressure (kJ/kg ^{0}C)

Hv — heat of vaporization of the liquid (kJ/kg)

Ts — storage or operating liquid temperature (^{0}C)

Tb — normal liquid boiling point (^{0}C)

Pv — vapour pressure of the liquid (kPa)

$$\mathrm{AQg} = 4.751 \times 10^{-6} \mathrm{D}^2 \ \mathrm{Pa} \sqrt{\frac{\mathrm{MWavg}}{\mathrm{T} + 273}}$$

$$\mathrm{L} = 9.44 \times 10^{-7} \mathrm{D}^2 \sqrt{1000\mathrm{Pg} \times \rho_1}$$

$$\mathrm{AQf} = \left(\frac{\mathrm{Cp}}{\mathrm{Hv}}\right) (\mathrm{Ts} - \mathrm{Tb}) \times \mathrm{L}$$

Wp= 900L

Ap= 100Wp/ρ_1

$$\mathrm{AQp} = 9.0 \times 10^{-4} \mathrm{Ap}^{0.95} \ \mathrm{Pa} \frac{\mathrm{MWavg}}{\mathrm{T} + 273} \mathrm{Pv}$$

Step 1

It is vapour phase operation so AQg should be calculated.

$$\mathrm{AQg} = 4.751 \times 10^{-6} 6.35^2 \times 486.4 \sqrt{\frac{53.8}{623}} = 0.023$$

Step 2

It is also vapour phase operation so AQg should be calculated.

$$\mathrm{AQg} = 4.751 \times 10^{-6} 6.35^2 \times 374.9 \sqrt{\frac{76.5}{623}} = 0.24$$

Step 3

It is liquid phase operation and operating temperature is less than boiling point. The AQp should be calculated.

$$\mathrm{L} = 9.44 \times 10^{-7} 6.35^2 \sqrt{1000 \times 623.15 \times 947.9}$$

Wp= 900L

Ap= 100Wp/ρ_1

$$\mathrm{AQp} = 9.0 \times 10^{-4} \mathrm{Ap}^{0.95} \times 724.5 \frac{83.65}{358} \times 4.79 = 0.071$$

$$\mathrm{AQacc} = \sum_{i=1}^{n} \frac{x_i \times m_{AQ}}{\mathrm{VF} \times \mathrm{STEL}_i}$$

VF = 966.3

$$\mathrm{HAQacc} = \mathrm{Max}\,\{\mathrm{AQacc1}, \mathrm{AQacc2}, \mathrm{AQacc3}, \ldots\}$$

Table A.6: The AQacc for TBA route

Step	**Chemical**	**xi**	**m_{AQ}**	**(xi)×m_{AQ}/VF (10^{-6} kg/m^3)**	**STEL (10^{-6} kg/m^3)**	**AQacc**
1	Tert But Alcohol	0.1192	0.023	2.81501	0.00045	0.006255577
	Oxygen	0.0514				
	Methacrolein	0.5445		12.8541	0.00029	0.044324391
	Water	0.2847				
					AQacc1=	**0.050579969**
2	Methacrolein	0.344118	0.024	8.65244	0.00029	0.029836007
	Oxygen	0.076299				
	Methacrylic Acid	0.579583		14.5729	0.00014	0.104092286
					AQacc2=	**0.133928293**

3	Methacrylic Acid	0.19	0.071	13.9101	0.00014	0.099357872
	Methanol	0.07		5.12477	0.000325	0.015768537
	Methyl Methacrylate	0.63		46.123	0.00041	0.112495049
	Water	0.11				
					AQacc3=	**0.22762146**

$$\mathrm{HAQacc} = 0.2276$$

11. Occupational health impact due to fugitive emissions

$$\mathrm{FEcon} = \sum_{i=1}^{n} \frac{m_{i,FE}}{\mathrm{VF} \times \mathrm{TWA}_i}$$

Table A.7: The FEcon for TBA route

Chemical	**$m_{i,FE}$(mg/s)**	**Q (m3/s)**	**$m_{i,FE}$ /Q**	**TWA**	**($m_{i,FE}$ /Q)/TWA**
Methacrolein	224.85	966.3	0.232692	145	0.001605
Methacrylic Acid	247.93		0.256577	70	0.003665
Methanol	72.78		0.075318	260	0.00029
Methyl Methacrylate	97.39		0.100787	205	0.000492
Oxygen	113.01		0.116951	0	0
Tert But Alcohol	124.36		0.128697	300	0.000429
Water	156.68		0.162144	0	0
				FEcon=	**0.00648**

12. Inventory

$$\mathrm{INVche} = \sum_{i=1}^{n} Q_i$$

Table A.8: The INVche for TBA route

Chemical	Qi
Methacrolein	41.1
Methacrylic Acid	34.9
Methanol	2024.5
Methyl Methacrylate	6309.3
Oxygen	7.0
Tert But Alcohol	4672.5
Water	9.9
INVche =	13099.4

13. Flammability

$$\text{FLAche} = \sum_{i=1}^{n} Y_i \times F_i$$

Table A.8: The FLAche for TBA route

Chemical	Yi	Fi	Yi × Fi
Methacrolein	0.003141765	4	0.012567
Methacrylic Acid	0.002666885	1	0.002667
Methanol	0.154548677	3	0.463646
Methyl Methacrylate	0.481652337	3	1.444957
Oxygen	0.000534615		0
Tert But Alcohol	0.356696472		0
Water	0.000759249	3	0.002278
		FLAche =	1.926

FLAche = 1.926

14. Explosiveness

$$\text{EXPche} = \sum_{i=1}^{n} Y_i \times E_i$$

Table A.10: The EXPche for TBA route

Chemical	**Yi**	**Ei**	**Yi*Ei**
Methacrolein	0.003141765		0
Methacrylic Acid	0.002666885		0
Methanol	0.154548677	30.5	4.713735
Methyl Methacrylate	0.481652337	10.4	5.009184
Oxygen	0.000534615		0
Tert But Alcohol	0.356696472	5.6	1.9975
Water	0.000759249		0
		FLAche =	11.7204

EXPche = 11.72

15. Operating pressure

$$\text{Ppro} = \text{Max}\{P_{1,g}, P_{2,g}, \ldots P_{j,g} \ldots\}$$

Ppro= Max (4.8, 3.7, 6.5) = 6.5

16. Operating temperature

$$\text{Tpro} = \text{Max}\{T_{1,g}, T_{2,g}, \ldots T_{j,g} \ldots\}$$

Tpro= Max (325, 325, 60) = 325

Appendix A.2

The STEL, TWA, LC50 and molecular weight values

Table A.11: The STEL, TWA, LC50 and molecular weight values

Chemical	Molecular Mass (g/mol)	TWA (mg/m3)	STEL (mg/m3)	LD50 (mol/m3)
Acetone Cyanohydrin	85.12			
Acetone	58.08	1200	1780	0.004189
Ammonia	17.03	17	27	0.0000206
Ammonium bisulphate	115.11	115	165	
Carbon dioxide	44.01	9000		
Carbon monoxide	28.01	55	110	
Ethylene	28.05	1.2	5.7	0.0105
Formaldehyde	30.03	0.92		0.000121
Hydrogen	2.02			0.0105
Hydrogen Cyanide	27.03	11	20	
Hydrogen fluoride	20.01			0.000056
Isobutylene	56.1	345	460	0.0105
Isobutyric Acid	88.1	35	55	
Isobutyryl fluoride	90.1			
Methacrolein	70.1	145	290	0.000089
Methacrylamide	85.12	205	410	
Methacrylamide Sulphate				
Methacrylic Acid	86.09	70	140	
Methane	16.04			
Methanol	32.04	260	325	0.001422
Methylal	76.09	3100	6000	0.000059

Methyl methacrylate	100.12	205	410	0.00969
Methyl propionate	88.1	180	360	
Nitrogen	28.02			
Oxygen	32			
Propionaldehyde	58.08		950	
Propylene	42.08	350	700	
Sulphur dioxide	64.06	5		
Sulphuric Acid	98.08	1		
Sulphur Trioxide	80.06			
Tertiary butyl alcohol	74.2	300	450	
Water	18.02			

Appendix B.1

Hazard potential calculation for primary parameters

An example calculation for a primary parameter considering GWIacc-che in ACH route:
GWIacc-che= 76052 kmol
The MGWI and HGWI fuzzy sets are included within the GWIacc-che.

Table B.1: Fuzzy sets of GWIacc-che and the shape of the input and output membership functions

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy Sets**
GWIacc-che (GHG Emission Kmol of CO_2 equivalence)	Very Low Global Warming Impact	VLGWI	Triangular	[0, 0, 22730]
	Low Global Warming Impact	LGWI	Triangular	[0, 22730, 45460]
	Medium Global Warming Impact	**MGWI**	**Triangular**	**[22730, 45460, 90920]**
	High Global Warming Impact	**HGWI**	**Triangular**	**[45460, 90920, 136380]**
	Very high Global Warming Impact	VHGWI	Triangular	[90920, 136380, 227300]
	Extremely high Global Warming Impact	EHGWI	Triangular	[136380, 227300, 227300]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy sets**
GWIACC-CHE (HP)	Very low hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low hazard	LH	Triangular	[0, 0.2, 0.4]

	Medium hazard	**MH**	**Triangular**	**[0.2, 0.4, 0.6]**
	High hazard	**HH**	**Triangular**	**[0.4, 0.6, 0.8]**
	Very high hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely high hazard	EHH	Triangular	[0.8, 1, 1.2]

Table B.2: Fuzzy IF-THEN rules for GWIacc-che

	IF (GWIacc-che)					
	VLGWI	LGWI	**MGWI**	**HGWI**	VHGWI	EHGWI
THEN (GWIACC-CHE (HP))	VLH	LH	**MH**	**HH**	VHH	EHH

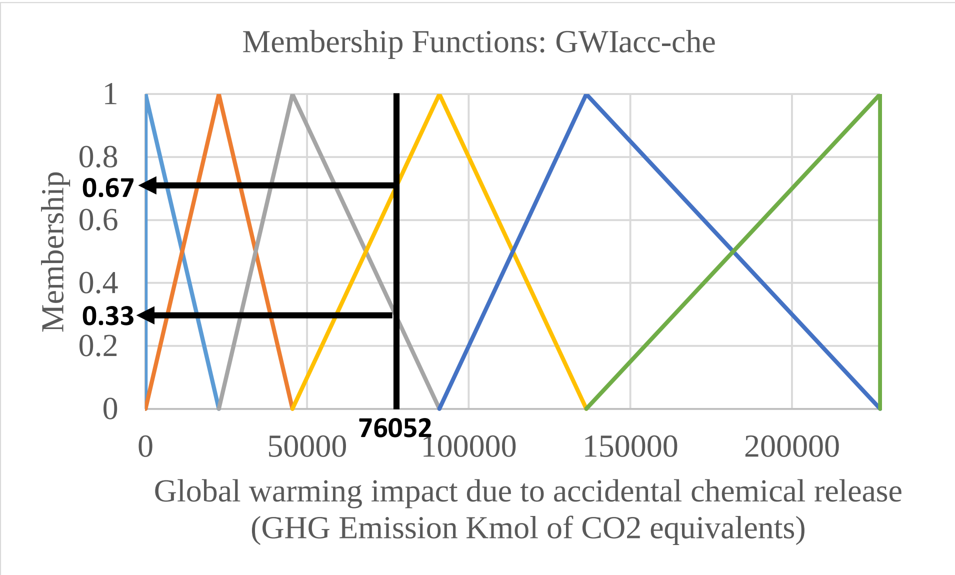

Figure B.1: Input memberships of GWIacc-che

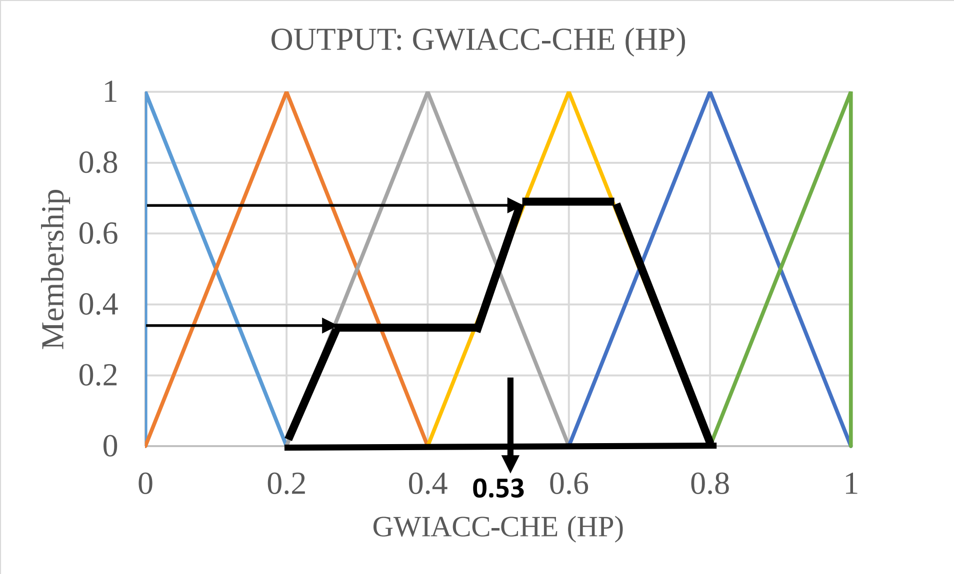

Figure B.2: Output memberships of GWIacc-che

Appendix B.2

Hazard potential calculation for intermediate parameters (pair wise comparison)

Table B.3: Fuzzy sets and shapes of input and output memberships for ENVACC

Inputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy sets**
ENVCHE (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.8]
	Low Hazard Potential	LH	Triangular	[0, 0.8, 1.6]
	Medium Hazard Potential	MH	Triangular	[0.8, 1.6, 2.4]
	High Hazard Potential	HH	Triangular	[1.6, 2.4, 3.2]
	Very High Hazard Potential	VHH	Triangular	[2.4, 3.2, 4]
	Extremely High Hazard Potential	EHH	Triangular	[3.2, 4, 4]
ENVFIRE (HP)	Very Low Hazard Potential	VLH	Triangular	[0, 0, 0.2]
	Low Hazard Potential	LH	Triangular	[0, 0.2, 0.4]
	Medium Hazard Potential	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard Potential	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard Potential	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard Potential	EHH	Triangular	[0.8, 1, 1]
Outputs	**Linguistic Description**	**Abbreviation**	**Shape**	**Fuzzy sets**
ENVACC (HP)	Very Low Hazard	VLH	Triangular	[-0.2, 0, 0.2]
	Low Hazard	LH	Triangular	[0, 0.2, 0.4]

	Medium Hazard	MH	Triangular	[0.2, 0.4, 0.6]
	High Hazard	HH	Triangular	[0.4, 0.6, 0.8]
	Very High Hazard	VHH	Triangular	[0.6, 0.8, 1]
	Extremely High Hazard	EHH	Triangular	[0.8, 1, 1.2]

IF-THEN rules

The IF-THEN rules for environment impact due to accidental release (ENVACC) represent the relationship between ENVCHE, ENVFIRE and ENVACC.

The general rule is: IF ("ENVCHE" is ___) AND ("ENVFIRE" is ___) THEN ("Hazard due to ENVACC" is ___).

The rules constructed for this aggregation are given in Table 3.32.

An example for an operation is: IF ("ENVCHE" is very low) AND ("ENVFIRE" is very low) THEN ("Hazard due to ENVACC" is very low).

Table B.4: Fuzzy IF-THEN rules for ENVACC

THEN (ENVACC (HP))		IF (ENVFIRE)					
		VLH	LH	MH	HH	VHH	EHH
AND (ENVCHE)	VLH	VLH	VLH	VLH	LH	MH	MH
	LH	VLH	VLH	LH	MH	MH	HH
	MH	VLH	LH	MH	MH	HH	VH
	HH	LH	MH	MH	HH	VH	EHH
	VHH	MH	MH	HH	VH	EHH	EHH
	EHH	MH	HH	VH	EHH	EHH	EHH

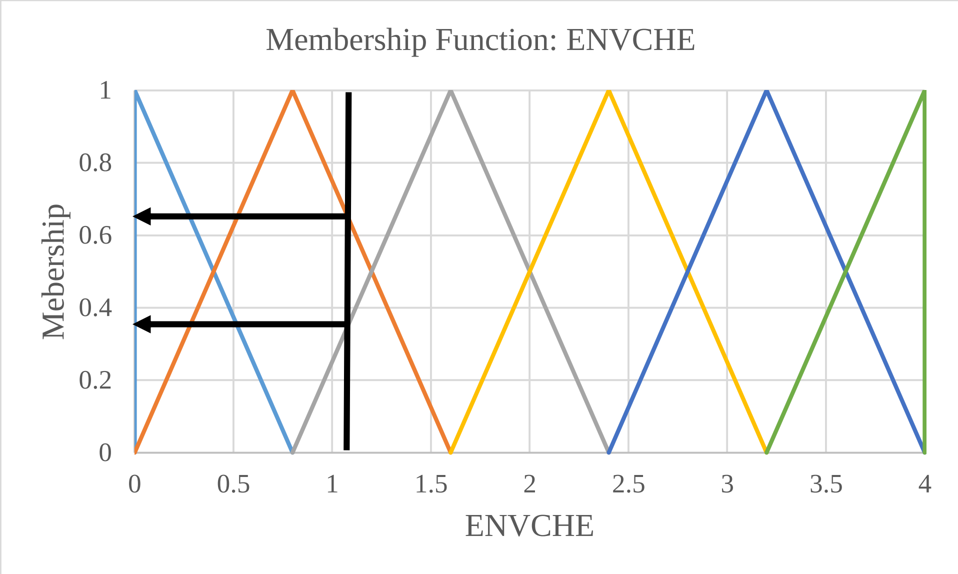

Figure B.3: Input membership for ENVCHE

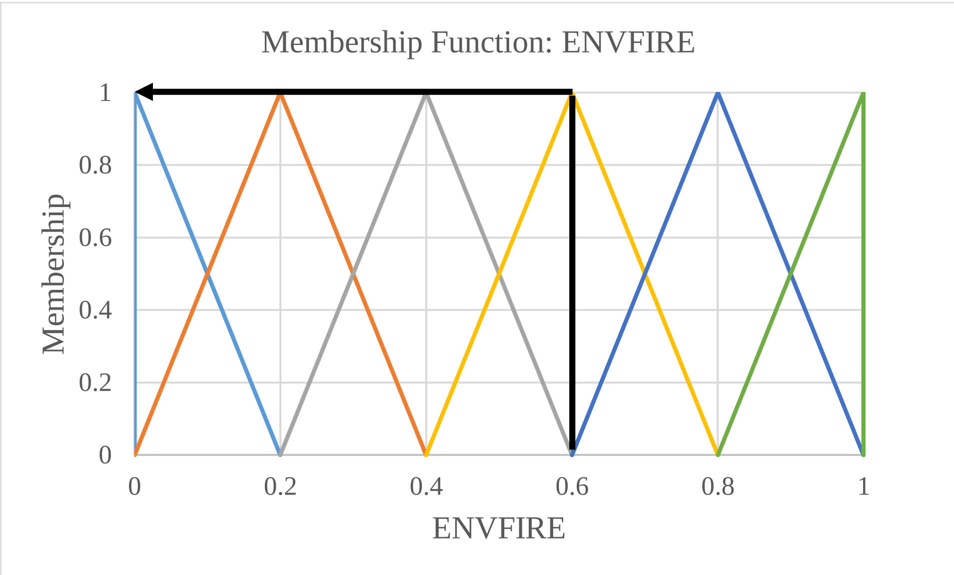

Figure B.4: Input membership for ENVFIRE

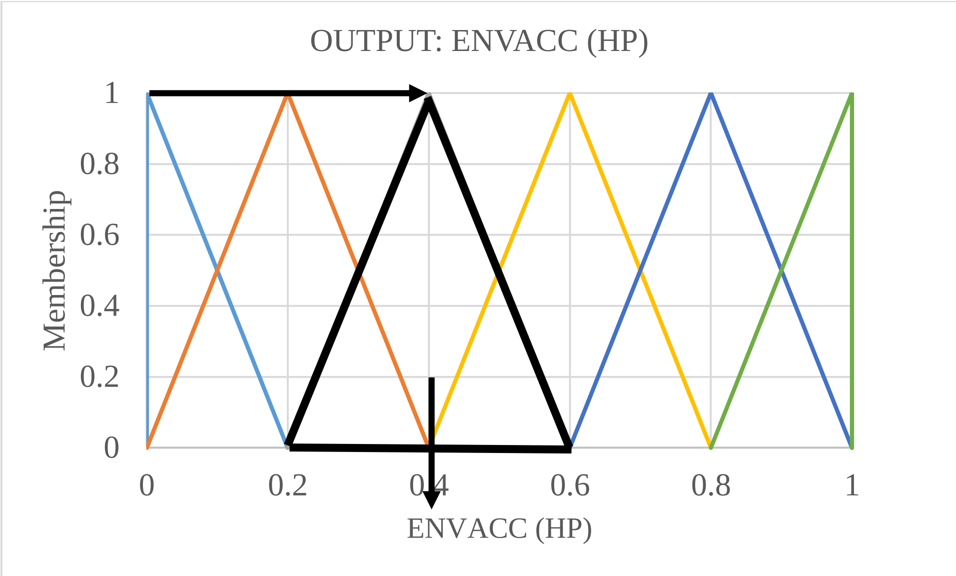

Figure B.5: Output membership for ENVACC