APPLICATIONS OF DYNAMIC SIMULATIONS IN THE PROCESS INDUSTRIES – A SAFETY CASE STUDY USING TEXAS CITY REFINERY EXPLOSION

by

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Abstract

Although process safety performance in petroleum refineries is much better today compared to several decades ago, major accidents still occur occasionally. The explosion and fires at Texas City refinery on 23 March 2005 is regarded as one of the worst industrial accidents in US history to date. Dynamic process simulation provides an effective means to collect, collate and analyze data from previous incidents and offer recommendations of good practice to further improve process safety outcomes.

A simulation of the sequence of events that led to the catastrophic explosions at Texas City refinery is presented in Aspen HYSYS. An initial steady state simulation of the operation of the raffinate splitter column at Texas City forms the basis for a subsequent dynamic simulation of the filling of the distillation column from 0213hrs until 1313hrs when the explosion occurred. A PID (proportional, integral, derivative) control scheme is implemented with appropriate tuning parameters.

The dynamic simulation of the overall tower filling dynamics from 1000hrs to 1320hrs when the explosion occurred revealed that the feed to the column vaporised at approximately 1310 hrs. This happened as a result of the additional heat input into the column through the feed-product heat exchanger. Subsequently, thermal expansion of the liquid in the column led to the filling of the overhead vapour line with hydrocarbon liquids and an increase in pressure as a result of the hydrostatic liquid head. Flammable hydrocarbon vapours subsequently flowed from the overhead line through the collection headers into the blowdown drum. An alternative accident pathway is presented as the basis for a quantitative hazard and operability study, HAZOP.

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My wife and lover Ufuoma has been an amazing pillar of support for the past 5 years. I often wonder how you manage to juggle being a wife, mother and employee and still have it all together. I am becoming a better man because of you.

Learning more about God's grace in the past months made me realize this could not have been possible apart from Him.

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List of Abbreviations

CBI	Chicago Bridge and Iron Co.
CDU	Crude Distillation Unit
CFD	Computational Fluid Dynamics
CSB	Chemical Safety Board (USA)
DCS	Distributed Control System
DOTS	Dynamic Operator Training Simulator
EOS	Equation of State
ETA	Event Tree Analysis
EYESIM	Immersive Virtual Reality Training System (Invensys)
FCCU	Fluid Catalytic Cracking Unit
FCV	Flow Control Valve
FIC	Flow Indicating Controller
HAZOP	Hazard and Operability Study
HSE	Health and Safety Executive (UK)
IChemE	Institution of Chemical Engineers (UK)
IEEE	Institute of Electrical and Electronic Engineers
ISOM Unit	Isomerisation Unit
LCV	Level Control Valve

LPG	Liquified Petroleum Gas
MOC	Management of Change
OTS	Operator Training Simulator
PFD	Process Flow Diagram
Pfd	Probability of Failure on Demand
PFS	Process Flowsheet
PHA	Process Hazard Analysis
PID	Proportional, Integral, Derivative
PR	Peng Robinson
PSSR	Pre Start-up Safety Review
SRK	Soave-Redlich-Kwong
VCE	Vapour Cloud Explosion
VDU	Vacuum Distillation Unit
VR	Virtual Reality

Chapter 1 Introduction

Dynamic process simulation has steadily become a mature tool for various applications in the process industries. Some areas where dynamic simulations are useful in the chemical process industries include process safety analysis, process design and optimisation, control systems design and operator training and competence assessment.

Failures in process plant equipment happen as a result of complex interactions of individual components that lead to loss of containment incidents which could have catastrophic consequences. Although protection barriers are usually in place to prevent or mitigate the effects of process safety incidents, they may not always function as intended on demand. Process safety analysis helps to identify weak points in a plants protection barriers in order to propose improved risk reduction measures. Dynamic process simulation offers extensive capabilities for such process safety analysis (Rizal *et al*. 2006).

Dynamic process simulations are used in training operators of capital intensive and safety critical equipment used in oil and gas production platforms, refineries, power stations, and nuclear reactors (Chatterjee, 2004). The increase in the use of dynamic process simulators (also called Operator Training Simulators, OTS) can be attributed to advances in computer speed, programming methods and human machine interfaces. These advances have made possible the development of robust, effective, and relatively inexpensive simulation models for operator training. The development of high fidelity simulators that closely match actual operating conditions in a process plant has extended the application of such simulators for use in engineering design, control system configuration, safety analyses and operational support.

Process engineering operations often require engineers and plant operators to work in hazardous environments and operate complex equipment with very little or no margins for error. This usually limits the amount of training that can be carried out safely on site without posing serious risks to personnel, plant equipment or the environment. It is therefore necessary to design safe systems and environments to train process industry personnel. Operator Training Simulators provide the opportunity to expose personnel to hazardous situations in a safe, highly visual and interactive manner (Nasios, 2002).

Dynamic process simulations can be used to teach chemical engineering concepts, from basic principles such as mass balancing, compression and heat exchange principles, to advanced process control concepts such as controller tuning. It can also be used to train process operators on routine operations such as plant start-up and shut-down and emergency response training. Dynamic process simulations can be used to develop and verify reliable, safe and effective operating procedures before the actual plant becomes available (Berruti, 2009). Dynamic simulators are used during the commissioning phases to verify control and safety logic, pre-tune instrumentation, and train process operations personnel. After the plant comes on line and normal operations begin, the simulator is used to improve everyday operations through testing, validating and instructing operators in basic good operating practices and optimisation theories, for anticipating upcoming production changes, and testing various operating scenarios. Dynamic process simulation is thus a relevant tool for improving safety and increasing asset operability, reliability and profitability in various process industries.

The dwindling numbers of experienced engineers and operators is a major source of concern for operating companies. There is also a constant emphasis on safe operations, and the ability to manage safety critical incidents. Furthermore, the increased prevalence of ageing installations and equipment mean reduced reliabilities and increase in the potential for major accident hazards that could harm people, assets or the environment. Lastly, improvements in standard of living for millions of citizens in developing countries necessitate the consumption of more energy. Arguably, this energy has to come from a variety of sources. One of these sources will undoubtedly be unconventional hydrocarbon sources.

The processing and refining of heavy crude oil from unconventional sources presents special challenges for refiners. It is therefore pertinent to devise innovative technologies that will re-tool experienced operators, train new engineers and operators, and ensure that operations are carried out in a safe manner to protect assets and people, and comply with stringent regulatory standards. Dynamic process simulation provides extensive capabilities for addressing these challenges.

There is therefore an opportunity to find innovative ways of using dynamic process simulations and simulators to address the needs identified above. This research effort will further explore the applications of process simulations with a major focus on using dynamic simulations for process safety analysis.

1.1 Safety in Refinery Operations

Petroleum refineries have evolved over the years into complex assets with many integrated units that produce different products. Maintaining safe operations and ensuring the safety of everyone in the refinery presents a huge challenge that refiners are always looking for innovative ways to address. There is a history of major accidents in oil and gas refineries with major financial losses and reputational damage (Schouwenaars, 2008). As a result, process safety has emerged as a disciplined framework for managing the integrity of operating systems and processes with large inventories of hazardous materials. Process safety relies on good design principles, and sound engineering and maintenance practises in order for it to be effective. While major incidents in the process industries is relatively rare, the industry cannot afford to rely on lessons from these alone. To strengthen layers of safety barriers and prevent major incidents from occurring at all, it is necessary to collect, collate and analyse data from previous incidents. Dynamic process simulations offer one such tool for data analysis and recommendation of good practice in the industry.

1.2 Key Refinery Operations

Petroleum refineries are huge, capital intensive manufacturing facilities with many complex processes. Typically, they convert raw crude into a variety of products including Liquefied Petroleum Gas (LPG), gasoline, kerosene, jet fuel, diesel, lubricating oils, and asphalt. It is estimated that over 660 refineries in 116 countries are currently in operation, producing more than 85 million barrels of refined products each day.

A simplified process flow diagram of a typical refinery is shown in figure 1.1. The main unit operations that take place in a refinery are summarized below.

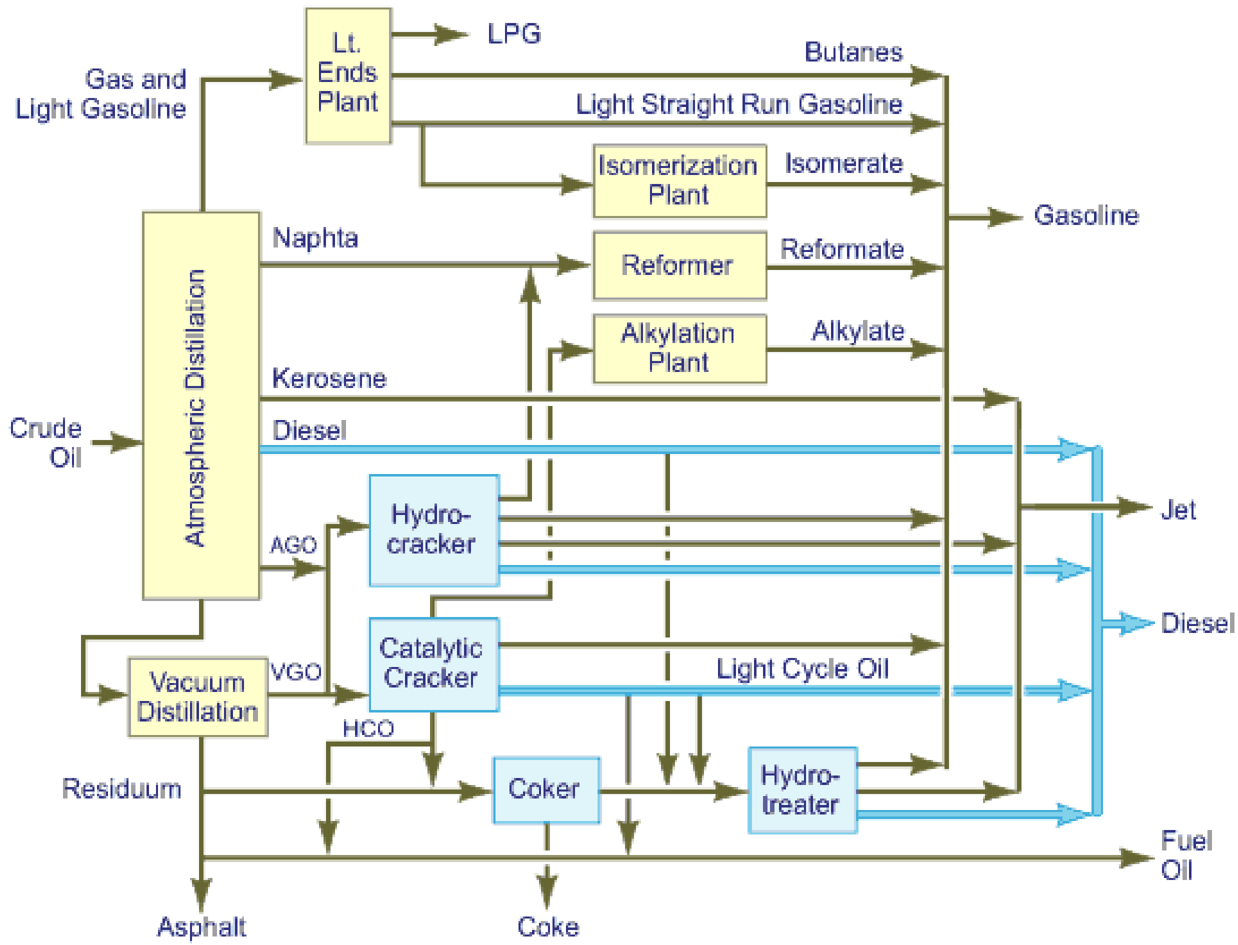


Figure 1.1 Simplified Refinery Process Flow Diagram (OSHA Technical Manual, 1999)

1.2.1 Raw Crude and Refined Products Storage

The crude storage area is designed to hold the many barrels of crude oil that are supplied to a refinery from pipeline, ship or barge. These tanks hold the crude oil until it is sent to the process units for upgrading into refined products that meet customer and government specifications. The crude storage area is necessary for any refinery to maintain a constant supply of crude oil to the process units and maximize production.

There are many different types of tanks available to store crude oil and refined products. Some products require storage at low temperatures, so they are stored in refrigerated tanks. Other highly volatile products, which could easily evaporate, are stored in spherical pressure vessels. To minimize environmental risks and maximize safety, the design of the tank must take into account the properties of the stored liquid. Crude oil is generally stored in flat bottom tanks in a refinery. Most flat bottom tanks are constructed out of steel plates that are formed into shape and welded together. One type of flat bottom tank has a fixed roof which is a stationary roof welded into place on top of the tank.

Besides fixed roofs, some flat bottom tanks have a floating roof, which means the roof of the tank moves up and down as the amount of liquid in the tank changes. Since there is no vapor space between the crude oil and the roof (except at very low liquid levels), evaporation effects are greatly reduced as well as the potential fire hazards (adapted from CBI Virtual Refinery, 2009).

1.2.2 Distillation (atmospheric and vacuum)

The atmospheric Crude Distillation Unit (CDU) is the first major processing unit in an oil refinery. Typically, all the crude oil entering a refinery passes through this unit, where it is distilled into different components, called fractions or cuts, based on their boiling points. These cuts are then routed to other parts of the refinery.

Before distillation, the crude oil first enters a desalter, where water, inorganic salts, trace metals and other impurities are removed. The desalted crude feedstock is then heated to temperatures ranging from 343°C to 399°C and fed into a distillation or fractionation column, also called a tower. All but the heaviest fractions flash into vapor, which rises in the tower, cooling as it goes up. Heavy fuel oil and asphalt residuals are drawn from the bottom of the tower, while other major products are drawn off the tower at successively higher points, including lubricating oil, heating oil, kerosene, gasoline and uncondensed gases. These cuts are subsequently routed to other parts of the refinery for additional processing or blending.

A Vacuum Distillation Unit (VDU) is often used to further refine heavy residuals after atmospheric distillation. The vacuum distillation unit relies on the same principle as the atmospheric unit but employs a vacuum so the heavy components will boil at lower temperatures. Both atmospheric and vacuum distillations are conducted at temperatures to avoid overly damaging the crude oil by cracking or coking. The heaviest cuts often are sent to a delayed coking unit for further processing (adapted from CBI Virtual Refinery, 2009).

1.2.3 Delayed Coking

A delayed coking unit uses a process called thermal cracking to convert heavy residuals or bottoms into lighter, higher-valued products such as naphtha and diesel fuel, leaving behind petroleum coke as a residual product. Cracking works by breaking complex hydrocarbon compounds into smaller molecules. Heavy residual oils from the atmospheric and vacuum distillation columns are heated in a furnace to approximately 448°C and then transferred to a large cylindrical vessel called a coke drum. Gas oil and lighter components separate from the liquid in a vapor phase, which is directed to a fractionation column where the fractions are drawn off. The liquid products are then routed to the hydrotreater or hydrocracker for further processing.

The uncracked residual liquids that remain in the drum eventually form petroleum coke, a solid carbon material. After water quenching, the top and bottom heads of the full coke drum are removed, and the coke is removed from the drum using mechanical or hydraulic methods. Typically, coke drums operate in pairs so that one is filling while the other is being opened and decoked. Petroleum coke can be used as a fuel and for the manufacture of electrodes, graphites and carbides (adapted from CBI Virtual Refinery, 2009).

1.2.4 Hydrocracking

Hydrocracking is a process that combines catalytic cracking in the presence of hydrogen. It uses high pressure, high temperature, a catalyst and hydrogen to crack heavier feedstocks into lighter, more valuable products, including diesel and jet fuels, as well as naphtha for gasoline blending. Products resulting from hydrocracking are nearly free of contaminants, as the process removes sulfur, nitrogen, oxygen and metals.

Hydrocracking is often a two-stage process. Feedstock is mixed with hydrogen, heated and sent to a reactor vessel, where fixed-bed catalysts convert sulfur and nitrogen compounds and limited cracking occurs. The hydrocarbon product is then cooled and partially condensed and sent to a separator, where the hydrogen is separated and recycled to the feedstock and the liquid is charged to a fractionation column. High-value fractions are drawn off and the bottoms are returned to a second reactor for further cracking under higher temperatures and pressures. Like the first stage, the second-stage product is separated from the hydrogen and charged to the fractionator.

In addition to the liquid product, hydrocracking yields light gases that can be used as fuel for the refinery or as petrochemical feedstocks. With heavier feedstocks, hydrocracking can improve the properties such that they become base lubricants. Other hydrocrackers deal with very heavy components, like bitumen, which can contaminate the catalyst, requiring regular regeneration of the valuable catalyst (adapted from CBI Virtual Refinery, 2009).

1.2.5 Fluid Catalytic Cracking

A Fluid Catalytic Cracking Unit (FCCU) upgrades heavy distillates from the crude distillation unit into lighter, higher-valued products such as high octane gasoline, light fuel oils and liquefied petroleum gas. It is one of the most widely used processes for increasing the ratio of light to heavy products from a refinery. A catalyst is a material that assists a chemical reaction but is not itself chemically changed. Catalysts used in refinery cracking units are typically solid materials, such as silica, alumina, clay and zeolites, that come in the form of powder, beads or pellets.

The FCCU uses a catalyst in the form of a very fine powder which flows like a liquid. Heavy feedstock from the CDU or the delayed coker is preheated and sprayed into the base of a vertical sloped pipe called a riser where it contacts extremely hot fluidized catalyst at 666°C to 760°C. The hot catalyst vaporizes the feed and facilitates the cracking reactions that break down the heavy hydrocarbons into lighter components. The catalyst/hydrocarbon mixture flows through the riser and then is separated by cyclones in a reactor separation vessel. The hydrocarbon stream is then routed to a fractionating column for separation into lighter products such as LPG, gasoline, light gas oil and heavy gas oil.

The used catalyst is sent to a stripper where it is contacted by steam to remove any remaining hydrocarbons and then to a regenerator, where the combustion residue is burned off and catalyst activity is restored. The regenerated catalyst then flows to the base of the riser, and the cycle is repeated. Since the catalyst is always flowing and is subjected to extreme temperatures, it may be damaged. Much of the process attempts to trap any catalyst from escaping the reactor/regenerator and recovering the valuable material (adapted from CBI Virtual Refinery, 2009).

1.2.6 Naphtha Hydrotreating

Hydrotreating, also known as hydrodesulfurization, is a process that removes contaminants such as sulfur, nitrogen, oxygen and metals from liquid petroleum fractions. As the fractions move through a refinery, these impurities can damage equipment, catalysts and the quality of the finished products. In addition, to improve air quality, many countries have imposed limits on the amount of sulfur in transportation fuels, and hydrotreating enables refiners to make products meeting these requirements. Hydrotreating also converts some hydrocarbons to saturated compounds, which can change certain properties.

Hydrotreating takes place under high pressure and temperature conditions with catalyst and hydrogen present. Pressurized feedstock is combined with hydrogen-rich gas, heated to the point of vaporization, and then passed through a fixed-bed of catalyst where several reactions occur: hydrogen combines with sulfur to form hydrogen sulfide, nitrogen compounds are converted to ammonia, any metals in the feedstock may be deposited on the catalyst, and saturated hydrocarbons are created. After cooling, the liquid/gas mixture is separated, and the hydrogen sulfide gas is routed to the sulfur recovery plant for further processing. The desulfurized liquid products are blended or used as feedstock for downstream processes like the catalytic reformer and FCCU. In addition to removing sulfur from gasoline and diesel fuel, hydrotreating can be used to improve the burning characteristics of middle distillates such as kerosene (adapted from CBI Virtual Refinery, 2009).

1.2.7 Catalytic Reforming

Catalytic reforming is a process that converts low-octane naphthas into high-octane gasoline blending components called reformates. Reforming also produces high-purity hydrogen that can be used for hydrotreating and other refining processes.

The reforming process literally reshapes, or reforms, the molecules in the feedstock in the presence of hydrogen and a catalyst that contains platinum and often another noble metal such as rhenium. The reaction requires a continuous supply of process heat to maintain reaction temperature in the catalyst beds, so the process is usually done with three or more reactors in series with furnaces in between. The naphtha feedstock, sourced from the crude distillation unit and the hydrotreater, is mixed with hydrogen, vaporized and passed through an alternating series of furnaces and reactors. The liquid-gas mixture from the final reactor is cooled and sent to a separator to remove the hydrogen gas. The liquid product from the bottom of the separator is sent to a fractionating column where reformate is drawn from the bottom and light ends from the top are sent to the refinery's saturate gas plant.

Since the catalyst is very expensive, the process conditions are carefully controlled and catalyst is often regenerated before it suffers much damage (adapted from CBI Virtual Refinery, 2009).

1.2.8 Hydrogen Plant

In many large refineries, high-purity hydrogen is required for the hydrocracking and hydrotreating operations. Hydrogen is produced as a by-product of several refinery processes, especially catalytic reforming, but this is often not enough to meet the total refinery demand. As a result, hydrogen must either be manufactured on site or acquired from external sources.

For those refineries that manufacture hydrogen on site, the most common process used to produce hydrogen is steam methane reforming. In this process, a gaseous hydrocarbon feedstock -- often natural gas or methane -- is pretreated for sulfur removal, mixed with steam and introduced to a reforming furnace, where it passes through tubes containing a nickel based catalyst. The reformed gas, which now consists of steam, hydrogen, carbon monoxide and carbon dioxide, is cooled and then passed through a shift converter containing an iron catalyst. Here, the carbon monoxide generated in the reformer is converted with the addition of steam to carbon dioxide and more hydrogen. The effluent from the shift converter goes next to a pressure swing adsorption unit, where carbon oxides and water are removed and high-purity hydrogen is the final product (adapted from CBI Virtual Refinery, 2009).

1.2.9 Sulphur Recovery

Crude oil can contain anywhere from 1% to 5% sulfur by weight, typically with sulfur imbedded in large complex molecules. This sulfur can be released during distillation, cracking, coking and hydrotreating processes. In addition, all of the combustion units in a refinery, such as boilers and furnaces, will produce sulfur dioxide if there is sulfur in the fuel. Also, many of the water streams throughout the refinery contain sulfur compounds that must be removed prior to discharge. The sulfur recovery facilities in a refinery are used to remove sulfur compounds from these liquid and gas streams.

Most sulfur recovery facilities include units for gas and liquids treating, sour water treating, sulfur recovery, tail gas treating and incineration. Removal of hydrogen sulfide from hydrocarbon streams is typically achieved by absorption using a solvent, or amine. Hydrogen sulfide and other acid gases from the amine treating unit are sent to the sulfur recovery unit. The sour water treating unit, which usually includes a sour water stripper, removes hydrogen sulfide, ammonia and other contaminants from various sour water streams using steam. The sour gas is sent to the sulfur recovery unit and the stripped sour water is sent to the water treatment plant.

The sulfur recovery unit converts hydrogen sulfide to elemental sulfur using both thermal and catalytic conversion reactions in what is known as the Claus process. Ammonia in the sour gas is destroyed as well. Effluent gas from the sulfur recovery unit is sent to the tail gas treating unit, where nearly all of the remaining sulfur is recovered. Any residual sulfur-containing gases are sent to a thermal incineration unit, where all sulfur species are converted to allowable limits of sulfur dioxide before release to the atmosphere. Since sulfur emission standards are very strict, the sulfur recovery processes must be very reliable and are sometimes configured with redundant units to make sure plant operations are not disrupted (adapted from CBI Virtual Refinery, 2009).

1.2.10 Product Blending

The product blending area in a refinery is where the product streams from various process units, and appropriate additives, are mixed together to provide fuels that meet customer and government specifications. This area includes short-term storage capacity and facilities for bulk loading of products to trucks, barges, ship or railcars for transportation.

With more and more specialized fuel blends that are required to meet environmental mandates or to accommodate seasonal temperature variations, the blending and storage area has become an increasingly important part of the refinery. Many refineries use sophisticated monitoring and control systems as part of their blending operation. In addition to storing finished products after blending, refineries use flat-bottom tanks to store the raw crude oil coming in to the refinery for processing. Also, refineries generally have facilities for storing intermediate stocks or unfinished material. Intermediate storage allows the refinery to run more smoothly and provides emergency storage for upsets (adapted from CBI Virtual Refinery, 2009).

1.3 Research objectives

The objectives of this research are to:

I. Develop a steady state simulation model of a refinery distillation unit operation using the commercial simulation tool Aspen HYSYS

II. Develop a dynamic simulation model of a refinery distillation unit operation using the steady state simulation developed in (i)

III. Implement a control scheme for the dynamic simulation using proportional, integral and derivative (PID) control philosophy

IV. Use Texas City refinery explosion as a case study for quantitative HAZOP

1.4 Thesis structure

This report has been organised in an orderly manner with each new chapter following on from the previous one.

Chapter 1offers an introduction to dynamic simulations and the safety issues that remain in modern refinery operations. The main unit operations that take place in a refinery are summarised using a simplified process flow diagram.

In chapter 2, a literature review is carried out on the various uses of dynamic process simulations in the chemical process industries. A theoretical framework of the main applications of dynamic process simulations is developed.

Chapter 3 presents a description of Texas City Refinery and the isomerisation distillation unit operation used as the basis for the safety case study presented in this report. A summary of the contributory factors that led to the incident is presented.

Chapter 4 presents a process simulation of the sequence of events that led to the catastrophic explosion that took place at Texas City Refinery on March 23, 2005. A process control scheme is implemented and a discussion of the simulation results is presented. The initial dynamic simulation is used as the basis for a subsequent quantitative HAZOP study.

The main conclusions from this study are presented in Chapter 5 and suggestions for future research work are made.

Chapter 2 Literature review

A literature survey was carried out to ascertain the current state of knowledge on the use of dynamic process simulations and simulators for safety and reliability analyses in refineries, and for other applications. The strategy involved searching for articles in peer-reviewed journals using electronic databases in the Hull University LibGuides for Engineering. These databases include Web of Science, Scopus, and Science Direct. Some articles were also found using Google Scholar, Institute of Electrical and Electronics Engineers (IEEE) Xplore. The engineering database Knovel was used to access electronic textbooks. There was no deliberate attempt to restrict the search results to a particular period or number of years.

Keywords and phrases used include dynamic process simulations and simulators and the related term Operator Training Simulators, plus searching within the results of the aforementioned searches for heavy oil processing, refinery safety and reliability analysis. This literature survey will continue throughout the course of this research work with the aim of developing a conceptual framework through synthesis and a thorough critique of the literature. This will involve identifying seminal papers and key authors who have made significant contributions, and looking through the list of references in key papers to identify significant papers for further study and inclusion.

The papers in this review were categorised into six groups based on the overarching theme addressed in each article, as follows:

1. The development of dynamic simulation models to different levels of rigour and fidelity
2. Use of dynamic process simulations for hazard identification and risk analysis

3. Dynamic simulations used primarily for operator training purposes (Operator Training Simulators, OTS)
4. Dynamic simulations used for engineering applications such as process control philosophy, optimisation studies, process design verification for new builds and retrofits
5. Operator Training Simulators that incorporate 3D virtual reality (VR) simulations
6. Applications of dynamic process simulators for reliability studies

The above groups and their key features are depicted in a theoretical framework (figure 2.1) that will form the basis of an extended literature review in the course of this research work.

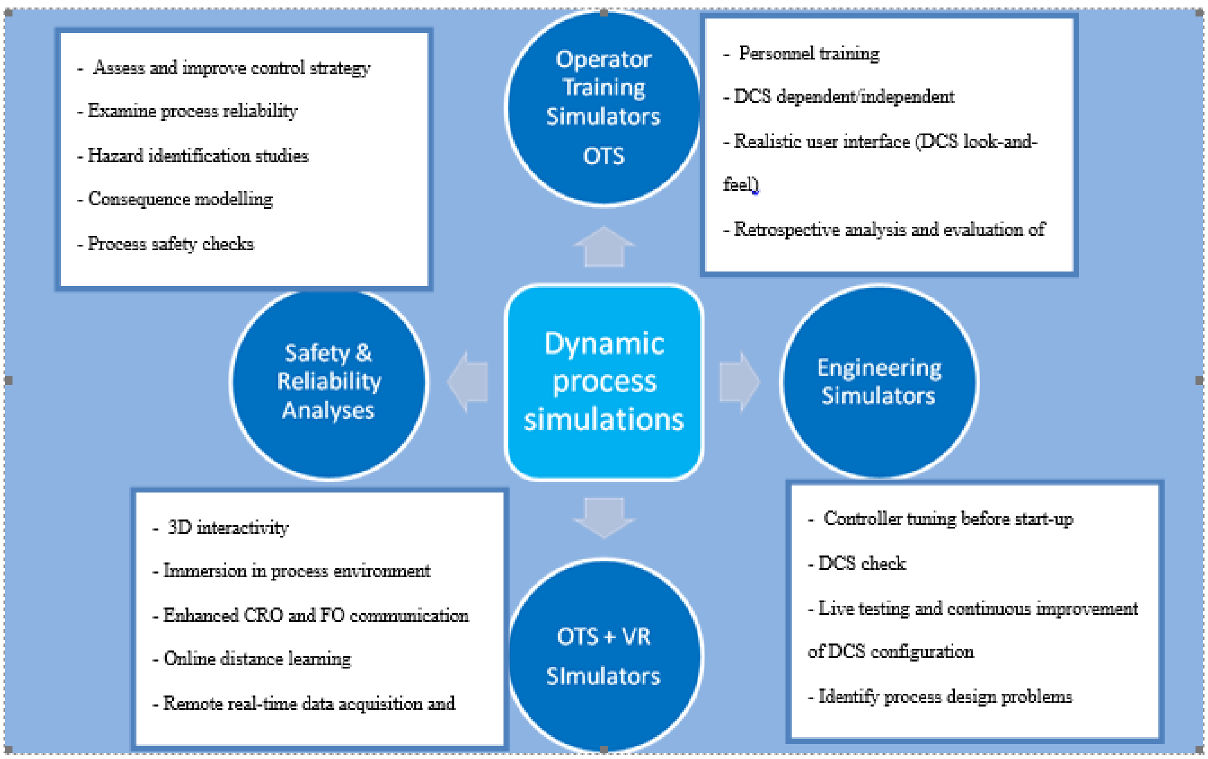


Figure 2.1 A theoretical framework for dynamic process simulations

2.1 Use of dynamic process simulations for hazard identification and risk analysis

In the last two decades, dynamic process simulations have increasingly become a mature tool for various process industry applications. This has facilitated the use of dynamic simulations for safety-related studies. This may be attributed to the increased legislative requirements and tough safety measures imposed by regulatory bodies charged with oversight for public safety. Incidents like Bhopal, Buncefield, Seveso and several others have increased the public's perception of risk associated with the chemical process industries. There is therefore increased emphasis on safety, and the use of sophisticated and complex systems to ensure asset and life protection.

One of the earliest demonstrations of the application of dynamic process simulations for hazard identification studies is that of Graf and Schmidt-Traub (1999) and Eizenberg et al. (2006). Although hazard and operability study (HAZOP) is widely regarded as a qualitative hazard identification procedure, Eizenberg et al. (2006) presented a method called "quantitative HAZOP" for identifying hazards in a batch process reactor. The main usefulness of the model, according to Eizenberg and his fellow researchers, is for the purpose of incorporating a strong safety orientation in chemical engineering undergraduate education. This approach is extremely valuable as regulatory pressures demand safer designs including the concepts of inherently safe design which can be identified using HAZOPS and other process safety analyses procedures.

The work of Eizenberg et al.(2006) is further extended by the contribution of Ramzan et al. (2007). Ramzan and his fellow workers demonstrated the use of commercial simulation software, Aspen Dynamics, for safety and reliability analyses. Their seminal work included a hazard and operability study (HAZOP) and event tree analysis (ETA) to troubleshoot operational failures in a distillation column. An important finding from this study was the observation that it is possible to increase the reliability of safety critical elements by reducing the probability of failure on demand (pfd) from 0.55 per annum to 0.00043 per annum.

The use of dynamic process simulations for incident investigation is presented by Manca and Brambilla (2012). Utilising rigorous process modelling in the commercial simulation package UNISIM, Manca and Brambilla (2012) developed a dynamic simulation of the events that led to the BP Texas city refinery accident on 23 March 2005. The report found loopholes in the sequence of events which led to the incident as reported previously by the US Chemical Safety Board. This application of dynamic process simulation provides further evidence of the applicability of such simulations, not only for identifying hazardous scenarios but also for root cause analysis (RCA) and accident investigations.

Tauseef et al. (2011) demonstrated the use of computational fluid dynamics (CFD) to successfully simulate a vapour cloud explosion (VCE) in a refinery Liquefied Petroleum Gas (LPG) tank farm. This consequence modelling approach using CFD or similar tools to quantify the risk resulting from the loss of containment of hazardous material in high hazard industries is a legislative requirement in the UK, and therefore merits further investigation in this research work, subject to the constraints of time and resources. A cursory overview of the applications of dynamic Operator Training Simulators in improving profits, safety and reliability in the process industries is presented by Guddeti et al. (2010). Gudetti et al. argue that in contrast to routine simulation packages, licensor developed OTS packages offer higher fidelities and better customisability to actual plant requirements, and may thus provide major additional benefits beyond operator training.

An extremely valuable account of the use of dynamic process simulation for safety, reliability and asset life cycle analyses applied to a refinery distillation unit is presented by Ramzan and Witt (2007). Their analysis provides a detailed account of a merged process based on multi-objective decision analysis technique (Promethee), extended HAZOP, reliability modelling, and life-cycle related cost modelling. Ramzan and Witt (2007) contend that because of the interconnectedness of the methodologies used in the process industries for safety analysis and reliability analysis, additional benefits may be obtained from merging both analyses, including better design and operation, and better cost benefit considerations when considering recommendations for protecting people and assets. Some of the combined methods for safety and reliability analyses include hazard and operability studies (HAZOP, What-if / Checklist analysis, failure modes, effects and criticality analysis, fault tree analysis, event tree analysis, master logic diagrams and reliability centred maintenance).

A novel application of dynamic process simulators for improved safety in chemical process plants is discussed by Nakaya et al. (2006). The online tracking simulator may be used for remote plant maintenance, predict future plant states by increasing simulation speed, and effectively reduce the stress and workload of field operators. Nakaya et al., however, failed to provide convincing evidence of the real-world applicability of their online simulation model. The case study presented in their paper applied to a simple heat exchanger and there are plans to extend the applicability of the model to more complex practical process systems.

2.2 Dynamic simulations used primarily for operator training

One of the earliest accounts giving a detailed description of the development and deployment of a dynamic process simulation for operator training is that given by Parmenter and Warshawsky (1981). In this major work which provided a pattern that has since been adopted in many OTS applications in the process industries, the authors describe a process simulator comprising a trainee console, instructor console, process control computer, and a programmer console. The simulation progamme, written in Fortran, is demonstrated by the regulation of simple airflow to a cooler compartment.

Since the initial work of Parmenter and Warshawsky (1981), several descriptions of the application of dynamic process simulators for training process industry operators have been given in the academic literature (Jones, 1992; Hotblack, 1992; and Dixon, 1992). Jones (1992) points out that the origin of training simulators can be traced to its use in the aircraft industries. Jones (1992) further lists the four major components of a training simulator as follows:

- The simulation platform comprising the hardware and software used to execute the model
- Actual models to represent plant equipment and control systems
- Human machine interface for interaction with trainee operators, and
- An instructor console with which the instructor or engineer conducts training sessions or implements model modifications

Furthermore**,** Operator Training Simulators can be configured in two ways. In an emulation configuration, the functions and features of an actual DCS are replicated with the simulator station “looking and feeling” like an actual DCS, but driven by a completely different software.

A link configuration, on the other hand, uses a plant's actual DCS software and hardware to provide the operator interface. This link configuration may use the actual control algorithms of the actual DCS or may be provided with a different process model (Jones, 1992).

Operator Training Simulations find useful applications in various process industry operations such as offshore and onshore production facilities, ethylene plants, catalytic cracking units, and ammonia plants, to mention a few. Most high fidelity simulators are deployed during the construction phase of a new plant, or when major equipment or control systems are installed during a plant turn-around. Jones' claim that simulators are not commonly used for existing plants, however, seems to contradict common practice today, although that may have been the case at the time of his writing. The following scenarios are suggested as those in which an OTS may be applied for operator training:

- Training to teach basic process operation and equipment operation principles
- Training operators to use DCS systems
- Bridging skills gap on plant operations during different operating conditions such as plant start-up and shut-downs
- Emergency and safety training to develop hazard identification skills
- Training on optimum operation strategies
- Refresher training to update skills throughout a plant's lifecycle

The development of a high fidelity dynamic simulation system for operator training using a commercial simulation package is presented in an article in Hydrocarbon Processing magazine (Harismiadis et al., 2011). The simulation models a diesel hydrotreating process from first principles and incorporates common unit operations such as compressor surge control and gas absorption columns. Some pre-configured operational upsets included in the model include loss of feed, steam failure, pump failure, and loss of fuel gas. The ability of operators to anticipate these problems and take the necessary corrective action is tested under high stress conditions. This research contradicts the claim by Jones that dynamic simulators may only be applied during the construction phase for new process plants. Harismiadis et al (2011) argue in this article that long production runs and a decrease in major process upsets dull operator competence and recommends that training simulators may be used to remedy this problem. Additionally, Ayral and De Jong (2013) present convincing evidence based on industry experience that OTS packages offer significant benefits when used in brownfield processing facilities. Some of these significant benefits include reduction in planned turnaround maintenance times, less abnormal situations and incidents arising from human error, improvements in advanced process control systems, and decreased repair costs for critical equipment. A real-world application of an OTS system for training process operators in a Greenfield refinery hydro-craking unit is presented in the account of Muravyev and Berutti (2007). The novelty in their approach involved the combination of a commercially available simulation package with high and medium fidelity modelling objects.

Worm et al. (2012) extended the application of dynamic process simulators for operator training in their research work. The research focuses on using simulators to enhance operator intervention in the slow process involved in drinking water purification. A pioneering dimension in the work of Worm et al. (2012) is the concept of a faster than real-time simulator. The researchers assert that the accelerated simulation training offers a faster and more accurate tracking of a target set-point compared to real time speed training (Guckenberger and Stanney, 1995). Accelerated simulation is also attributed with improvements in process performance, increased knowledge retention, and reduced stress in comparison to real-time simulation training.

> One problem associated with the acclaimed benefits of using dynamic process simulators for operator training is the difficulty in quantifying the benefits arising from their use. This assertion is corroborated by Hotblack (1992) in an account of his attempts to objectively quantify the benefits of OTS systems deployed in five BP sites in the UK. Using qualitative techniques, Hotblack identified savings of approximately £6m in lost production in one site and a payback time of less than one year in another site. It is therefore arguably safe to conclude that OTS packages deliver benefits to operating companies that use them.

2.3 Dynamic simulations for engineering studies

Another interesting dimension in the application of dynamic simulation models is the development of rigorous models for engineering studies in addition to operator training. Such rigorous models for refinery studies incorporate an array of algebraic and differential equations, with mass and energy balances for each tray, hydraulic pressure drop calculations and liquid and vapour flows. Olsen et al. (1997) implemented such a rigorous model for a distillation column which they claim was used for operator training and engineering investigations for a major hydrocarbon producing company in Norway. Olsen and his co-workers demonstrated that dynamic process simulations can be connected to actual DCS control systems for realistic operator training by connecting the distillation model to a Bailey Infi-90 DCS system. The DCS system used for engineering studies was an emulation of the actual system, probably to allow for more flexibility in engineering studies.

The use of dynamic process simulations for multiple purposes was also demonstrated by Takatsu et al. (2004) in their model of a refinery FCCU comprising a catalyst loaded reactor section and fractionation section. The assertion of the authors that their simulator offers tangible benefits throughout the plant's lifecycle for controller design, plant design and operations and operator training appears to have been vaguely corroborated by an economic optimisation study.

In recent times, there has been an increased interest in the use of dynamic process simulations for chemical engineering education in universities (Martin-Villalba et al., 2012; Komulainen et al., 2012; and Richmond and Chen, 2012). For example, Komulainen et al. (2012) describe the use of several simulation tools such as Matlab/Simulink, Aspen Plus, Aspen HYSYS to teach process control principles, distillation column principles, and biochemical engineering principles.

In summary, the following are some engineering benefits that may be obtained from dynamic process simulations:

- Validation of DCS control philosophy
- Design of process control strategies
- Detailed equipment operation validation, especially for pump and compressor performance and heat exchanger duty capacity.

2.4 Operator Training Simulators that incorporate 3D virtual reality (VR) simulations

In recent years, there has been an increasing trend to combine dynamic Operator Training Simulators with 3D virtual reality simulations for wider applicability. One of such innovative developments is the EYESIM Immersive Virtual Reality Training System created by Invensys. This simulator combines traditional Operator Training Simulators with VR gaming technology that emulates not only the hardware and software systems, but also the actual plant layout and DCS consoles. This offers an interactive 3D environment for training, testing, and process engineering simulation studies. Some of the benefits of the EYESIM trainer touted by Invensys include provision of a more realistic environment for trainees, fast and accurate reaction to high stress scenarios, improved performance of safety-critical tasks such as emergency shutdowns, and improved team training and communication. Although there are claims of up to 30 – 40% time savings for operator training and 1 – 3% savings in maintenance costs, one envisaged difficulty with this type of integrated simulation system is the reluctance of operating companies to commit the time and resources required to deploy such sophisticated packages. Another drawback may be that the increased complexity detracts from the usefulness of the system.

Although earlier reported instances of using VR technology for operator training (especially in electrical power systems) are available in literature (Okapuu-von Veh, et al. 1996; Goh et al., 1998), a recorded instance of research work on the development of an integrated process industry OTS systems that incorporate VR technology is reported by Manca et al. (2013) where a strategic training approach leading to increased safety and productivity is presented. One benefit of this system is the possibility to train both control room and field operators simultaneously. Manca and his co-workers (2013) pointed out additional benefits of an OTS over engineering simulators such as replication of actual control room environment, and the flexibility to speed-up or slow down the simulation based on the competence level of the trainee. Previous applications of VR and augmented reality are reported to have occurred in the military and in the construction industries. Figure 2.2 shows a typical VR environment for field operator training. An extended application of the integrated system involves its use in hazard identification and consequence analysis studies.

Figure 2.2 Operator training in a 3D virtual reality environment [Source: Virthualis company, www.virthualis.com]

Similarly, Yang et al. (2001) report the creation of a dynamic Operator Training Simulator (DOTS) that combines interactivity between field operators and control room operators. Yang et al. (2001) present detailed modelling procedures and parameters for various operational scenarios ranging from normal start-up and shut-down to emergency upset scenarios. The authors assert that the pseudo-dynamic DOTS simulator contributes to improved process safety as it allows operators to practise rare emergency scenarios and become better prepared to take corrective action to mitigate their consequences.

An interesting account of the combination of virtual reality and dynamic process simulation in a refinery model is given by Zhou et al. (2011). The authors postulate that this refinery model can assist researchers and key decision makers acquire information about production data, and gain an intuitive impression about refinery operations. Educational benefits include enhanced visualisation, exploration and interactivity with the refinery in a 3D learning environment and the possibility to use the VR refinery model for long distance online education.
An emerging area of interest in the development of dynamic process simulations is in heavy oil refining (Remesat, Young, and Svrcek, 2009; Mederos, Ancheyta, and Elizalde, 2012; Rodriguez, Elizalde, and Ancheyta, 2012). Today, rapid growth in emerging economies means an insatiable demand for energy from all available sources. This increase in demand has required refineries to upgrade heavy crude oils, such as bitumen sources and others, into synthetic crude oils. There is also an increasing trend towards processing heavier conventional crudes. Important refinery operations that are significantly important in processing heavy crude oil are delayed coking and hydrotreating operations. There is therefore an opportunity to develop simulation models for these operations, and extend the models for training, safety and reliability applications.

2.5 Conclusion

This literature review has demonstrated the various applications of dynamic process simulations to include operator training, engineering studies, safety analyses – including accident investigations and hazard identification. Although there is an increasing trend to combine dynamic Operator Training Simulators with virtual reality technology, there is insufficient evidence that this will become a mature application anytime soon. Lastly, dynamic simulations have been variously deployed for common refinery operations, especially CDUs, and for refinery operator training. There appears to be no evidence to show copious applications of dynamic Operator Training Simulators for the processing of heavy crude.

This research work will provide initial validation for the use of Aspen HYSYS for simulating process safety related incidents in refineries. This will be done by comparing simulation results from HYSYS with those available in the literature. This will form the basis for further safety studies.

Chapter 3 Texas City Refinery

Texas City refinery was one of BP's largest refineries where an explosion and subsequent fires took place on 23 March 2005. The refinery is located 30 miles south east of Houston and has a capacity of 10 million gallons of gasoline per day (38,000 m^3/day). In addition to gasoline, the refinery also produced jet fuels, diesel, and several chemical raw materials. The refinery had 29 oil refining sections and four units for chemicals production covering an area of about 5 square kilometres. At the time of the explosion in 2005, the company had a workforce of 1800 employees and 800 contractors (US Chemical Safety Board, 2005).

Texas City Refinery was built in 1934 but had not been maintained for several years. The refinery was the second largest refinery in Texas, and the third largest in the United States with an input capacity of 460,000 barrels (73,000 m3) per day as of January 1, 2000. BP acquired Texas City Refinery as part of its merger with Amoco in 1999 (Lyall, S. 2010).

3.1 Process Description

The isomerisation unit of the refinery where the incident occurred was installed in the mid-1980s to provide higher octane components for unleaded gasoline. The unit consists of 4 sections namely:

(i) Desulphuriser section

(ii) Reactor section

(iii) Vapour recovery and liquid recycle section

(iv) Raffinate splitter section

The purpose of the isomerisation unit was to convert straight chain normal C5 and C6 hydrocarbons to branched chain isomers with higher octane numbers. This improved hydrocarbon stream was blended with straight run gasoline to improve its octane rating or used as chemicals feedstock. The explosion and fires on March 23rd occurred in the Raffinate Splitter (US Chemical Safety Board, 2005).

3.1.2 Raffinate splitter section

The rafinnate splitter section comprised several process equipment that included a feed surge drum, a distillation tower, a furnace, air-cooled condensers and an overhead reflux drum. Several pumps and heat exchangers were also present in this section. The purpose of the raffinate splitter was to separate the raffinate feed from the aromatics recovery unit into light raffinate and heavy raffinate, and it had a capacity of 45,000 bbls per day (5,000 m^3/day) of raffinate feed.

3.1.3 Raffinate Splitter Distillation Column

The Process Flow Diagram, along with corresponding instrument and equipment tag numbers, in figure 3.1 is used for the following description. The distillation tower was a vertical column with an inside diameter of 3.8m and a height of 52m with an approximate liquid volume of 586,000 L (586 m^3). It was a tray column with 70 stages. Raffinate feed was introduced into the tower at tray 31. A flow control valve (F5002) that was normally set in automatic mode was used to modulate the feed rate into the column. The temperature of the incoming feed was raised to that required for component separation in the tower using an initial product-feed heat exchanger (C1104 A/B) and then a reboiler (B1101). The reboiler had four burners and was fired using refinery fuel gas. A bottoms product pump (J1103/1103A) was used to re-circulate a side product stream back into the furnace through the reboiler and also send finished product to storage tanks. An automatic level control valve (L5100) downstream of the bottoms product pump was used to maintain the liquid level at the bottom of the tower at the required set point. A level transmitter (G in fig 3.2) at the bottom of the tower provided a column bottom level reading to the Distributed Control System (DCS) to keep control room operators abreast with the level at the bottom of the distillation tower. Two high level alarms (E and F in fig 3.2) and a single low level alarm also provided readings to the DCS to notify operators when the tower level was rising above its operating design envelope.

The top section of the distillation column consists of a 45m long overhead pipe section that fed overhead vapours from the top of the tower, through air-cooled condensers (CA1101), prior to collecting in an overhead reflux drum (F1102). The flooded reflux drum provided reflux back into the column as a means of increasing the purity of the top products. As a means of maintaining a high level of process safety, the reflux drum was fitted with low level and high level alarms, and a pressure relief valve that was set to lift at 4.8 barg. A bypass line located upstream of the reflux drum provided a route for the collection of non-condensable gases (such as nitrogen) into the header collection system.

In line with guidelines for process safety in the design of distillation columns, three pressure relief valves (I in fig 3.2) were fitted on the overhead vapour line to protect the process lines and associated equipment from anticipated overpressure scenarios. The outlet of the relief valves discharged into a common header that was piped to a blowdown drum and vent stack (B in fig 3.2).

Several commentators (Fisher, H.G. 1991; US Chemical Safety Board, 2005; Kaszniak, M. 2010; Murphy, J.F. 2012) have argued extensively about the adequacy of the blowdown drum and vent stack, as there was no flare system connected to the vent stack. The disposal system was simply designed to receive liquid and vapour hydrocarbon streams from process vents and emergency blowdown systems and send them to the blowdown drum for a simple two phase separation. Separated liquids collect at the bottom of the blowdown drum and are discharged into the refinery's sewer system through a manual gate valve that was locked open (to prevent operators from accidentally closing the valve). Entrained vapours were simply released through the vent stack to atmosphere with no facility for hydrocarbon vapour combustion in a flare system (US Chemical Safety Board, 2005). Figure 3.1 below shows a simplified Process Flow Diagram of the isomerisation unit at Texas City refinery. The Blowdown drum section of the ISOM unit is shown in figure 3.2.

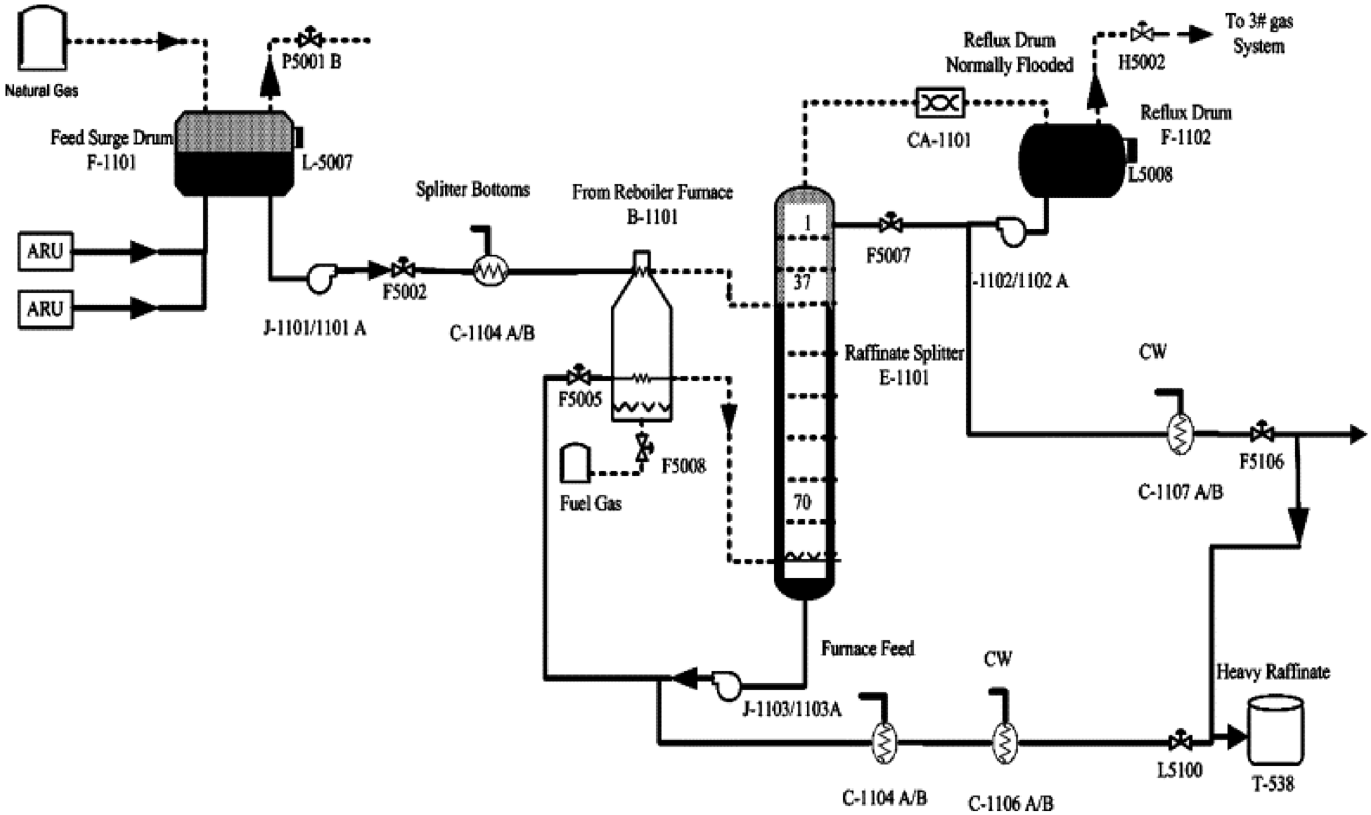
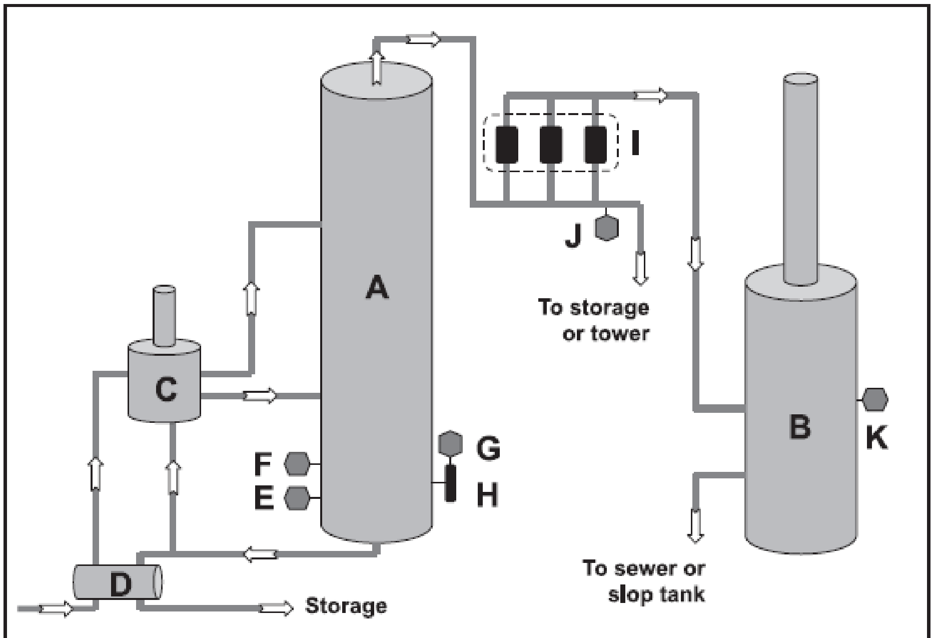


Figure 3.1 Simplified Process Flow Diagram of Raffinate Splitter (Khan and Amyotte, 2007)



A	Raffinate splitter tower	G	Level transmitter
B	Blowdown drum	H	Sight glass
C	Reboiler furnace	I	Safety relief valves
D	Heat exchanger	J	Pressure transmitter
E	High-level alarm	K	Blowdown drum alarm
F	Redundant high-level alarm		

Figure 3.2 Raffinate Splitter showing Blowdown Drum (Saleh et al 2014)

3.2 Incident description

The explosion that occurred at BP's Texas City Refinery on 23 March 2005 remains one of the most catastrophic incidents in the history of the process industries. The explosion resulted in the death of 15 persons, and over 180 were injured. It is estimated that economic losses of up to US$1.5b resulted from the incident and follow-up efforts at reconstruction. This incident has been the subject of several process safety analyses, and the lessons learned from the thorough incident investigation has been used by process industries around the world for improving technical safety, and for developing better process safety management processes. The US Chemical Safety Board (US CSB, 2005) reports that the incident was due to organisational and safety deficiencies at all levels of the organisation as warning signs were present for many years.

The incident happened as the raffinate splitter section of the isomerisation unit (ISOM unit) was being re-started after a turnaround maintenance. Evidence suggests that the start-up procedure was being carried out contrary to instructions in BP's start-up procedures after a major turnaround maintenance. The operators proceeded to fill the raffinate tower with hydrocarbon liquid feed for over three hours with no liquid outflow from the tower. This resulted in the tower overheating and overfilling as a result of thermal liquid expansion. In addition to operator negligence and error, incorrect functioning of critical instrumentation and control devices also contributed to the sequence of mis-steps that led to the catastrophic explosion (US Chemical Safety Board, 2005.

3.3 Incident Contributory Factors

A number of safety failings (Qi et al, 2012) have been identified as holes in the safety barriers at Texas City refinery that led to the catastrophic failure and loss of containment of hydrocarbon vapours and liquid.

3.3.1 Turnaround Maintenance

At the beginning of 2005, some major turnaround work was taking place at the ISOM unit of the refinery. A number of contractors were supporting the turnaround and required temporary trailers to be located on site to accommodate the extra manpower requirements. In addition, turnaround work was also taking place at the aromatics recovery unit of the refinery. These two major turnarounds significantly increased the number of BP and contractor personnel present on site (Mogford, J. 2005).

3.3.2 Staffing requirements

During normal operations, the ISOM unit was manned by one control room operator and three outside operators. The control room operator monitored all sections of the ISOM unit from a central control room. In each operating team, there was an experienced frontline supervisor and another process technician (Mogford, 2005).

While the turnaround maintenance was taking place, each team worked 12 hour shifts. As a result of the turnaround, two additional outside operators were added to the three operators present during normal operations, making available one control room operator and five outside operators for each crew. One of the more experienced outside operators was assigned as the lead operator for the start-up of the ISOM unit following the turnaround work. However, clear lines of responsibility and command were not defined for the crew. Three of the outside operators present for the ISOM unit start-up were inexperienced and had been on the plant for less than 8 months (Mannan et al., 2007).

3.3.3 Pre-start up safety review (PSSR)

There was a standing requirement for all plant start-ups following a major turnaround to go through a PSSR. However, during the start-up in March 2005, the process safety coordinator responsible for implementing this procedure was inexperienced and lacked the skills required for an effective PSSR. No PSSR was therefore carried out prior to the start-up of the ISOM unit. The

PSSR required that an experienced technical team verified the appropriateness of all safety systems and equipment, including procedures, training, process safety information, alarms, instrument testing and calibrations (Saleh et al., 2014).

3.3.4 Critical instrumentation and equipment

Prior to start-up, important column instrumentation and equipment were identified as malfunctioning and in need of repair. Crucially, the level transmitter and level sight glass (fig 3.2) at the base of the column needed repair. It was not possible for these repairs to be carried out while the unit was online as the block valves required for process isolations were leaking. The leaking valves were not repaired because plant supervisors decided there was too little time available to effect the repairs before bringing the plant back online.

A few days before the unit start-up, operators discovered that a pressure control valve was not functioning correctly. Attempts to open the valve from the central control room demonstrated the valve was not responding and so could not be opened. In spite of this, the supervisor who authorised the start-up procedure signed off to say that all control valves had been tested and were in perfect working order. It was also mandatory to ensure that all alarms were tested and functioning correctly before start-up. This procedure was also omitted (MacKenzie et al., 2007).

3.3.5 Shift handover

On the night of the incident, the lead operator for the night shift left the refinery at 5.00am, one hour before the end of his shift. He verbally informed his supervisor that he was leaving and simple recounted the actions he had initiated as part of the unit start-up process. At handover, the control room operator for the day shift received very little information from his counterpart on the night shift. Because the lead operator who left the refinery early was the one in charge of the control room for most of the night shift, there was little or no information that his late relief could pass on to the day crew. The shift supervisor for the day crew arrived an hour late, after handover procedures had been completed and was therefore unaware of what had gone on during the night shift (Mogford, 2005).

3.3.6 Management of change

Plant changes were frequently made without recourse to the management of change, MOC, procedures written down for the asset. MOC procedures help to provide clear instructions for safely operating process plant and equipment. There was a standing policy at BP that all procedures were reviewed frequently to reflect current operating practices, and certified as being up to date and accurate. The MOC policy at Texas City also stated that MOCs should be used when modifying or revising an existing startup procedure or when a system is intentionally operated outside the existing safe operating limits (Pitblado, 2011).

However, BP management permitted plant operators and supervisors to change procedural steps without appropriate management of change to assess the risks arising as a result of the changes. This practice of permitting operators to make changes without adequately assessing the risks created a dangerous work environment where procedures were not regarded as strict instructions and deviations from established procedures are accepted as normal.

3.3.7 Location of temporary trailers

The siting of temporary trailers close to the ISOM unit contributed to the high number of fatalities. It is reported that all personnel who lost their lives a result of the blast were located close to the temporary trailer. The siting of the trailers was done as a matter of convenience without regard to the risk and hazards that contractor personnel were potentially being exposed to (Kaszniak and Holmstrom, 2008).

Chapter 4 Process Simulation of Texas City Refinery Explosion

The simulation of the sequence of events that led to the catastrophic explosions at the BP Texas City refinery is based on the hypothesis that the raffinate splitter (distillation column) overfilled (Manca & Brambilla, 2012). Subsequently, liquid in the column spilled over the top into the overhead pipe, leading to over pressurisation and opening of the relief valves upstream of the blowdown vessel. It has been pointed out (Palacin-Linan, 2005; US Chemical Safety Board, 2005) that because of significant deviations from normal distillation column operations on the day of the incident, standard distillation column models in proprietary process simulation software cannot be used to simulate the sequence of events and process upsets that led to the disaster. The simulation approach adopted in this study is, therefore, a simplified approach that replaces the distillation column model in Aspen HYSYS with a tank separator.

The tank separator is modelled as a vertical vessel with a total liquid volume of 583 m3. The volume of the separator is taken as the difference between the total internal volume of the actual distillation column less the volume occupied by column internals such as trays, weirs and downcomers (Manca and Brambilla, 2012).

Prior to the explosion on 23 March 2005, at 01:13pm, it is reported that the column was completely liquid full (flooded) with a layer of sub-cooled liquid at the top with the condenser and reflux drum filled with pressurised nitrogen. No vapour flowed out of the column, and there was no reflux into the column. Indeed, laboratory tests of liquid samples recovered from the column feed, bottoms product, and overhead samples demonstrated that no separation took place in the column on the day of the incident (US Chemical Safety Board, 2005). This justifies the approach used in this study where the distillation tower is replaced with a tank separator that is simply filling up with liquid feed. It has also been suggested that the behaviour of the vapour generated in the column on the day of the incident cannot be accurately predicted, as the prevailing process conditions are outside the range of standard empirical models of distillation tray separation available in commercial simulation packages such as Aspen HYSYS.

The approach used in simulating the sequence of events that led to the explosions sought to demonstrate the following:

1. Liquid over-fill in the distillation column
2. Liquid thermal expansion in the column as a result of feed pre-heat
3. Feed vaporisation dynamics in the distillation column

4.1 Feed Composition

According to data provided by BP (Palacin-Linan, 2005), the feed to the column was a mixture of 35 light hydrocarbons (Appendix 1). However, for the purpose of this simulation, the components have been lumped into three pseudo components; C5, C6 and C7. All the components with 5 carbon atoms have been lumped in the C5 category, while components with 6 and 7 carbon atoms have been lumped into the hexane and heptane categories. In addition to hydrocarbons, nitrogen is included in the components list as nitrogen was used to pressurise and test the system for leaks prior to the introduction of hydrocarbon feed. Also, water is included in the component list, as the column was steamed out following nitrogen purge. The list of components and their mass fractions is shown in table 4.1 below.

Table 4.1 Distillation Column Feed Composition

Component	Mass fraction
Nitrogen	0.004506
Water	3.87E-05
Pentane	0.3872
Hexane	0.4915
Heptane	0.1208

4.2 Thermodynamic Correlations

Rigorous fluid packages are available in HYSYS that help to predict physical and transport properties of mixtures at different temperatures and pressures. The equation of state (EOS) models are used to handle hydrocarbon systems like the one involved in this study. The two EOS models available in HYSYS are Peng Robinson (PR) and Soave-Redlich-Kwong (SRK), including several modifications of these base EOS models. The SRK package contains enhanced binary interaction parameters for hydrocarbon-hydrocarbon pairs, as well as most hydrocarbon-nonhydrocarbon pairs, like the ones encountered in this simulation. The SRK EOS model is therefore chosen as the property package for this simulation study. Predictions of vapour-liquid binary compositions for two key fractions in the feed (pentane and hexane) at different temperatures and pressures using SRK and Peng Robinson EOS models was carried out (Appendix 2). The VLE (vapour-liquid equilibrium) predictions are similar for both models. It is therefore acceptable to use either SRK or Peng Robinson EOS model for this simulation study.

The formulation used in HYSYS for parameter prediction in the SRK EOS model is given below.

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \qquad (4.1)$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \qquad (4.2)$$

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i j_i \, (a_i a_j)^{0.5}(1 - K_{ij}) \qquad (4.3)$$

$$b = \sum_{i=1}^{N} x_i \, b_i \qquad (4.4)$$

$$A = \frac{aP}{(RT)^2} \qquad (4.5)$$

$$B = \frac{bP}{RT} \qquad (4.6)$$

Where

P = Pressure [MPa]

V = Molar Volume [m^3/mole]

T = Absolute Temperature [K]

R = Universal Gas Constant [J mol^{-1} K^{-1}]

Z = Compressibility Factor

$x_i x_j$ = mole fraction of component i, j in mixture

$a_{ij} b_i$ = SRK interaction parameters for components i, j

Kij = Binary interaction parameter for components i, j

4.3 Process Flowsheet

The Process Flowsheet (PFS) used in HYSYS for the simulations are shown in figures 4.1 and 4.2 below. It comprises the tank separator used to model the distillation column and a simple TEE separator used to simulate the separation of light raffinate from nitrogen used to pressurise the system prior to the introduction of feed.

For the purpose of dynamic simulation, two flow control loops each comprising a sensor, flow controller and a control valve are included in the flowsheet: FIC-1 is used to control the inflow of feed into the column, and FIC-2 is used to control the outflow of product from the column. The actual distillation column had a level control controller for manipulating the flow of product from the bottom of the column to storage but on the day of the incident, this level controller malfunctioned.

Figure 4.1 below shows the PFS for the initial steady state simulation while figure 4.2 is the subsequent flow sheet used for dynamic simulations.

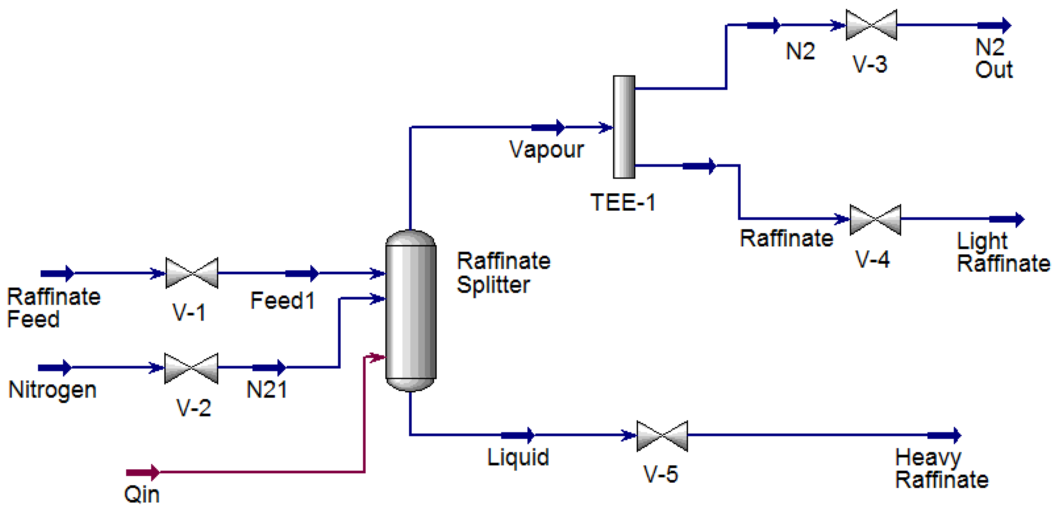


Figure 4.1 PFS used for initial steady state simulation

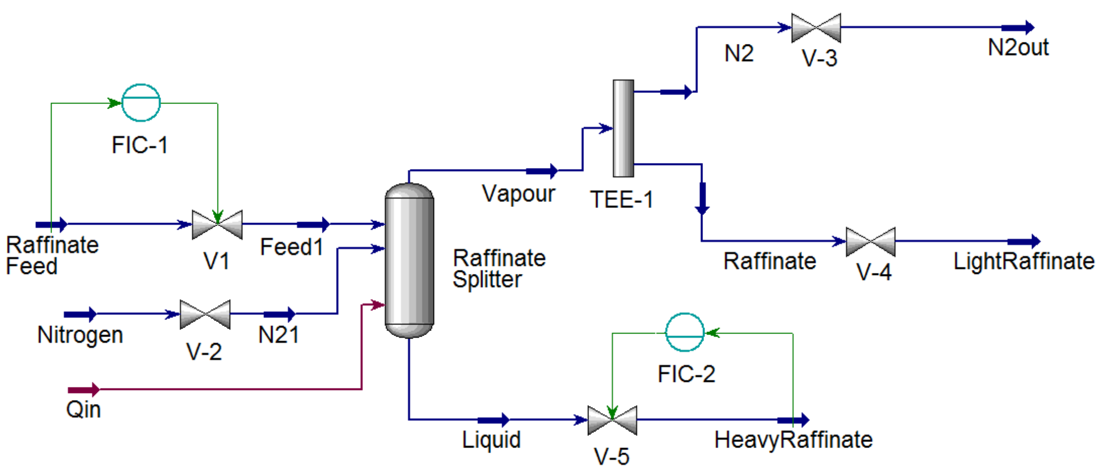


Figure 4.2 PFS used for dynamic simulation

4.4 Steady State Simulation

The initial conditions used for the steady state simulation are those available in several published documents about the process conditions at the start-up of the raffinate splitter tower on 23 March at the end of the turn-around maintenance (Palacin-Linan, 2005; US Chemical Safety Board, 2005, Baker, Levenson, and Bowman, 2007). The results of the flash calculation gave the initial feed composition used for subsequent dynamic simulations of the sequence of events leading up to the explosion. The flash calculation results are shown in Table 4.2. There are variations in the values obtained in this simulation and those those obtained by Palacin-Linan who used gPROMS as his simulation tool. This is likely due to the different models for predicting multi-component interactions used in both simulation packages. Appendix 3 shows an Aspen HYSYS output stream table showing the initial process conditions for all streams in the steady state simulation while Appendix 4 shows Aspen HYSYS output mass and energy balances for all inlet and outlet streams.

Table 4.2 Initial flash calculation showing composition in the column at start of the process

Components	Liquid mass fraction	Vapour mass fraction	Liquid mass fraction	Vapour mass fraction
	HYSYS Simulation		Palacin-Linan (gPROMS)	
Water	0.00	0.00	0.00	0.00
Methane	0.00	0.14	0.00	0.00
Pentane	0.39	0.53	0.37	0.36
Hexane	0.49	0.20	0.50	0.14
Heptane	0.12	0.01	0.13	0.01
Nitrogen	0.00	0.12	0.00	0.49
Total	1.00	1.00	1.00	1.00

4.5 Dynamic Simulation

The simulation covers the period from 0213hrs to 1320hrs on 23 March 2005, corresponding to the time raffinate feed was introduced into the tower and when the explosion occurred, respectively.

In order to carry out dynamic simulations in Aspen HYSYS, several modifications have to be made to the preliminary steady state simulation. Although it is also possible to commence with a dynamic simulation, the simulation approach in this study involved first creating a steady state simulation that was converted to a dynamic simulation. Dynamic simulation in Aspen HYSYS is especially useful for modelling a variety of scenarios such as plant start-up, plant shut-down, and pressure relief amongst others. Because the simulation was converted from a steady state to a dynamic simulation, the same input data and thermodynamic models were used for the dynamic simulation.

The first step in converting from steady state to dynamic simulation involved adding resistance nodes to the simulation, and specifying the pressure-flow correlations. This realistically creates a pressure-drop across all units in the simulation and establishes relevant flows. Valves V-1 to V-5 were used to create the required resistance between adjacent pressure nodes to ensure the right flow was established. Besides making it possible to run the dynamic simulation, these additional features are also more representative of the actual physical state of the plant.

Pressure specifications for boundary streams were also specified. No pressure specifications are required for internal streams as these are computed from surrounding equipment. The PFS showing the pressure specifications for all boundary streams is shown in Figure 4.3.

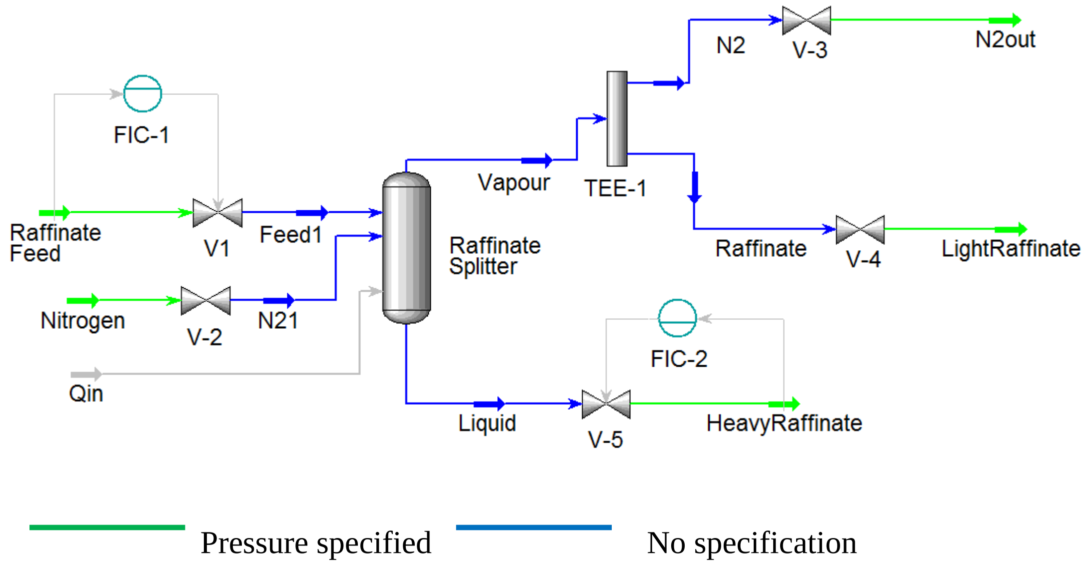


Figure 4.3 PFS showing pressure specifications for boundary streams

Other adjustments made to the steady state simulation model include sizing the raffinate splitter and adding flow controllers to the raffinate feed inlet stream and heavy raffinate outlet stream. The raffinate splitter was sized for a liquid volume hold-up of 585 m^3.

4.6 Process Control Strategy

Flow controllers FIC-1 and FIC-2 were used to control flow fluctuations for the raffinate feed and heavy raffinate streams. The proportional, integral, and derivative (PID) control strategy was implemented in this study. The PID equation used by Aspen HYSYS for this control scheme is shown below.

$$Controller\ Output = K_c E(t) + \frac{K_c}{\tau_i}\int E(t)dt + K_c \tau_d \frac{dE(t)}{dt} \tag{4.7}$$

Where E(t) = error (difference between the setpoint and process variable)

K_c = controller gain

τ_i = integral time constant

τ_d = derivative time constant

An iterative procedure was used to determine the appropriate values for the controller gain, integral time constant and derivative time constant for the flow controllers in the dynamic simulation. The values used in the simulation are shown in Table 4.3.

Table 4.3: Controller settings

	FIC-1	FIC-2
Kc	0.1	1
Ti	2	5
Td	0	0

4.7 Plant Start-up

The first simulation is for the sequence of events from 0213hrs to 1000hrs when the night shift crew started introducing raffinate feed into the raffinate splitter from the aromatics recovery unit. Because of variations in the reported feed rate to the column during the start-up procedure, an average feed flowrate of 16.3 kg/s was used for the simulation. An isothermal temperature regime was assumed for this stage of the simulation as no heat input to the splitter is reported. The feed enters the column at temperature of 23°C.

The raffinate splitter at Texas City had a level transmitter at the bottom of the tower that was designed to alarm when the level reached 2.3m, and a second redundant alarm was programmed to go off at a level of 2.4m. However, only the first alarm sounded during the start-up of the tower. This alarm was ignored as had been done routinely in previous start-ups. After filling the tower to a height of approximately 9m, the start-up procedure was stopped around 0320hrs on the 23rd of March. The unit was later re-started by the day shift.

The dynamics of the initial vessel filling as simulated in Aspen HYSYS is shown in Figure 4.4.

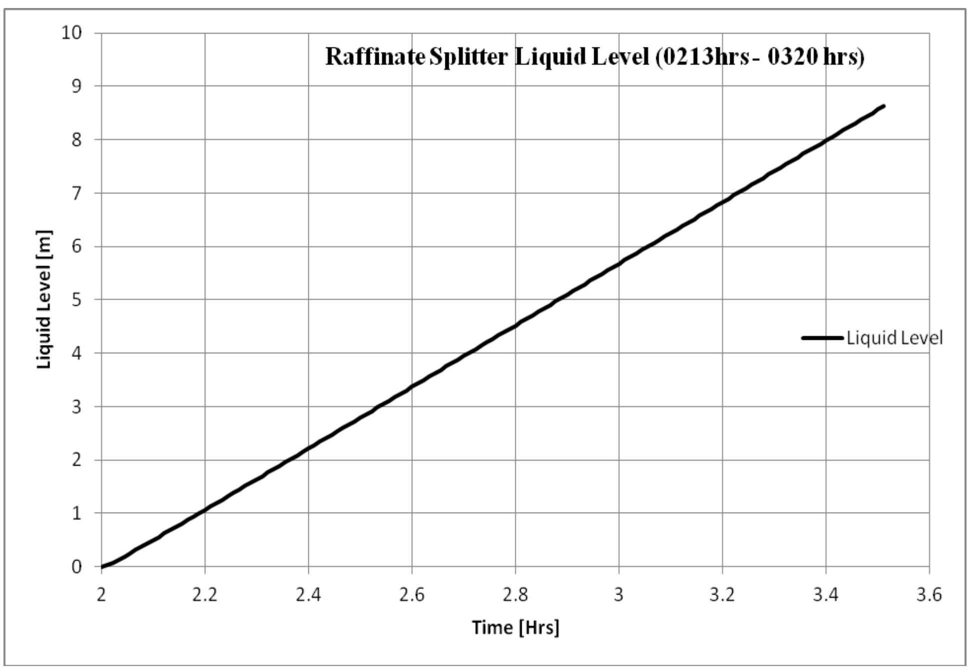


Figure 4.4 Liquid level dynamics during initial plant start-up

4.8 Feed Pre-Heat

Following crew changeover at 0600hrs, the raffinate splitter start-up procedure was resumed at approximately 1000hrs on the morning of 23 March, 2005. At this stage, the fuel gas supply to the reboiler furnace was initiated and the first two burners were lit. Feed pre-heat subsequently occurred by convective heat transfer in the top section of the furnace, increasing the temperature of the feed at a rate of 8.5°C per hour (Manca and Brambilla, 2012). The dynamics of the feed temperature increase as simulated in HYSYS is shown in Figure 4.5.

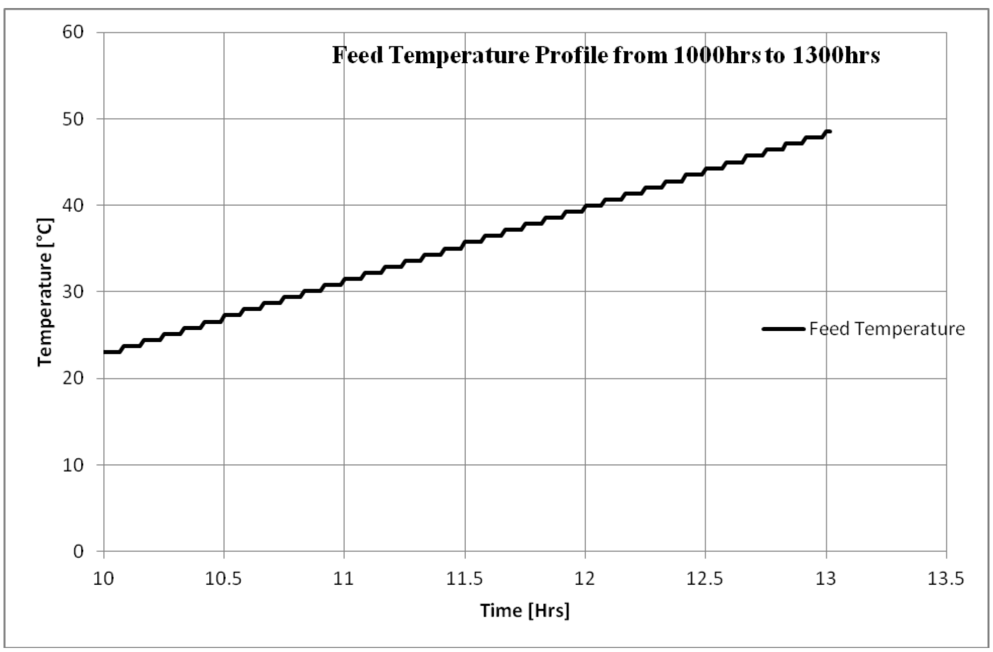


Figure 4.5 Feed Pre-heat Dynamics from 10am to 1pm

The observed temperature profile obtained from Aspen HYSYS dynamic simulation closely matches that reported by the simulations of Manca and Brambilla (2012) which was implemented in UNISIM. At 1300hrs, the feed temperature had risen to 48.5°C, and the vapour fraction was 0.015.

During this period in the start-up sequence, the level control valve at the outlet of the raffinate splitter remained closed, contrary to BP's start-up procedures. The correct procedure required that the level control valve was left at 50% open in automatic mode, to establish heavy raffinate flow to storage. Operators had previously complained that leaving the level at 50% was not ideal (contrary to what is stated in the start-up procedure). They maintained that if the level was left at 50%, a drop in liquid level could result in completely loosing heavy raffinate flow from the tower, resulting in a trip to the feed supply, and costly interruption to the start-up procedure. The raffinate splitter level filling dynamics from 1000hrs to 1300hrs obtained in Aspen HYSYS is shown in Figure 4.6.

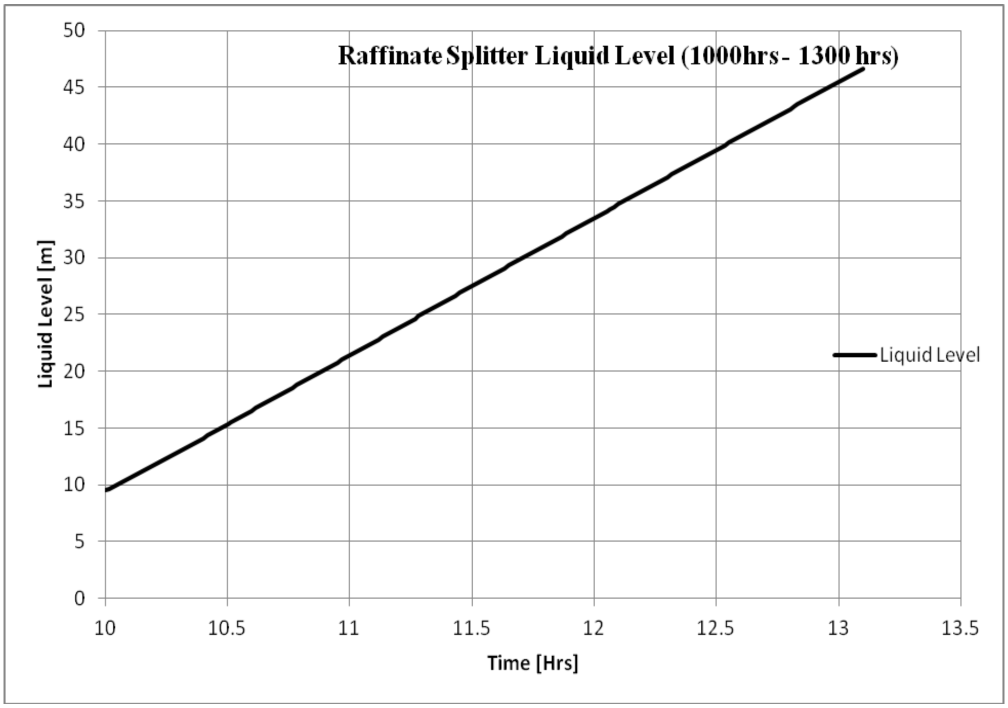


Figure 4.6 Tower Liquid level filling dynamics from 10am to 01pm

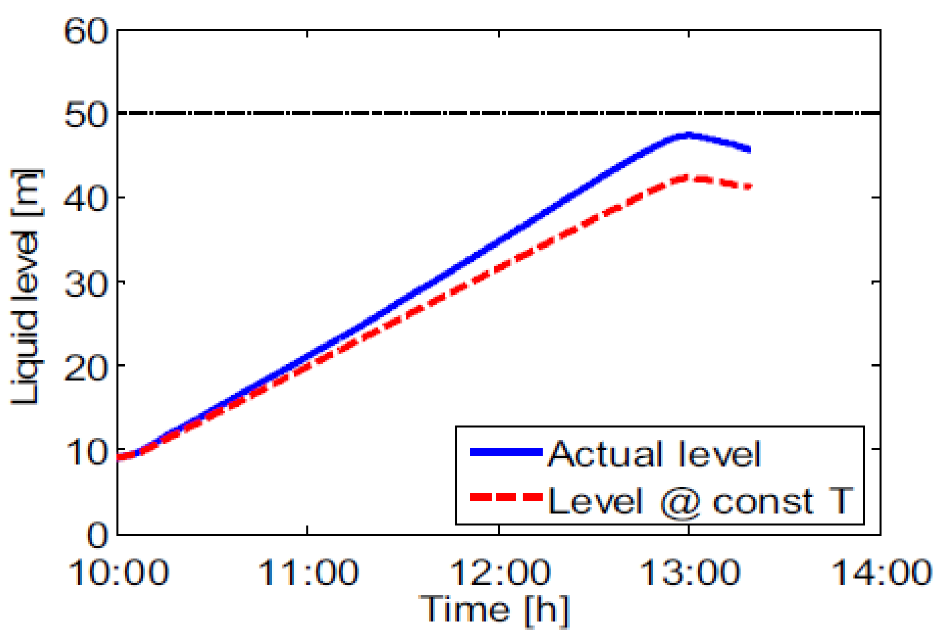
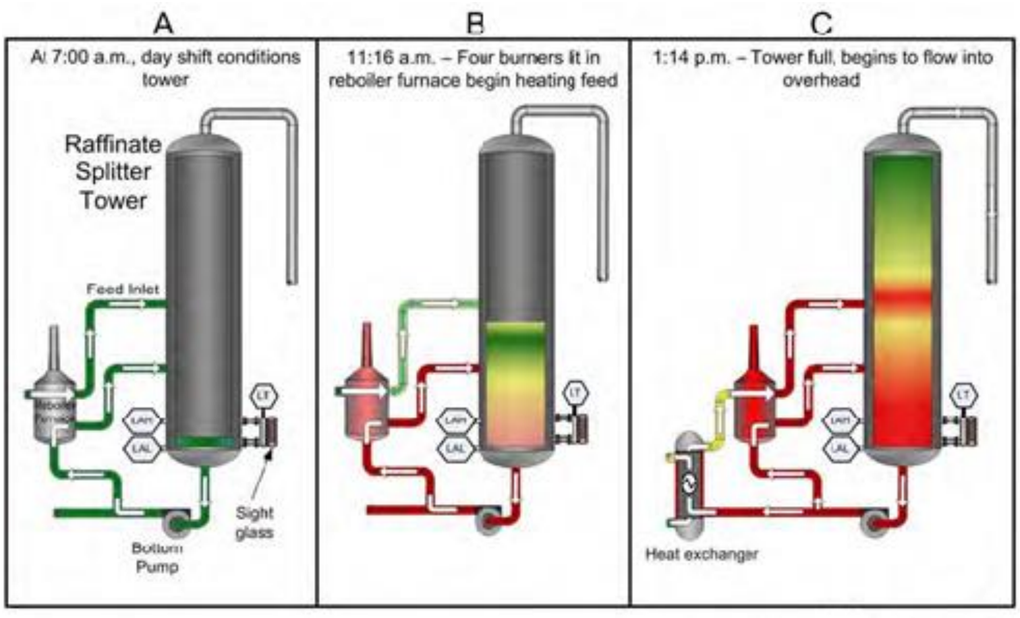


Figure 4.7 Tower Liquid level filling dynamics from 10am to 01pm (Manca & Brambilla, 2012)

The tower liquid level obtained from the Aspen HYSYS dynamic simulation, again closely matches that reported by Manca and Brambilla (2012) as shown in figure 4.7. According to the CSB investigation report, the liquid level in the tower at 11am is estimated to have been 30 m. The result obtained in this simulation gives a liquid level of 30.7 m at 11:50 am. The CSB liquid level estimates differ from those obtained in this simulation. There is however a very close match between the simulation results in this study and those obtained by Manca and Brambilla (2012) using a similar simulation tool. There is no indication in the CSB report of the simulation tool used to obtain the liquid level profile estimate, making it difficult for direct comparison with the results obtained in this study.

4.9 Feed Vaporisation

At 1302hrs, the LCV on the raffinate splitter bottom was opened to 70% to initiate product transfer to storage. At 1304, the heavy raffinate flowrate is reported to have exceeded the feed inflow into the column. The liquid level in the 52 m high tower was reported as 48 m at this time. Although the total liquid inventory in the tower began to decrease as product outflow began, thermal expansion of the heated liquids inside the column caused the level to continue to increase until it completely filled the column and spilled over into the overhead vapour line to the relief valves and condenser. The faulty level transmitter at the bottom of the tower erroneously indicated a healthy column level of 2.4 m, 45.6 m less than the actual level. At 1314hrs, it is reported that sub-cooled hydrocarbon liquids flowed out of the top of the column into the vertical overhead vapour line. At this stage, it is reported that the rate of temperature increase of the feed into the tower was at an additional 7.5 °C per minute This is because the heavy raffinate product flow transferred additional heat to the feed through the feed-product heat exchanger located upstream of the reboiler. This led to a situation where the column contained a stream of heated liquid at the bottom of the tower while a layer of cold liquid remained at the top section of the column as shown in figure 4.8.



= temperature >
= temperature >
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Figure 4.8 Tower temperature profile at 1314hrs (CSB, 2005)

4.10 Explosion

The filling of the overhead vapour line with hydrocarbon liquids led to an increase in pressure as a result of the hydrostatic liquid head. The pressure in the tower at this point is reported to have been about 4.3 barg. The combined liquid static head and the tower pressure led to an increase in pressure in the overhead vapour line higher than the relief valve lift set pressures of 2.76, 2.83 and 2.90 barg.

Flammable hydrocarbon vapours subsequently flowed from the overhead line through the collection headers into the blowdown drum. It is reported that liquids flowed from the raffinate splitter tower into the blowdown vessel at a rate of 509, 500 gph (2000 m^3/h), resulting in a discharge of approximately 51,900 galons (200 m^3) of liquids into the blowdown drum in six minutes. Once the blowdown drum overfilled, flammable liquid spilled to the ground and created a vapour cloud around the ISOM unit. The vapour cloud exploded at 1320hrs and the likely ignition source is reported to most likely have been an idling diesel pickup truck.

A dynamic simulation of the overall tower filling dynamics from 1000 to 1320 when the explosion occurred revealed that the feed to the column vaporised at approximately 1310 hrs. This happened as a result of the additional heat input into the column though the feed-product heat exchanger. The liquid level in the column from 1000hrs to 1320 hrs is shown in Figure 4.9.

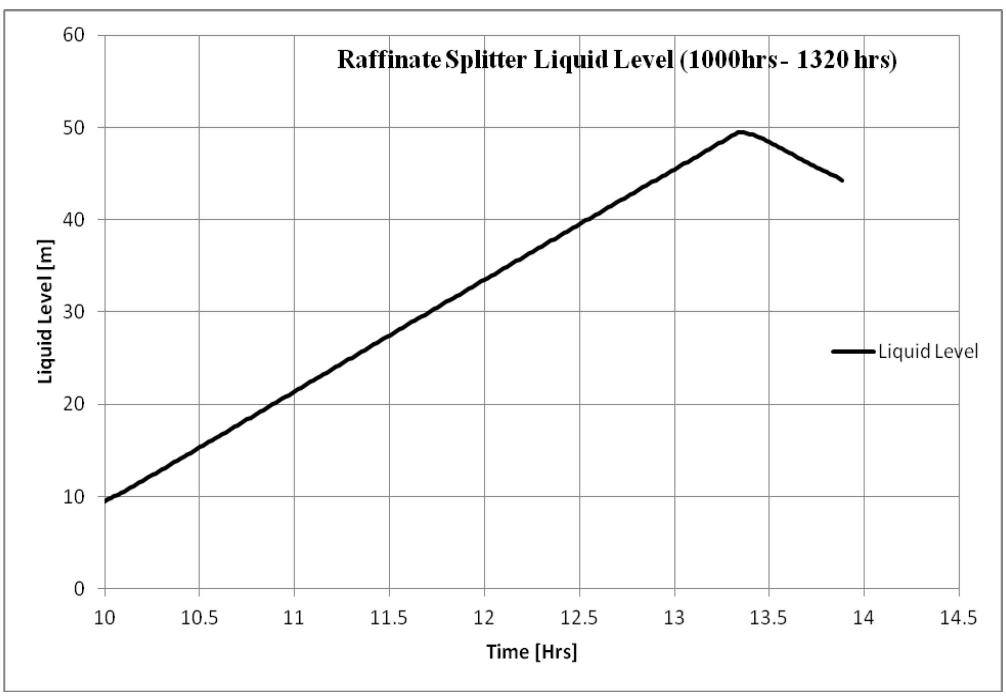


Figure 4.9 Column liquid level filling dynamics from 1000hrs to 1320hrs

The dynamics of the feed vapourisation as the rate of feed pre-heat increased at 1300hrs is shown in Figure 4.10. The feed completely vaporises at 1310hrs. This is expected to occur and agrees with reported observations on the day of the incident, and from simulation results by other researchers (Manca and Brambilla, 2012).

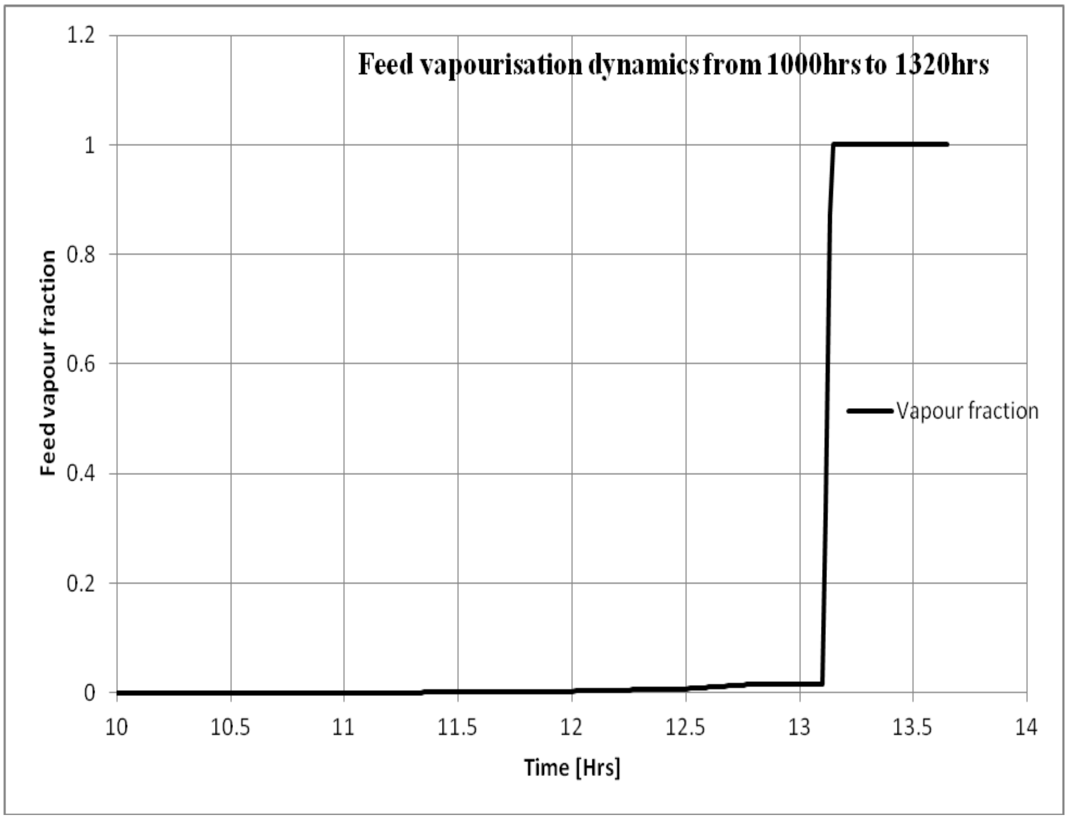


Figure 4.10 Feed vapourisation dynamics

From 10am, a linear increase in feed temperature is observed as shown in figure 4.11. This corresponds to the time that two burners in the reboiler furnace were lit. After 1.00pm, there is a marked exponential increase in the feed temperature, outside the normal operating envelope. At such high temperatures, liquid thermal expansion of the feed will occur in the raffinate splitter. This corroborates the hypothesis that the presence of superheated liquid led to tower overfill and subsequent carryover of hydrocarbon liquid into the overhead vapour line. This observation is seen just before the explosion occurs.

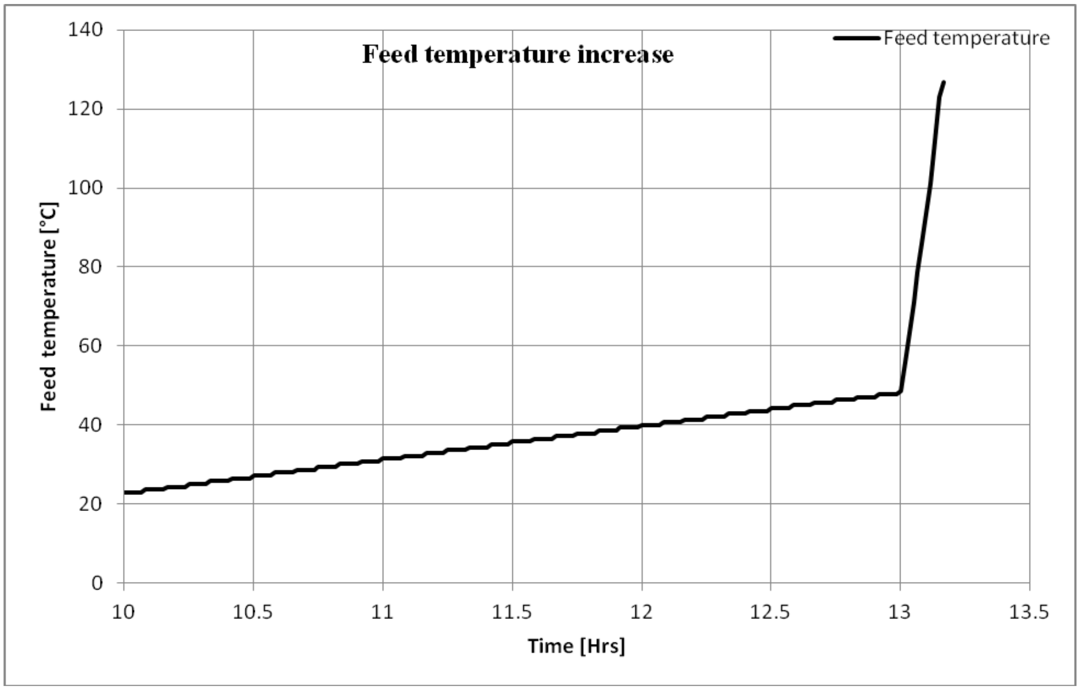


Figure 4.11 Feed temperature increase

4.11 Quantitative HAZOP

Process hazard analysis involves identifying potential hazards in a facility and the possible scenarios that could lead to loss of containment incidents or other undesirable outcomes.

One of the outcomes of the Baker panel report into the Texas City refinery incident is the recommendation for robust process hazard analysis (PHA) in process plants. Hazard and operability study (HAZOP) is regarded as one of such PHA tools for the systematic identification and assessment of process and operability hazards (Herbert, 2011). The effectiveness of a

HAZOP team depends on the creativity and experience of the participants in discovering unforeseen effects that might result in a major accident hazard. This is not an easy task as the team works with final design documents prepared by clever engineers who would have thought of most credible hazard scenarios. In addition to being creative, the team therefore needs to be highly critical in order to identify latent/hidden errors in design. To do this, the team must systematically probe the process design in a sustained manner over many hours of debating process design errors.

It has been suggested (Mahnken, 2001) that case histories from previous accidents can be a powerful tool in stimulating and sustaining the creativity of HAZOP team members. Mahnken suggests that in addition to presenting the basic sequence of events of the incident, a hypothetical HAZOP worksheet that illustrates how the accident might have been foreseen in a HAZOP study should also be considered. A dynamic HAZOP of the Texas City accident has therefore been undertaken in this study to investigate an alternative potential incident pathway on the day of the accident.

It is reported (Willard, 2009) that Texas City refinery engineers used the "What-if" hazard identification method for the first and subsequent process hazard reviews of its raffinate splitter column that exploded on 23 March 2005, killing 15 people and injuring several others. Even with this less rigorous method of hazard identification, a flare stack was repeatedly recommended as necessary to replace the blowdown stack. This recommendation was repeatedly ignored by management. The need to learn from past incidents is also highlighted by Kletz (1999). Kletz argues that it is better to illuminate the hazards we have passed through than not illuminate them at all, as we may pass the same way again, but we should try to see them before we meet them. Kletz concludes that unfortunately, we do not always learn from the hazards we have passed through.

In order to extend the use of the dynamic simulation, an additional simulation scenario was investigated. It has been established that the simulation approach employed in this study is a tank model that replicates the dynamic filling of the raffinate splitter like it happened on the day of the incident. This approach is also used in the dynamic HAZOP study. The initial dynamic simulation has been used to establish that it is possible to replicate the column feed temperature and vapour fraction profiles, and the column liquid level dynamics observed on the day of the accident.

The significance of this methodology is not in the rigorous simulation of the sequence of events, but in the extrapolation of the model for use in dynamic HAZOP studies. It can be argued that the benefits obtainable from such an approach exceed whatever gain may be obtained from developing more accurate models. Such benefits include a visual representation of the quantified level of risks resulting from incorrectly designed equipment, or not following adequate operational procedures.

A conventional HAZOP involves using guidewords to qualitatively investigate the hazards and operability issues that would result from incorrect operations. Examples of such guidewords include “more flow”, “high temperature”, “no flow”, “less pressure”, and so on. For the purpose of this study the guideword used is “high temperature”. According to the accident investigation report, the observed temperature profile occurred as a result of heat input from two burners in the reboiler which were lit at approximately 1000hrs.Two additional burners were lit at 1117hrs. The

HAZOP scenario explored in this study therefore considers the case where increased heat input to the column began at 1000hrs with all four burners lit. A qualitative assessment of this scenario would obviously identify the associated hazard of increased temperature input and likely overpressure of the column. Appropriate safeguards would be the pressure relief valves and the blowdown drum and stack which will protect the column from any overpressure scenario. The additional lapses that occurred on the day of the incident such as leaving the LCV at the bottom of the column closed are also included in this scenario. The resulting dynamic process conditions from this simulation are shown in figures 4.12 to 4.14.

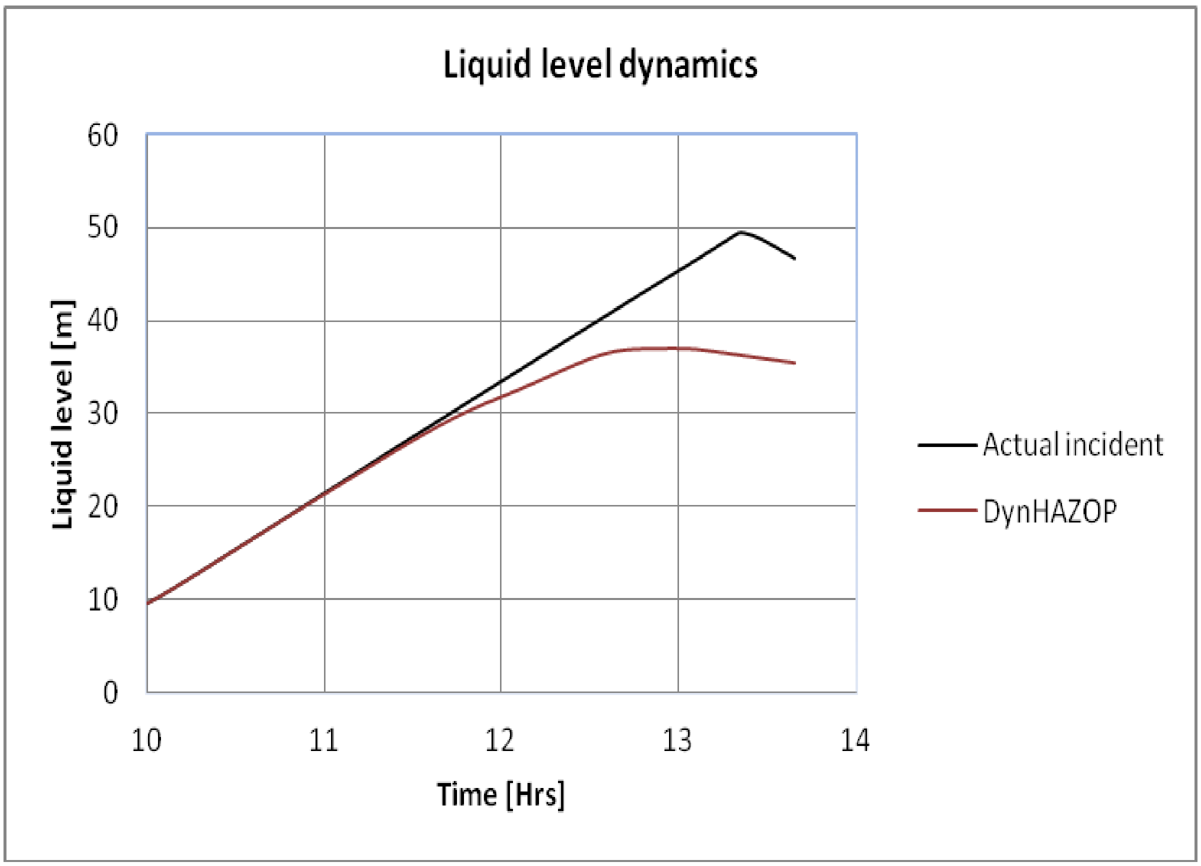


Figure 4.12 Liquid level dynamics for quantitative HAZOP

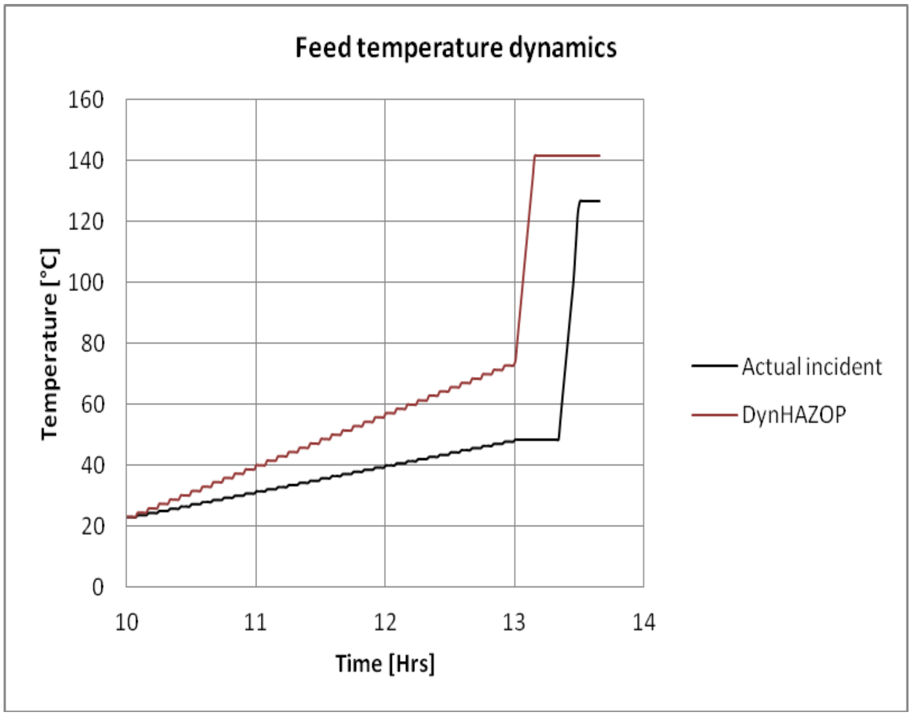


Figure 4.13 Feed Temperature dynamics for quantitative HAZOP

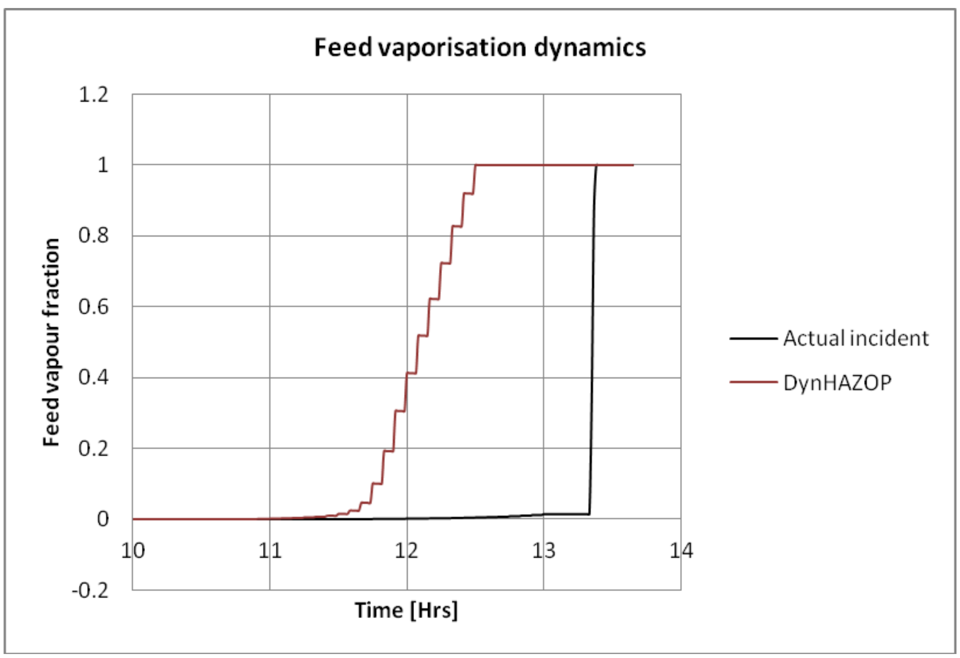


Figure 4.14 Feed Vaporisation dynamics for quantitative HAZOP

The dynamic HAZOP simulation demonstrated an alternative pathway for the sequence of events leading up to the accident. As can be observed in figures 4.13 and 4.14, an additional temperature increase of 43% occurred at 12 noon, leading to a mixed phase feed flow with a vapour fraction of 0.4. It is noteworthy that the rise in liquid level in the column is less than that which supposedly took place on the day of the incident as shown in figure 4.12. Complete vaporisation of the feed takes place at 1230pm in the alternative accident pathway, much earlier than the reported feed vaporisation time on the day of the incident as can be seen in figure 4.14. The conclusion from the above is that the explosion may have occurred earlier if all four burners had been lit. There is also the possibility that the faster rate of temperature excursion above the normal operating envelope may have alerted operators to potential dangers, thereby prompting them to take corrective actions such as controlled plant shut down.

The dynamic HAZOP in this study has demonstrated an alternative pathway for the evolution of process variables if additional safety barriers were breached on the day of the incident. Establishing the evolution of the process variables downstream of the column has not been considered in this study. However, it has been demonstrated that a dynamic HAZOP may help secure management buy-in by demonstrating the likely consequences of deviations from standard operating procedures or other hazards in process plants.

It has been pointed out (Anderson, 2005) that many major accidents in the process industries happen as a result of HAZOP actions that are not closed out effectively. This is often as a result of diverting resources to other areas where management considers to be of higher priority. A dynamic HAZOP can be an effective visual tool for convincing management to spend the time and resources required to close out HAZOP actions.

Chapter 5 Conclusions and Recommendations for Future Work

5.1 Conclusions

The dynamic simulation of the sequence of events and the resulting process conditions preceding the explosion and subsequent fire at Texas City refinery sought to demonstrate the use of process simulators for process safety analysis. The liquid level, temperature profile and feed vaporisation dynamics obtained in the accident simulation closely match those available in published literature.

The dynamic simulation demonstrated that the initial start-up process from approximately 0200hrs filled the column to a height of 9m before the procedure was discontinued and restarted at 1000hrs. The observed temperature profile obtained from Aspen HYSYS dynamic simulation closely matches that reported by the simulations of Manca and Brambilla (2012) which was implemented in UNISIM. At 1300hrs, the feed temperature had risen to 48.5°C, and the vapour fraction was 0.015.

This work has demonstrated the likely causes of the explosion that took place at Texas City refinery. Although operating procedures required that the level control valve at the bottom of the tower is opened during start-up, an operator deviated from this practice and continued pumping liquid into the tower with a closed outlet valve. The tower was thus filled for over three hours with no liquid flowing out. A simple mass balance check should have revealed to the operators that something was wrong but this did not happen. Continuous filling of the tower led to flooding and high pressure in the tower, which activated relief valves that sent flammable liquid and vapour to an improperly designed blow-down system.

The malfunctioning of critical instrumentation in the distillation tower contributed to the incident. The level indicator at the bottom of the tower showed that level was declining when it was actually overfilling. A second high level alarm that should have alerted operators to the danger also malfunctioned. As a result of improvements in legislation and developments in the field of process safety, these failures are unlikely to happen today. In addition to having basic process control and instrumentation installed, critical process equipment and operations are fitted with trips and automatic shutdown systems that will prevent the undesirable situation that happened at Texas City from ever happening. Although these trip and shutdown systems are designed with very high reliabilities (low probability of failure on demand), there is still the need for adequate planned and preventive maintenance regimes to ensure reliability. The safety integrity level of advanced control systems provides a guide to the level of maintenance rigour required to keep a safety instrumented system at the required level of reliability.

The incident at Texas City also underscored the need for properly trained operators and rigorous supervisory oversight in the process industries. Although a staffing assessment had recommended that an extra operator was required due to the increased workload during the start-up period, nothing was done to reduce staff workload. Fatigue and work overload may well have contributed to the incident. There was very poor communication between supervisors and operators during the start-up process shift handover, which meant that critical information was not passed on. Operator training simulators using dynamic process simulations are an important tool for addressing the gap in knowledge and experience of process operators. It was identified that the training programme at Texas City was grossly inadequate: training staff numbers had been reduced from 28 to 8, and simulators were not available for operators to handle abnormal situations and critical deviations that typically occur during plant start-ups.

5.2 Recommendations for future work

This work has not simulated the flow of fluids from the relief discharge header to the blowdown drum and the subsequent filling of the blowdown drum. One reason for this is the lack of available data on the sizes of the relief valves and other information about the lines to the blowdown system. It may be possible for additional work to be carried out using the pressure profiles at the pressure transmitters and the temperature profile at the column head to simulate the discharge rate from the relief valves. Although attempts have been made in literature to explain the filling dynamics of the blowdown drum, results did not match the incident description. It might therefore be possible to develop rigorous models that would help explain the overfilling of the blowdown system.

References

Anderson, M. (2005) Behavioural Safety and Major Accident Hazards: Magic Bullet or Shot in the Dark? *Process Safety and Environmental Protection*, 83 (2), 109-116.

Ayral, T and De Jonge, P, 2013, Operator training simulators for brownfield process units offer many benefits, *Hydrocarbon Processing*, 92(2).

Baker, J.A., Levenson, N., Bowman, F.L. (2007) *The report of the BP US refineries independent safety review panel.* Available online: http://www.absa.ca/IBIndex/TheBakerPanelReport.pdf [Accessed Feb. 4th, 2013].

Berutti, M, 2009, Operator Shortage Crisis and the Use of Dynamic Process Simulation, Available: http://www.mynah.com/content/operator-shortage-crisis-and-use-dynamic-process-simulation, [Accessed Mar. 2nd, 2013].

CBI, Chicago Bridge & Iron Company (2009) *CBI Virtual Refinery*. Available online: http://www.cbi.com/virtual-refinery [Accessed Jan. 15th, 2013].

Chatterjee, S G, 2004, Software Architectures and Tools for Computer Aided Process Engineering: B. Braunschweig, R. Gani (Eds.), Elsevier Inc., P.O. Box 945, Madison Square Station, New York, NY 10159-0945, USA/Elsevier B.V., P.O. Box 211, 1000 AE Amsterdam, The Netherlands, *Separation and Purification Technology*, 35(2), pp 169-173.

Chemical Safety Board, U. (2005) *Investigation report, refinery explosion and fire (15 killed, 180 injured).* Available online: http://www.csb.gov/assets/1/19/csbfinalreportbp.pdf [Accessed Sep. 23rd, 2012].

Dixon, M, 1992, Training simulators, *Operator Training Simulators, IEE Colloquium on*, pp 1/1-1/6.

Eizenberg, S, Snacham, M and Brauner, N, 2006, Combining HAZOP with dynamic simulation - Applications for safety education, *CHISA 2006 - 17th International Congress of Chemical and Process Engineering*, .

Fisher, H.G. (1991) An overview of emergency relief system design practice. *Plant/Operations Progress*, 10 (1), 1-12.

Goh, S, Chang, B, Jeong, I, Kwon, H and Moon, I, 1998, Safety improvement by a multimedia operator education system, *Computers & Chemical Engineering*, 22, Supplement 1(0), pp S531-S536.

Graf, H and Schmidt-Traub, H, 1999, Process hazard identification during plant design by qualitative modelling, simulation and analysis, *Computers & Chemical Engineering*, 23, Supplement(0), pp S59-S62.

Guckenberger, D and Stanney, K, 1995. Enhancing the fidelity of virtual environments through the manipulation of virtual time, in Anonymous Advances in Human Factors/Ergonomics, Elsevier, pp 505-510.

Guddeti, R, Ramdoss, P, Esparragoza, J V and Dasgupta, S, 2010, Improved margins, safety and reliability through licensor developed operator training simulators, *Chemical Engineering World*, 45(8), pp 52-56.

Harismiadis, V I, AlDaiel, A T, AlMulla, M M, AlNajrani, M A, Chaitanya, K and Deshpande, A, 2011, Fine-tune diesel hydrotreating operations, *Hydrocarbon Processing*, 90(10).

Health and Safety Executive, UK HSE, 2007, *BP Texas City incident - Baker review*, Available: http://www.hse.gov.uk/leadership/bakerreport.pdf, [Accessed Jun. 18th, 2013].

Herbert, I L, 2011, Learning the Lessons - Retrospective HAZOPs, *OFFSHORE EUROPE - CONFERENCE PROCEEDINGS-; 2; 771-778 Offshore Europe oil & gas Conference, Offshore Europe*, Aberdeen, UK, 6 - 8 Sep. 2011, Society of Petroleum Engineers.pp 771-778.

Hotblack, C C, 1992, Training simulators-quantification of benefits and lessons learnt: a user's perspective, *Operator Training Simulators, IEE Colloquium on*, pp 2/1-2/6.

HSE, 2006, *An independent review of HSE methodology for assessing societal risk*, Available: http://www.hse.gov.uk/societalrisk/review.pdf, [Accessed Nov. 7th, 2012].

Invensys, 2013, *EYESIM Immersive Virtual Reality Training System* , Available: http://iom.invensys.com/UK/Pages/SimSci-Esscor_EYESIMImmersiveVirtualRealityTrainingSystem.aspx, [Accessed Apr. 3rd, 2013].

Johnson, R W, 2010, Beyond-compliance uses of HAZOP/LOPA studies, *Journal of Loss Prevention in the Process Industries*, 23(6), pp 727-733.

Jones, D R, 1992, Current application of simulators in the process industries and future trends, *Operator Training Simulators, IEE Colloquium on*, pp 3/1-3/4.

Kalantarnia, M, Khan, F and Hawboldt, K, 2010, Modelling of BP Texas City refinery accident using dynamic risk assessment approach, *Process Safety and Environmental Protection*, 88(3), pp 191-199.

Kaszniak, M. & Holmstrom, D. (2008) Trailer siting issues: BP Texas City. *Journal of Hazardous Materials*, 159 (1), 105-111.

Kaszniak, M. (2010) Oversights and omissions in process hazard analyses: Lessons learned from CSB investigations. *Process Safety Progress*, 29 (3), 264-269.

Khan, F I and Amyotte, P R, 2007, Modeling of BP Texas City refinery incident, *Journal of Loss Prevention in the Process Industries*, 20(4–6), pp 387-395.

Kletz, T, 1999, Hazop and Hazan: Identifying and Assessing Process Industry Hazards, 4th edition, UK: IChemE.

Komulainen, T M, Enemark-Rasmussen, R, Sin, G, Fletcher, J P and Cameron, D, 2012, Experiences on dynamic simulation software in chemical engineering education, *Education for Chemical Engineers*, 7(4), pp e153-e162.

Lyall, S. (2010) In BP's Record, a History of Boldness and Costly Blunders, *The New York Times, NYT.* Available: http://www.nytimes.com/2010/07/13/business/energy-environment/13bprisk.html?pagewanted=all&_r=0, [Accessed Sep. 17th, 2013].

Lyons, William C.,Zaba, Joseph., (1996) Standard handbook of petroleum & natural gas engineering. Volume 1 Volume 1.

MacKenzie, C., Holmstrom, D. & Kaszniak, M. (2007) Human Factors Analysis of the BP Texas City Refinery Explosion. *Proceedings of the Human Factors and Ergonomics Society Annual Meeting*, 51 (20), 1444-1448.

Mahnken, G E, 2001, *Use case histories to energize your HAZOP*, Available: http://people.clarkson.edu/~wwilcox/Design/hazopcas.pdf, [Accessed 08/28 2013].

Manca, D and Brambilla, S, 2012, Dynamic simulation of the BP Texas City refinery accident, *Journal of Loss Prevention in the Process Industries*, 25(6), pp 950-957.

Manca, D, Brambilla, S and Colombo, S, 2013, Bridging between Virtual Reality and accident simulation for training of process-industry operators, *Advances in Engineering Software*, 55(0), pp 1-9.

Mannan, M.S., West, H.H. & Berwanger, P.C. (2007) Lessons learned from recent incidents: Facility siting, atmospheric venting, and operator information systems. *Journal of Loss Prevention in the Process Industries*, 20 (4–6), 644-650.

Martin-Villalba, C, Urquia, A and Dormido, S, 2012, Development of virtual-labs for education in chemical process control using Modelica, *Computers & Chemical Engineering*, 39(0), pp 170-178.

Mederos, F S, Ancheyta, J and Elizalde, I, 2012, Dynamic modeling and simulation of hydrotreating of gas oil obtained from heavy crude oil, *Applied Catalysis A: General*, 425–426(0), pp 13-27.

Mogford, J (2005) Texas City Refinery Fatal accident investigation report, isomerization unit explosion final report. Available: http://cip.management.dal.ca/publications/final_report.pdf , [Accessed 08/28 2013].

Muravyev, A and Berutti, M, 2007, Operator training system for hydrocracking unit: Real world questions and answers, *AIChE Annual Meeting, Conference Proceedings*, .

Murphy, J.F. (2012) Safety considerations in the chemical process industries. *Handbook of Industrial Chemistry and Biotechnology*, 47-105.

Nakaya, M, Fukano, G, Onoe, Y and Ohtani, T, 2006, On-line Simulator for Plant Operation, *Intelligent Control and Automation, 2006. WCICA 2006. The Sixth World Congress on*, pp 7882-7885.

Nasios, K, 2002, *Improving Chemical Plant Safety Training Using Virtual Reality*, PhD edition, [Online] Available: http://etheses.nottingham.ac.uk/39/1/CostasThesis.pdf: University of Nottingham. [Accessed Oct. 8th, 2012].

Okapuu-von Veh, A, Marceau, R J, Malowany, A, Desbiens, P, Daigle, A, Garant, E, Gauthier, R, Shaikh, A and Rizzi, J -, 1996, Design and operation of a virtual reality operator-training system, *Power Systems, IEEE Transactions on*, 11(3), pp 1585-1591.

Olsen, I, Endrestøl, G O and Sira, T, 1997, A rigorous and efficient distillation column model for engineering and training simulators, *Computers & Chemical Engineering*, 21, Supplement(0), pp S193-S198.

OSHA, Occupational Safety & Health Administration (1999) *OSHA Technical Manual Section IV: Petroleum Refining Processes.* Available: https://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html [Accessed Aug. 21st, 2013].

Palacin-Linan, J, 2005, *Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas - Final technical report.* Available online: http://www.psenterprise.com/news/data/bp_fatal_accident_report.pdf [Accessed Aug. 25th, 2013].

Parmenter, D V and Warshawsky, J, 1981, Cement Plant Simulator Trainer, *Industry Applications, IEEE Transactions on*, IA-17(1), pp 90-94.

Pitblado, R. (2011) Global process industry initiatives to reduce major accident hazards. *Journal of Loss Prevention in the Process Industries*, 24 (1), 57-62.

Qi, R., Prem, K.P., Ng, D., Rana, M.A., Yun, G. & Mannan, M.S. (2012) Challenges and needs for process safety in the new millennium. *Process Safety and Environmental Protection*, 90 (2), 91-100.

Ramzan, N and Witt, W, 2007, Combining disturbance simulation and safety analysis techniques for improvement of process safety and reliability, *Computer Aided Chemical Engineering*, 24, pp 1259-1264.

Ramzan, N and Witt, W, 2007, Merging safety and reliability analysis for process safety and reliability improvement, *Revista de Chimie*, 58(4), pp 379-386.

Ramzan, N, Compart, F and Witt, W, 2007, Application of extended Hazop and event-tree analysis for investigating operational failures and safety optimization of distillation column unit, *Process Safety Progress*, 26(3), pp 248-257.

Remesat, D, Young, B and Svrcek, W Y, 2009, Improving vacuum gas oil hydrotreating operation via a lumped parameter dynamic simulation modeling approach, *Chemical Engineering Research and Design*, 87(2), pp 153-165.

Richmond, P and Chen, D, 2012, A model predictive control package for undergraduate education, *Education for Chemical Engineers*, 7(2), pp e43-e50.

Rizal, D., Tani, S., Nishiyama, K. & Suzuki, K. (2006) Safety and reliability analysis in a polyvinyl chloride batch process using dynamic simulator-case study: Loss of containment incident. *Journal of Hazardous Materials*, 137 (3), 1309-1320.

Rodríguez, M A, Elizalde, I and Ancheyta, J, 2012, Modeling the performance of a bench-scale reactor sustaining HDS and HDM of heavy crude oil at moderate conditions, *Fuel*, 100(0), pp 152-162.

Saleh,J, Haga, R, Francesca M. Favarò, Efstathios Bakolas, (2014) Texas City refinery accident: Case study in breakdown of defense-in-depth and violation of the safety–diagnosability principle in design, *Engineering Failure Analysis* 36:121-133

Schouwenaars, E. (2008). DNV energy, the risks arising from major accident hazards. Refining Management Forum Copenhagen, June. Available: http://www.researchgate.net/publication/238674574_The_Risks_Arising_From_Major_Accident

_Hazards_Lessons_From_The_Past_Opportunities_For_The_Future [Accessed Aug. 26th, 2013].

Takatsu, H, Nozaki, T and Okada, K, 2004, Application of simulation technology to plant optimization and control, *Control Applications, 2004. Proceedings of the 2004 IEEE International Conference on*, pp 1312-1317 Vol.2.

Tauseef, S M, Rashtchian, D, Abbasi, T and Abbasi, S A, 2011, A method for simulation of vapour cloud explosions based on computational fluid dynamics (CFD), *Journal of Loss Prevention in the Process Industries*, 24(5), pp 638-647.

Willard, D. (2009) Safety statistics can get you into a scape: focusing on minor accidents can foster false perceptions. Putman Media, Inc. *Chemical Processing Magazine,* 03 Dec.

Worm, G I M, van der Wees, M, de Winter, J C F, de Graaf, L, Wieringa, P A and Rietveld, L C, 2012, Training and assessment with a faster than real-time simulation of a drinking water treatment plant, *Simulation Modelling Practice and Theory*, 21(1), pp 52-64.

Wu, J, Zeng, J C and Sun, G J, 1997, The assessment of the fidelity of Operator Training Simulator for chemical industrial processes, *Simulators International Xiv*, 29(3), pp 178-181.

Yang, S H, Yang, L and He, C H, 2001, Improve safety of industrial processes using dynamic operator training simulators, *Process Safety and Environmental Protection*, 79(B6), pp 329-338.

Zhou Zewei, Feng Yiping, Rong Gang and Wu Yucheng, 2011, Virtual Reality Based Process Integrated Simulation Platform in Refinery: Virtual Refinery and Its Application, *China Petroleum Processing & Petrochemical Technology*, 13(3), pp 74-84

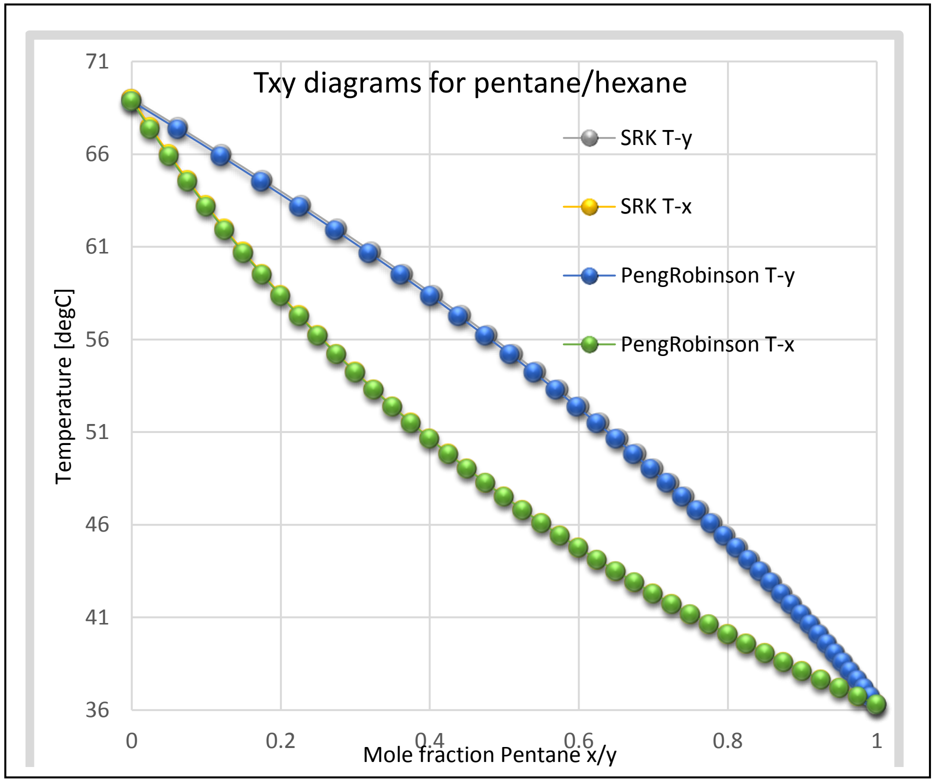
Appendix 1 Hypothetical List of 35 C1 to C10 Light Hydrocarbons present in Texas City Refinery Isomerisation Unit Feed

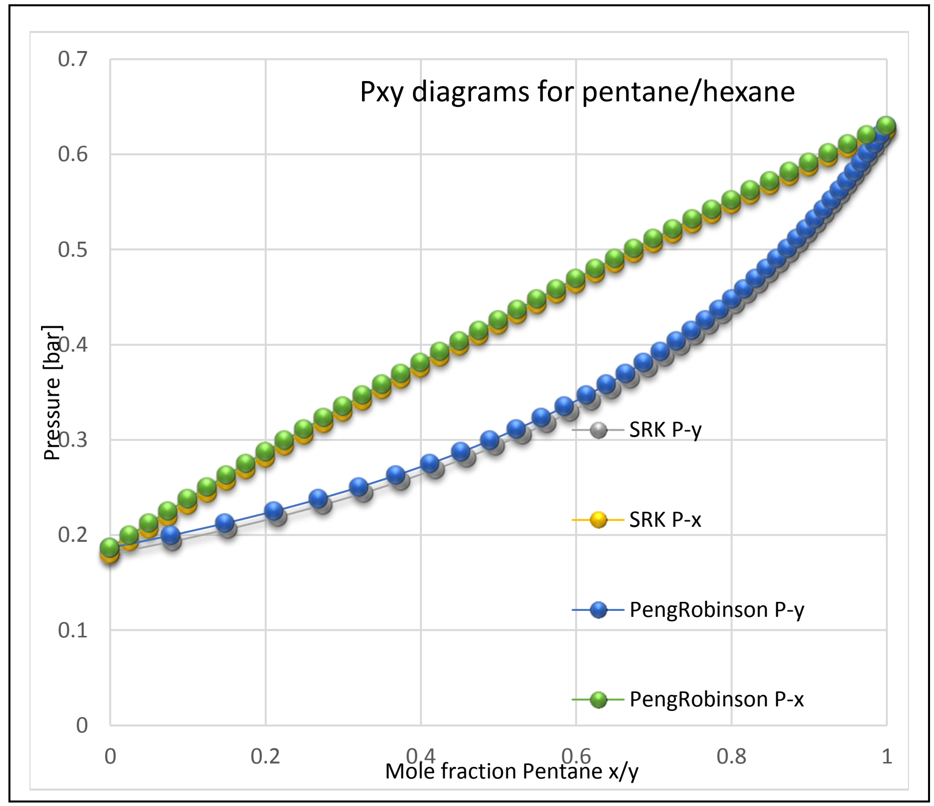
S/No.	Compound	Formula	Molecular Mass
1	Methane	CH_4	16.043
2	Ethane	C_2H_6	30.07
3	Ethene	C_2H_4	28.054
4	Propane	C_3H_8	44.097
5	Propene	C_3H_6	42.081
6	n-Butane	C_4H_{10}	58.124
7	IsoButane	C_4H_{10}	58.124
8	1-Butene	C_4H_8	56.108
9	1,2-Butadiene	C_4H_6	54.029
10	1,3-Butadiene	C_4H_6	54.029
11	n-Pentane	C_5H_{12}	72.151
12	IsoPentane	C_5H_{12}	72.151
13	NeoPentane	C_5H_{12}	72.151
14	Cyclopentane	C_5H_{10}	70.135
15	1-Pentene	C_5H_{10}	70.135
16	Isoprene	C_5H_8	68.119
17	n-Hexane	C_6H_{14}	86.178
18	2-MethylPentane	C_6H_{14}	86.178
19	2,3-Dimethylbutane	C_6H_{14}	86.178
20	Cyclohexane	C_6H_{12}	84.162
21	n-Heptane	C_7H_{16}	100.205
22	2-Methylhexane	C_7H_{16}	100.205
23	3-Methylhexane	C_7H_{16}	100.205
24	3-Ethylpentane	C_7H_{16}	100.205
25	2,2-Dimethylpentane	C_7H_{16}	100.205
26	2,4-Dimethylpentane	C_7H_{16}	100.205
27	3,3-Dimethylpentane	C_7H_{16}	100.205
28	2,2,3-Trimethylbutane	C_7H_{16}	100.205
29	n-Octane	C_8H_{16}	114.232
30	Isoctane	C_8H_{18}	114.232
31	Diisobutyl	C_8H_{18}	114.232
32	2,3-Dimethylhexane	C_8H_{18}	114.232
33	2,3-Dimethylhexane	C_8H_{18}	114.232
34	n-Nonane	C_9H_{20}	128.259
35	n-Decane	$C_{10}H_{22}$	142.286

Source: Lyons, C., and Zaba, . (1996). *Standard Handbook of Petroleum & Natural Gas Engineering.*

Appendix 2 Comparison of SRK and Peng Robinson Equation of State Models

An analysis of binary VLE equilibrium data for pentane and hexane was carried out using Aspen Plus. This is to justify the choice of EOS model used in this simulation study.





Appendix 3 Stream tables showing process conditions for initial steady state simulation

	Unit	Feed	Nitrogen	Vapour	Liquid	Heavy Raffinate	Light Raffinate	N2 Out
Vapour Fraction		0	1	1	0	0.00028	1	1
Temperature	C	23	23	22.90431	22.90431	22.885019	22.843286	22.84329
Pressure	psia	15	14.7	12.52444	12.52444	11.799246	11.799246	11.79925
Molar Flow	kgmole/h	722.1047	0.356977	0.99239	721.4693	721.469319	0.396956	0.595434
Mass Flow	kg/s	16.3	0.002778	0.012024	16.29075	16.290753	0.00481	0.007215
Liquid Volume Flow	m3/h	90.01616	0.012401	0.076709	89.95185	89.951853	0.030684	0.046025
Component mole fractions								
		Feed	Nitrogen	Vapour	Liquid	Heavy Raffinate	Light Raffinate	N2 Out
n-Heptane		0.097937	0	0.006399	0.098014	0.098014	0.006399	0.006399
H2O		0.000175	0	0.011579	0.000159	0.000159	0.011579	0.011579
Methane		0.002284	0	0.380736	0.001763	0.001763	0.380736	0.380736
n-Pentane		0.436098	0	0.318273	0.436044	0.436044	0.318273	0.318273
n-Hexane		0.463507	0	0.099207	0.463779	0.463779	0.099207	0.099207
Nitrogen		0	1	0.183806	0.000242	0.000242	0.183806	0.183806

Appendix 4 Mass and Energy balance for steady state simulation

Mass balance

	Inlet flows (Kg/s)	Outlet Flows (Kg/s)
Raffinate Feed	16.3	
Nitrogen	10	
Heavy Raffinate		13.01
Light Raffinate		5.316
N2 Out		7.974
Total	26.3	26.3

Energy balance

	Inflows (KJ/h)	Outflows (KJ/h)
Qin	0	
Raffinate Feed	-1.38E+08	
Nitrogen	-8.32E+04	
Heavy Raffinate		-1.12E+08
Light Raffinate		-1.02E+07
N2 Out		-1.53E+07
Total	-1.38E+08	-1.38E+08

Appendix 5 Publication

Isimite, J & Rubini, P, 2014, Dynamic simulation of Texas City Refinery explosion for safety studies., in *Proceedings of Hazards 24 Process Safety Conference*, 7 – 9 May 2014, Edinburgh, UK. Institution of Chemical Engineers, IChemE.