

Appendix 12

Documentation

Documentation

The following relevant documentation was collected for review:

- Operations log books (Shift Supervisor log, Board Operator log)
- PI records for the past 5 years and DCS records for 15 days prior to the accident
- Startup Procedure (for March 23, 2005)
- Trailer Siting MOC/Facility Siting Plan
- Witness statements and transcripts
- Training records
- Maintenance records
- MOC records
- Hazard analysis records
- HSE policies and procedures
- Staffing studies
- Witness Statements
- Organization Chart/Manning
- Process Safety Information, including Process & Instrument Diagrams and Engineering Drawings
- Process Hazard Analysis and Risk Assessments (Hazops and MARS etc.)
- Operating Procedures
- Safe Work Practices
- Authorization To Work (ATW) Permits issued at the time of the incident
- Equipment Isolation Procedures and Certificates (LOTO)
- Training Guides and records
- Mechanical Integrity, including equipment inspection records
- Management of Change records
- Incident Investigations, including records of past incidents
- Emergency Response logs
- Technical Reports
- Process Safety Booklets
- Plot plans
- Aerial photographs
- Video clips
- Refinery budgets and plans
- Facility siting plans

Appendix 13
Chronology of Additional Evidence

FATAL ACCIDENT INVESTIGATION REPORT

CHRONOLOGY OF ADDITIONAL EVIDENCE

Event Date	Event Start Time	Event or Condition	Source
1985		Splitter RVs	No. 1 Ultraformer Calculation Book Vol 2
1986		Pressure relief system study includes most of the existing RV's. F-20 Modification 18 inch - 150# connection added for new RV header. RV study states that existing 12" headers were at capacity.	Dwg B-4550-K-2629 Rev 2
12/19/1986		F-20 P&ID Approved For Construction	B-4550-G-2399
1986 - 1994		Process Safety Standard No. 6 Text "or when major modifications are made to the existing facility" added. "Major modification" not defined.	e-mail
9/16/1992		Amoco Oil Co., Engineering Spec 990-1 States "construction of new blowdown systems which discharge directly to atmosphere are not permitted."	Document
9/29/1993		HAZOP Action Item 46 Resolution-Add purge of 1240 SCFH of N2 split between 4 main headers. A Standard Operating Instruction should be written to inform Operations why, where and how much purge gas should be used. Inspection of the purge system should be added to an existing periodic unit checklist to ensure it is in service and operating correctly.	Letter
1994		Process Safety Standard No. 6 (current version) Section E states "1) New blowdown stacks which discharge directly to the atmosphere are not permitted.; 2) When the size of the existing facility is outgrown or when major modifications are made to the existing facility, existing blowdown systems which are still necessary should be replaced with connections to depressurize via another processing unit, hydrocarbon - recovery system, or flare."	e-mail
1994		F-20 Modification Multiple RV lines added to header to F-20 blowdown stack	DWG-4550-G-1378 REV 27
7/8/1994		Modification 3 inch relief valve line and relief valve VA 586-G (J50/50A discharge to 14 inch RV-3502-40 header) added.	B-4550-G-2636
7/15/1994		Modification RV-1199G and 3 inch RV-5711-40 (discharge of reflux pumps) added.	B-4550-G-2622 Revision 6
7/18/1994		F-20 Modification 2 inch nitrogen line added to F-20	B-4550-G-2746
12/29/1994		F-20 P&ID Approved for Construction	B-4550-G-2399
5/1/1995		API Recommended Practice 752 Recommended Practice was developed as a tool to aid compliance with 29 CFR 1910.119 Process Safety Management of Highly Hazardous Chemicals (PSM) requirements for addressing facility siting as part of a process hazards analysis (PHA).	Document

FATAL ACCIDENT INVESTIGATION REPORT

Event Date	Event Start Time	Event or Condition	Source
2Q 1995		Facility Siting Study	Report
1997		ISOM Control Room in Zone 2 (acceptable risk) F-20 Maintenance Vessel rebuilt/replaced	U1 Data Form - Eng Office
1997		1997 Facility Siting Review Locations of trailers endorsed.	Document
March 1997		API Recommended Practice 521 Guidance on design of atmospheric vent systems.	Document
11/5/1997		HAZOP Action Item 33: F-20 Blowdown Drum was evaluated and found to be adequate.	Letter
11/5/1997		HAZOP Action Item 33: Results of HAZOP study and Litwin relief valve documents indicated existing pressure relief systems are adequate.	Letter
4/24/1998		HAZOP Revalidation Consider connecting the temperature indicator on F-20 Blowdown stack (TE367) to DCS to help operator monitor operation. Alerts operator when there is a release of hot material.	HAZOP Report
4/24/1998		HAZOP Revalidation Consider locking open the valve in F-20 Blowdown Stack goose-neck overflow line to help prevent the valve from being closed which could cause high liquid level.	HAZOP Report
4/24/1998		HAZOP Revalidation Node 63. Identified an undesired consequence of major hydrocarbon release to blowdown drum, if the 8 inch bypass around Splitter relief valves was opened during startup.	HAZOP Report
4/24/1998		HAZOP Revalidation Node 63. Identified an undesired consequence of hydrocarbon release if there was a high level in the Splitter.	HAZOP Report
4/24/1998		HAZOP Revalidation Node 60. Identified an undesired consequence of hydrocarbon release to atmosphere if the quench valve to F-20 was closed.	HAZOP Report
4/24/1998		HAZOP Revalidation Node 63. Previous incident involved 8" inch chain-operated valve left open at startup. Installed sign at chain operator and modified startup procedure to slow tower warm up so that valve not needed.	HAZOP Report
March 1999		Splitter Modification Converted Splitter to operate with flooded accumulator, reconfigure Honeywell level alarms, and "use B-1101 furnace firing rate to control tower pressure".	MOC-ISOM-1998-009
4/12/1999		Operations Guidance Automatic control of the level in the Blowdown Drum is accomplished via the goose neck seal leg.	Training Guide 31
4/12/1999		Operations Guidance The preferred method of disposing of the liquid in the Blowdown Drum is via F-204 Charge Drum.	Training Guide 31

FATAL ACCIDENT INVESTIGATION REPORT

Event Date	Event Start Time	Event or Condition	Source
2000		Incident Investigation High discharge temperature on Recycle Gas Compressor due to opening of the "balancing line" between the suction and discharge. Not part of written procedure. Recommendations were: 1) training personnel in the AU2/ISOM/ARU complex on how to retrieve the most up-to-date procedures, 2) having a pre-startup meeting to improve communication, 3) reviewing and revising startup procedure, include alarm check list, and verify that balancing line block valve closed.	INV-ISOM-2000-001
10/16/2000		Organizational Change Consolidation of ISOM & AU2 optimization operator positions. Verify safe-off execution proficiency of both ISOM Asset & Optimization Operator. Optimization operators demonstrate proficiency via testing. Asset operators reviewed the safe-off scenarios.	MOC-ISOM-1999-006-016
10/16/2000		Organizational Change Perform ISOM safe-off gun drills on an annual basis, including review of procedures and physical walk-through of the action steps	MOC-ISOM-1999-006-017
10/16/2000		Organizational Change Revise ISOM planned startup and shutdown procedures to require an independent/dedicated Optimization operator during critical transitions.	MOC-ISOM-1999-006-023
2001		2 Board Operators required during "abnormal conditions". MOC action states "extend the requirement to have two control board operators for any planned startup or planned shutdown activities to include the NDU." Resolution was "added NDU to the required training matrix." MOC supersedes the staffing study, which was prior to NDU construction.	MOC-NDU-2001-002-012
6/1/2001		BPSH Relief System Design Guide Guidance issued for RV studies.	Document
2002		Incident Investigation Runaway thermal excursion of Penex reactor. Operators bypassed the reactors because of high MTBE results. Step in procedure missed when block valve not closed and feed continued to the reactor. Corrective actions were: 1) training all operators on the location of unit procedures and the need to use procedures for all tasks, 2) use of gun drills and other training techniques that will train operators in potential unit upset situations, and 3) operator review of safe-offs more frequently.	INV-ISOM-2002-001
1/18/2002		Trailer MOC Fluor construction trailer temporarily sited at catalyst warehouse during NDU Construction.	MOC-PWR2/OSU-2001-022
7/18/2002		2002 Facility Siting Review Locations of trailers endorsed including Fluor Daniels trailer west of ISOM.	Study report
9/1/2002		Operating Procedure SOP 201.0 for Splitter startup following a TAR created.	Document
9/23/2002		Operating Procedures SOP 201.0 and 201.1 (startup following a temporary outage) specify 'conduct a pre-startup review of the procedure with all crew members'.	SOP 201.1 & 201.0

FATAL ACCIDENT INVESTIGATION REPORT

Event Date	Event Start Time	Event or Condition	Source
11/18/2002		MOC Procedure Issued for all BPSH sites	MOC Procedure SH-PSM-10
12/11/2002		Clean Streams Project. New ISOM wet & dry maintenance drums. Scope did not include Splitter tower relief system.	Define Stage DSP Project R2-004P4 ISOM
2003		Operations Guidance. "The drain at each low point must be opened and left open until all condensate has drained."	Process Safety Booklet 4 "Safe Ups and Downs for Process Units"
2003		Internal Inspection of F-20. Shed trays collapsed. Corrosion found throughout vessel.	PCMS-ISOM-F-20
1/22/2003		Splitter Modification MOC approved for Splitter derating from 75 psig to 40 psig. Action to update startup procedures, but procedure on the server not updated prior to the incident. Procedure in Startup/Shutdown log book had been updated by hand.	MOC-ISOM-2003-005
1/31/2003		Splitter Modification Relief valve capacity reviewed. Springs changed out & set pressures staggered to 40, 41, & 42 psig.	MOC-ISOM-2003-005
2/1/2003		PHA Checklist Item 2 "Is the trailer located at least 350 feet from any process unit? If no, perform a facility siting analysis."	PHA Checklist
2/1/2003		PHA Checklist Item 9 "Were the following issues considered in regards to the proposed trailer locations: a) Types/quantities of product or hazardous chemicals?; b) Types of reactions and processes?; c) Ignition sources?; d) Direction and velocity of prevailing winds?"	PHA Checklist
2/7/2003		Splitter Derate MOC Consequence of tower pressure spikes above 40 psig identified as tower rupture. Safeguards identified as relief valves and operator awareness. No follow up actions.	MOC What If? Checklist
March 2003		ISOM Project Project for new wet and dry maintenance drums cancelled.	Project No. R2-004 PH DSP
3/4/2003		PHA Revalidation Action to conduct full ISOM unit RV study to verify adequate sizing of all RVs. Target date - 3/31/2005. Still open.	PHA report
3/4/2003		Operating Procedures SOP certification by Superintendent	Certification Form
3/25/2003		Maintenance Work Order Install derate tag on Splitter	SAP Order # 30030165207
4/1/2003		Major Accident Risk Assessment Top 80 risks identified, did not include ISOM.	MAR Assessment report
3/3/2004		Splitter Modification Derate MOC approved to commission	MOC-ISOM-2003-005
9/1/2004		Merit Trailer Installed prior to MOC being initiated.	Interview, MOC

FATAL ACCIDENT INVESTIGATION REPORT

Event Date	Event Start Time	Event or Condition	Source
9/1/2004		Merit Trailer Sited without MOC having Supt's approval to commission.	MOC-NDU-2004-008; MOC Procedure SH-PSM-10
9/17/2004		Merit Trailer Trailer checklist was completed. No mitigating actions for blast scenario.	MOC Checklist
9/27/2004		Merit Trailer MOC initiated to install a TAR trailer east of the NDU.	MOC-NDU-2004-008
9/29/2004		Merit Trailer MOC PHA report sent to Supt via e-mail & cc to PSM admin with request for Supt to approve the MOC to proceed	MOC-NDU-2004-008; e-mail
10/6/2004		Merit Trailer MOC approved to proceed	MOC-NDU-2004-008
10/6/2004		Merit Trailer MOC PHA actions assigned	MOC-NDU-2004-008
2/23/2005		ATW Permit issued to pull steam out blinds on F-1101	ATW
2/23/2005		ATW Permit issued to pull steam out blinds on F-1102	ATW
March 2005		Operating Procedures Procedures certified as current and accurate by the Superintendent	Interview
March 20 - 23, 2005		Shift Director's Log No direct reference to Splitter startup	Shift Director's Minutes
3/21/2005		Operations Supt Weekly Meeting No reference to Splitter startup.	Interview, Meeting minutes

Appendix 14

Scenario Assessment

**ASSESSMENT OF POTENTIAL CAUSES
OF RAFFINATE SPLITTER RELIEF EVENT
AT THE
BP, TEXAS CITY REFINERY ISOMERIZATION UNIT**

BakerRisk Project No. 01-1093-002-05

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August 24, 2005



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FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
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August 24, 2005*

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FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
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*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

Table of Contents

1.0 INTRODUCTION.....	1
2.0 POTENTIAL SCENARIOS	2
2.1 Scenario 1: Water Present in Column Bottom at Beginning of Startup	2
2.2 Scenario 2: Water Present in Upper Column Trays at Beginning of Startup	2
2.3 Scenario 3: Water Enters the Column with the Feed	3
2.4 Scenario 4: Temperature Rise in Preheater Flashes the Feed	3
2.5 Scenario 5: Light Ends (Butane) Enter the Column with the Feed	3
2.6 Scenario 6: Column Overflows with Liquid, Compressing Vapor in the Overhead System to a Pressure Above the PRVs Set Pressures	4
2.7 Scenario 7: Extension of Scenario 6 with Vapor Bubble Pushing Liquid Overhead....	4
2.8 Scenario 8: Water Enters the Column Prior to Starting the Heater Charge Pumps	5
2.9 Scenario 9: Water Enters Through Utility Line	5
2.10 Scenario 10: Light Hydrocarbon Enters the Column Via a Temporary Connection	6
3.0 EVALUATION OF WATER-BASED SCENARIOS	7
3.1 Temperature and Pressure Profiles.....	7
3.2 Theoretical Framework	8
3.3 Temperature Data Implications	9
3.4 Water Vapor Pressure and Flashing Could Explain Observed Pressure	14
3.5 Stage-Wise Calculations Develop Compositions Capable of Producing Sudden Surge in Pressure and Vapor Fraction Using Observed Temperatures	16
3.6 Postulated Flash Fraction	21
4.0 SUMMARY.....	26

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

List of Tables

Table 1. Identification of Instruments in Figure 1	7
Table 2. Temperature Data Analysis	9
Table 3. Tabulated Data and Comments.....	12
Table 4. Ideal Stage Calculations of Flooded Column Heated at the Bottom.....	17
Table 5. Predicted Flash Fraction at Observed Pressure and Temperatures.....	19
Table 6. Predicted Vapor Pressure at Observed Pressure and Temperatures	19
Table 7. Postulated Variables and Corresponding Temperatures	23
Table 8. Discharge Rates Through PRVs	23
Table 9. Summary of Piping and Vessel F20 Holdup Volumes	24
Table 10. Cumulative Discharge by Postulated Scenario	24

List of Figures

Figure 1. Temperatures and Pressure Data from PI System	7
Figure 2. Temperatures Near Feed Tray	10
Figure 3. Time for Feed Temperature Change to Reach Trays 27 and 33.....	11
Figure 4. Predicted Column Liquid Level	15
Figure 5. Observed Pressure Plotted Against Tray 59 Temperature Compared with Hydrocarbon Vapor Pressure Curve	15
Figure 6. Calculated Masses of Vapor and Nitrogen in the Column Vapor Space	16
Figure 7. Calculated Flash Curves at Ideal Stages Developing in Raffinate Splitter	18
Figure 8. Mass Fraction of Flashed Vapor for Ideal Stage Compositions at Tray 33 Temperature and Column Pressure	20
Figure 9. Vapor Pressure Curves for Ideal Stage Compositions	20
Figure 10. Water Vapor Pressure and Vapor Flash Fraction for 10% Water, Stage 2	21
Figure 11. Column Level with Postulated Flash Fraction	22

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

1.0 INTRODUCTION

In support of the team investigating potential causes of the explosion that occurred at BP's Texas City refinery Isomerization unit (Isom) on March 23, 2005, Baker Engineering and Risk Consultants (BakerRisk) was asked to assist in identifying and evaluating scenarios that could explain the events in the Raffinate Splitter. A list of potential failure mechanisms and a cursory evaluation of each is presented below in Section 2. A more detailed evaluation of the scenarios involving flashing of water follows in Section 3. It should be understood that the objective of this work was to evaluate a range of "what if's," considering the physical and chemical aspects of the Raffinate Splitter column. This work is intended to support the BP investigation committee, who are expected to consider a broader range of factors than analyzed here.

This analysis was developed using data provided to BakerRisk shortly after the incident. The analysis of water-based flash scenarios did not take into account recent suggestions that the overhead pressure indication PT5002 may not have been measuring the actual Raffinate Splitter column pressure. The analysis that follows should be interpreted in this light.

FATAL ACCIDENT INVESTIGATION REPORT

BP Americas, Inc.
TXC Isom Potential Cause Assessment

BakerRisk Project No. 01-01093-002-05
August 24, 2005

2.0 POTENTIAL SCENARIOS

The following is a list of scenarios to potentially explain what caused the Raffinate Splitter tower relief valves to lift and release material that caused the March 23, 2005 explosion. Each of these scenarios is described below, and evidence is discussed that supports or refutes the scenario.

2.1 Scenario 1: Water Present in Column Bottom at Beginning of Startup

In this scenario, water from earlier steam-out operations collected in the bottom of the Raffinate Splitter tower. During the course of the startup, some of this water gradually migrated to the upper trays of the column by vapor/liquid equilibrium. When a higher temperature reached the water, it flashed, resulting in an expanding vapor surge that pushed the liquid above it to the top of the column and into the rundown line.

Evidence in Support

After the incident, water was found in a splitter tower bottoms sample. If water was present and vapor/liquid equilibrium occurred at the bottom trays, water would have moved upward and concentrated higher in the column. This is because water has a larger equilibrium constant than the hydrocarbon feed components. Data recorded during the startup showed a pattern of increasing temperatures moving higher in the column. The sudden flash vaporization of water could have lifted a large column of liquid to the top of the column.

Evidence Against

The hydrostatic pressure profile, assuming all liquid, is higher than would be consistent with flashing water to vapor in the lower part of the column, which argues against this scenario. This would also require an explanation for the flashing occurring when the bottoms were cooling, rather than earlier. The possibility of water flashing is still open, but the evidence against this scenario predominates.

2.2 Scenario 2: Water Present in Upper Column Trays at Beginning of Startup

In this scenario, water from earlier steam-out operations collected at one or more trays in the upper part of the column. This water was heated and flashed by a hot temperature front coming from the reboiler or feed. The water flashed and generated a vapor surge that pushed liquid to the top of the column. This is similar to Scenario 1 except that the water was initially assumed to be in upper trays.

Evidence in Support

Scenario 2 is similar to Scenario 1 except that it does not require the vapor/liquid equilibrium mechanism to move the water from the bottom to higher locations in the column. In terms of explaining the relief through the PRVs, Scenario 2 is indistinguishable from Scenario 1. Tray 24 had a seal pan that could have prevented water from draining following the earlier steam-out operation.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

Evidence Against

The type of tray that could trap and hold liquid water exists only at Tray 24. The maximum amount of water that Tray 24 could hold is 3 inches in the trough for the downcomer, which is insufficient to displace the quantity of raffinate that flowed into the overhead line. The same uncertainty applies about whether the local temperature would have been high enough to flash water at the hydrostatic pressure.

2.3 Scenario 3: Water Enters the Column with the Feed

In this scenario, water enters the column with the feed. This water either flashes immediately in the feed heater or, after some delay, flashes when the feed temperature increases.

Evidence in Support

There is no supporting evidence.

Evidence Against

The water would have to pass through the bottoms stream of two distillation columns upstream of the Raffinate Splitter. There would have been noticeable upsets or unusually low temperatures in the bottom of these two columns, neither of which are supported by process data. The same uncertainty applies about whether the local temperature would have been high enough to flash water at the hydrostatic pressure.

2.4 Scenario 4: Temperature Rise in Preheater Flashes the Feed

Scenario 4 postulates that the feed began flashing just before the incident due to an increase in the feed temperature from heat exchange with the bottoms rundown flow. In this scenario the flashed vapor would lift the liquid above it to the top of the column and into the rundown line.

Evidence in Support

The recorded feed temperature was increasing substantially just before the pressure relief valves (PRVs) opened. The feed temperature increase resulted from both the action of the feed preheater and heat exchange with the column bottoms. The column bottoms flow had just begun when the feed temperature increase began.

Evidence Against

It is uncertain to what extent incoming vapors would collapse upon contact with cold column liquid.

2.5 Scenario 5: Light Ends (Butane) Enter the Column with the Feed

This is similar to Scenario 3 except that light hydrocarbons are introduced instead of water. The light hydrocarbon could result from an upset in the upstream distillation columns or from misrouting in upstream piping. The light hydrocarbon would have flashed in the feed preheater

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

if introduced just before the overpressure event, or it could have been introduced earlier and flashed when a hot temperature front reached it in the column.

Evidence in Support

For the column pressure to exceed the set point of the PRVs would require a substantial amount of butane in the feed, but the vapor pressure of butane could reach the pressure required in this scenario. Additional pentane in the feed would not provide enough vapor pressure. Propane is unlikely to be have been present.

Evidence Against

As with Scenario 3, for butane to have been present in the feed in abnormal amounts requires that it pass through the bottoms of two upstream distillation columns. There is no evidence of an upset in these upstream columns just prior to the PRVs opening in the Raffinate Splitter. There is also no evidence of a temporary upset in the feed drum.

A review of the P&IDs indicated no piping lineups that would introduce butane into the Raffinate Splitter. Candidate lines, such as the 8-inch line 0-1011-40 and the 6-inch line 0-1010-40 to the pump-out header shown on the right side of Drawing B-4550-893, should normally flow away from, not toward the column. There is no evidence that they were open to the Raffinate Splitter.

2.6 Scenario 6: Column Overflows with Liquid, Compressing Vapor in the Overhead System to a Pressure Above the PRVs Set Pressures

In this scenario the column fills with liquid and overflows into the overhead reflux rundown line. Overflowing liquid traps gases in the overhead condenser and reflux drum and compresses them until the pressure exceeds the relief pressure.

Evidence in Support

Liquids were shown to have passed overhead from the column into the reflux drum.

Evidence Against

To obtain the observed pressure spike, this scenario requires a high flow rate or plug flow of liquid in the overhead line, rather than an overflow that would allow gas to counter flow. At the time of the incident, bottoms rundown was underway, with a net reduction in mass of raffinate in the tower. Even without the rundown, the feed flow rate was insufficient to supply the material that discharged through the PRVs.

2.7 Scenario 7: Extension of Scenario 6 with Vapor Bubble Pushing Liquid Overhead

This scenario assumed that a vapor “bubble” developed, such as in Scenario 1, in which water was suddenly vaporized. This pushed the liquid above the flash point up the column and into the vapor overhead line. This sudden outflow generated the plug flow needed to compress gases in

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

the accumulator.

Evidence in Support

The evidence supporting this scenario is the same as for Scenario 6. This scenario overcomes the plug flow arguments against Scenario 6.

Evidence Against

The hydrostatic pressure profile, assuming all liquid, is higher than would be consistent with flashing water to vapor.

2.8 Scenario 8: Water Enters the Column Prior to Starting the Heater Charge Pumps

In this scenario, water leaked into the column bottoms system via a tube leak in C-1106A/B Heavy Raffinate Product Coolers. The raffinate is usually the high-pressure side of this heat exchanger, but prior to 9:41 a.m. on March 23, 2005, the J-1103A/B Heater Charge Pumps (i.e., the bottoms pumps) were not turned on. If cooling water was being supplied to the C-1106A/B tubes and there was a tube leak, there would be pressure to drive cooling water into the bottoms system. If the product rundown were blocked in, this could back into the column.

Evidence in Support

Water was found in a column bottoms sample. Depending upon the circumstances, enough water could be available in this scenario to support a water-flashing scenario.

Evidence Against

The evidence against previous scenarios involving flashing water is also against this scenario. The bottoms pump(s) would need to be lined up for operation (unblocked), and the check valves on the pump discharges would have to leak through.

2.9 Scenario 9: Water Enters Through Utility Line

A 6-inch service water line that ties directly into the column bottom could have leaked.

Evidence in Support

Water was found in a column bottom water sample.

Evidence Against

The evidence against previous scenarios involving flashing water is also against this scenario. This would require an unlikely lineup mistake, and there is no evidence of such a water leak.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

2.10 Scenario 10: Light Hydrocarbon Enters the Column Via a Temporary Connection

This scenario assumes that light hydrocarbons entered the column through a temporary hookup that is not shown on the P&IDs. Such hookups are sometimes used during startups, although there has been no suggestion that such a lineup took place in this case.

Evidence in Support

There is no evidence supporting this scenario.

Evidence Against

There is no precedent for using such a temporary hookup during previous startups of the Raffinate Splitter. In addition, since the overpressure event occurred several minutes after the feed temperatures increased, this indicates that either: (a) the temporary hookup would have to have been made at the same time as other process moves (an unlikely coincidence), or (b) butane accumulated in the column after an earlier connection, in which case its vapor pressure should have been observed earlier as the column warmed.

3.0 EVALUATION OF WATER-BASED SCENARIOS

BakerRisk was asked to evaluate the credibility of a “water flashing” scenario, as described in several scenarios presented in Section 2. This case presupposes that water has entered the splitter through some means. An evaluation of such a scenario is presented below.

3.1 Temperature and Pressure Profiles

Data from the PI process data system are shown in Figure 1. The data channels are identified in Table 1.

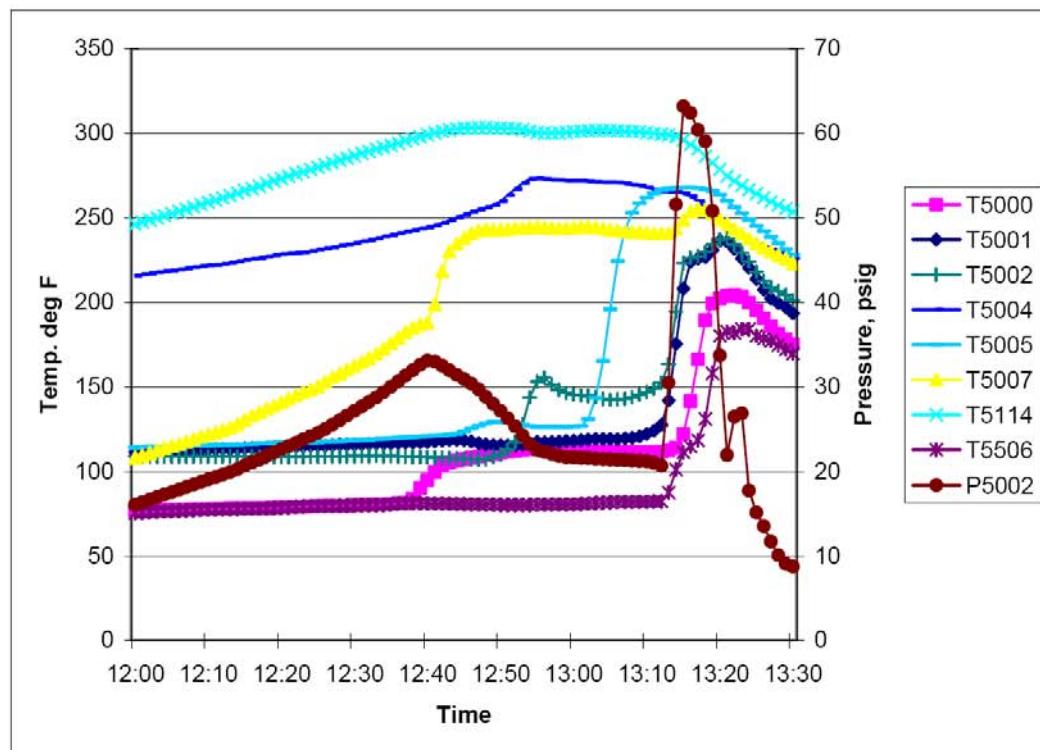


Figure 1. Temperatures and Pressure Data from PI System

Table 1. Identification of Instruments in Figure 1

Instrument	Description	Elevation Above Column Bottom (ft)
T5506	Overhead temperature	--
P5002	Overhead pressure	--
T5000	Tray 13 temperature	140.2
T5001	Tray 27 temperature	108.7
T5005	Feed temperature (feed enters at Tray 31)	--

FATAL ACCIDENT INVESTIGATION REPORT

BP Americas, Inc.
TXC Isom Potential Cause Assessment

BakerRisk Project No. 01-01093-002-05
August 24, 2005

Instrument	Description	Elevation Above Column Bottom (ft)
T5002	Tray 33 temperature	95.2
T5007	Tray 48 temperature	63.7
T5004	Tray 59 temperature	40.7
T5114	Bottoms temperature	--

3.2 Theoretical Framework

By about 12:00 p.m., the Raffinate Splitter is assumed to have been filled with liquid above the feed tray and heated by the reboiler. This could give rise to essentially a partial distillation column inside the actual column. The hot liquid in the bottom of the column would reach a saturation point and vapor would be generated. The vapors would condense in the cold liquid slightly higher in the column. That is, in some trays vapor/liquid flows act like a column at total reflux. Lighter components are enriched in the condensing liquid and heavier components accumulate in the lower section.

Figure 1 shows approximate step temperature “waves” that move progressively up the column. A scenario considered was that the timing and amplitudes of the step changes indicated vapor condensing higher and higher in the column. With this interpretation, an internal temperature (and therefore concentration) gradient was being established.

There is a local temperature inversion from about 12:00 to 12:40, when Tray 27 (TI5001) is warmer than Tray 33 (TI5002). The likely explanation for this anomaly is that this is when the operators manually vented the column. During the resulting pressure decrease, hydrocarbon vapors could have flashed and displaced nitrogen farther up the column.

If water was initially present in the bottom of the column, it can be shown that water could concentrate into the vapor phase and be driven up the column. The K_e value (vapor/liquid mole fraction) for water ranges from 5.2 at the column bottom temperatures to 1.2 at the mid-column temperatures. Water would condense by contact with cold liquid farther up the column, and tend to accumulate in the cold liquid. This could also happen with light hydrocarbon components.

An accumulated concentration of water would flash much differently than a broad range mix of hydrocarbons. It would behave more like a single component. Instead of the flash fraction gradually increasing with the increasing temperature, the flash fraction of a water mixture could increase to above 50% by mass over a small temperature range. If water accumulated below a large section of colder liquid, the sudden flash of water vapor could drive the liquid above it, compressing the vapor space above. This might produce both the pressure pulse that caused the PRVs to open and an initial outflow of liquid.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

3.3 Temperature Data Implications

Temperature “waves” are evident in Figure 1 at the times listed in Table 2 below.

Table 2. Temperature Data Analysis

PI Time	Sensor	Observation
12:40	T5007 (yellow) P5002 (brown circles)	Temperature wave passes Tray 48. As a vent valve is opened, the column pressure drops, and the temperature below Tray 48 warms by \approx 50 °F.
12:40	T5000 (pink)	Tray 13 also warms (\approx 35 °F) as warm hydrocarbon vapor replaces nitrogen.
12:42	T5002 (light blue)	Tray 33 (two trays below feed) also warms by about 10 °F.
12:52	T5002 (light blue)	Tray 33 warms by \approx 30 °F.
12:52	T5004 (medium blue)	Tray 59 warms by \approx 25 °F.
13:02	T5005 (pale blue)	Feed temperature to Tray 31 begins a fast rise, but temperatures above feed (Tray 27) and below feed (Tray 33) lag considerably.
	Postulate	Heavy raffinate flow begins generating hotter feed by heat exchange. Feed flashes so part of the feed goes up the column and part down.
13:12	T5002 (light blue)	Tray 33, below feed tray, warms by 110 °F.
13:12	T5001 (dark blue)	Tray 27, above feed tray, warms by 80 °F.
	Conclude	Feed temperature increase is felt above and below feed tray at times consistent with the discussion below using Figures 2 and 3, implying some fraction of the feed moves up the column as vapor.
13:14	T5000 (pink)	Tray 13 warms by 80 °F to level out 25 °F under that of Trays 27 & 33.
13:14	T5506 (purple)	Overhead line increases by 100 °F to peak and then levels out just under that of Tray 13.
13:14	Conclude	The liquid-filled column is replaced by a more normal temperature profile representative of vapor/liquid equilibrium.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

Figure 2 focuses on temperatures near the feed tray at the time of the major increase in feed temperature. The influence of flashing of the feed can be inferred from the increase in temperatures at Trays 27 and 33.

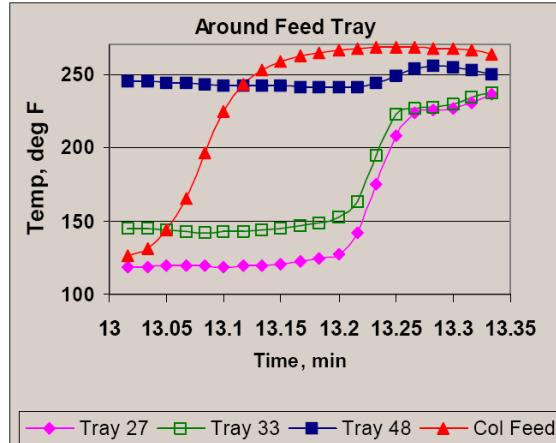


Figure 2. Temperatures Near Feed Tray

There is some indication in the temperature profiles that the column may have had vapor flow as well as liquid flow shortly before the release. To evaluate this, first assume the column below the feed tray is liquid-filled, and the feed experiences a step increase in temperature. A lower interface of hot liquid from the feed tray would move downward at a velocity, u_L . This velocity is simply the outflow of heavy raffinate, F_{HR} , divided by the cross-sectional area of the column, A_{col} .

$$u_L = \frac{-F_{HR}}{A_{col}}$$

The hot liquid accumulates above this lower interface, so the velocity of the upper hot interface, u_{up} , has the contribution of the liquid (unflashed) feed, $(1-x)F_D$, where x is the flash fraction of feed, or:

$$u_{up} = \frac{(1-x)F_D - F_{HR}}{A_{col}} .$$

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

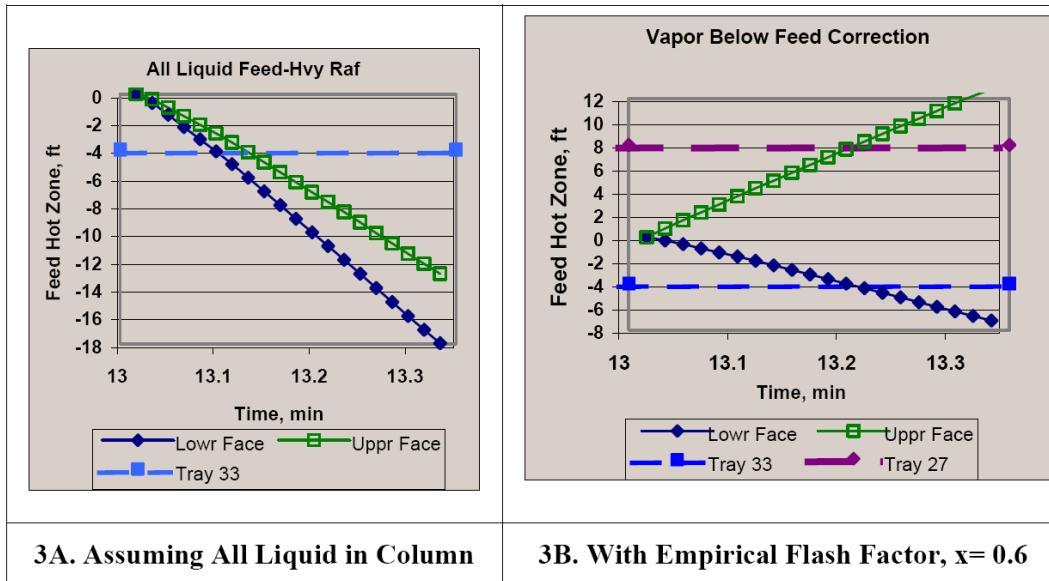


Figure 3. Time for Feed Temperature Change to Reach Trays 27 and 33

After 13:00 hrs, the heavy raffinate discharge exceeded the feed rate, so both u_L and u_{Up} would be negative if the feed was entirely liquid. The upper and lower interfaces, shown in Figure 3A, would decrease so neither interface reaches Tray 27 and Tray 33 at the observed time. Clearly, there must be a mechanism to move the interfaces upward. Vapor flow is one viable mechanism.

An empirical relationship that provides the correct overall interface velocities is:

$$u_L = \frac{-0.4F_{HR}}{A_{col}} \quad \text{and} \quad u_{Up} = \frac{1.6F_D - 0.4F_{HR}}{A_{col}}$$

These interface velocities were used to plot Figure 3B, in which the interface arrival times at Trays 27 and 33 match observations. By analogy, the empirical relationships imply that the vapor rate decreases the downward velocity of the lower interface and increases the upward velocity of the upper interface by 60%.

Additional evidence concerning temperature waves is discussed in Table 3 with added comments.

Table 3. Tabulated Data and Comments
(red entries denote significant change in a reading)

3/23/2005	I1F5000.pv	I1F5015.pv	I1F5007.pv	I1P5002.pv	I1T5005.pv	I1T5506.pv					I1T5114.pv	
	Feed	Raff Splitter Bottoms Prod R/D	Tower Reflux	Raff Split. OH Press.	Tower Feed Temp.	Raff Split. OH Temp	Tray #13	Tray #27	Tray #33	Tray #59	Raff Split.Btm Temp	INTERPRETATION
3/23/2005 12:50	19.5	3.1	0	27.52	129.2	80.4	112.0	116.5	136.5	269.6	303.0	
3/23/2005 13:00	19.8	4.6	0	21.66	126.2	80.7	111.6	119.0	143.7	270.7	300.7	
3/23/2005 13:05	20.5	27.8	0	21.43	179.8	81.7	111.6	119.0	142.0	270.9	301.7	Start of increase in feed temp, which corresponds to a slowly declining bottoms temp as the heat from the bottoms is transferred to the feed tray.
3/23/2005 13:06	20.5	27.8	0	21.38	211.8	82.0	111.5	118.9	142.4	270.7	301.5	
3/23/2005 13:07	21.0	27.7	0	21.33	235.2	82.0	111.5	119.3	142.8	270.1	301.5	
3/23/2005 13:08	20.6	30.2	0	21.28	248.6	82.1	111.4	119.7	143.6	269.4	301.0	
3/23/2005 13:09	21.0	31.0	0	21.24	256.1	82.1	111.3	120.5	145.1	268.8	301.0	The feed temperature has increased ≈130°F since 13:00, yet the tray temperatures above and below respond more slowly. The feed rate is about 14 bbl/min, and the space between Trays 27 and 33 is about 300 bbl. Thus a considerable quantity must be warmed.
3/23/2005 13:10	21.0	31.0	0	21.19	260.3	82.2	111.2	121.9	146.6	267.8	300.7	
3/23/2005 13:11	21.0	31.0	0	21.14	263.2	82.2	111.3	124.0	148.8	266.4	300.1	
3/23/2005 13:12	21.0	31.0	0	20.82	265.3	82.3	111.5	127.4	152.3	265.5	299.6	

3/23/2005	I1F5000.pv	I1F5015.pv	I1F5007.pv	I1P5002.pv	I1T5005.pv	I1T5506.pv				I1T5114.pv	
3/23/2005 13:13	21.0	31.0	0	20.50	266.8	82.3	112.3	141.7	163.4	265.1	299.1
3/23/2005 13:14	20.9	31.0	0	40.68	267.6	94.3	113.8	175.2	194.3	264.9	298.5
3/23/2005 13:15	21.0	31.1	0	62.37	267.5	108.1	121.8	208.0	222.8	264.4	297.3
3/23/2005 13:16	21.0	32.6	0	63.62	267.8	113.1	141.3	223.7	226.1	262.5	294.4
3/23/2005 13:17	21.0	32.3	33.9	61.08	267.7	115.7	166.0	225.8	227.0	259.5	292.4
3/23/2005 13:18	21.1	31.8	35.7	59.69	267.2	121.2	189.3	226.4	229.5	256.0	288.4
3/23/2005 13:19	21.0	31.5	35.7	58.34	266.6	142.4	199.1	230.7	233.8	252.6	284.3
3/23/2005 13:20	19.2	30.9	35.7	42.90	264.8	174.0	202.0	236.2	236.8	248.8	280.9
3/23/2005 13:21	20.7	30.4	35.7	24.44	261.9	182.6	203.7	235.7	237.5	244.8	276.1
3/23/2005 13:22	20.9	30.2	35.7	19.65	258.0	181.1	204.2	231.3	233.9	241.0	273.2

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

At just after 13:12, the indicated overhead pressure increased rapidly and the PRVs lifted. Potential mechanisms for the pressure increase were discussed in Section 2, including:

- 1) The liquid level in the column rises suddenly by material balance (more feed in and less product out) and compresses the vapor space in the top of the column.
- 2) A temperature wave moves up the column and reaches the point where water has accumulated, and suddenly the partial pressure of water becomes significant.
- 3) The temperature wave moves up the column and heats the water above its saturation point. The water suddenly flashes and drives upward the liquid above, compressing the vapor above the liquid.
- 4) A change of feed composition occurs so light components are suddenly introduced into the column.
- 5) Feed vaporizes due to heat exchange with heavy raffinate rundown. Hydrocarbon vapors in the feed lift liquid above the feed level and cause liquid to flow out the overhead line.

Alternative 1) can be ruled out by calculating the column level using a material balance on the column, making assumptions about the actual vs. recorded flows. This is done with a spreadsheet model, assuming non-flashing liquid build up. All flows to and from the column are included in the balance, including reflux and discharge rates. For reflux rate, a single pump design rate of 1509 gpm was used instead of the meter reading that was pegged at maximum. (A full reflux accumulator could deliver at the pumping rate for about four minutes.) The column was divided into five zones centered on the available thermocouples. The thermocouples are:

- 1) T5004 (just under Tray 59)
- 2) T5007 (just under Tray 48)
- 3) T5002 (just under Tray 33)
- 4) T5001 (just under Tray 27)
- 5) T5000 (just under Tray 13)

The locations of these thermocouples are described in Table 1. Liquid densities, calculated using a 15-component raffinate feed composition, were used in the spreadsheet as a function of temperature to give the predicted column level profile shown in Figure 4.

3.4 Water Vapor Pressure and Flashing Could Explain Observed Pressure

In the period between 13:12 and 13:20, the indicated overhead pressure rose rapidly, the PRVs opened, and a substantial mass discharged through the PRVs. In this period it is necessary to explain what caused the high pressure and whether the liquid level was pushed to the top of the column, giving a liquid discharge from the column.

The observed pressure is plotted in Figure 5 against the Tray 59 temperature and compared with the vapor pressure curve of the raffinate mixture. The difference between the observed and theoretical curves may be accounted for by the partial pressure of nitrogen. After 13:12, the indicated pressure exceeded the vapor pressure curve and then settled down to the vapor pressure curve after the nitrogen had been discharged.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

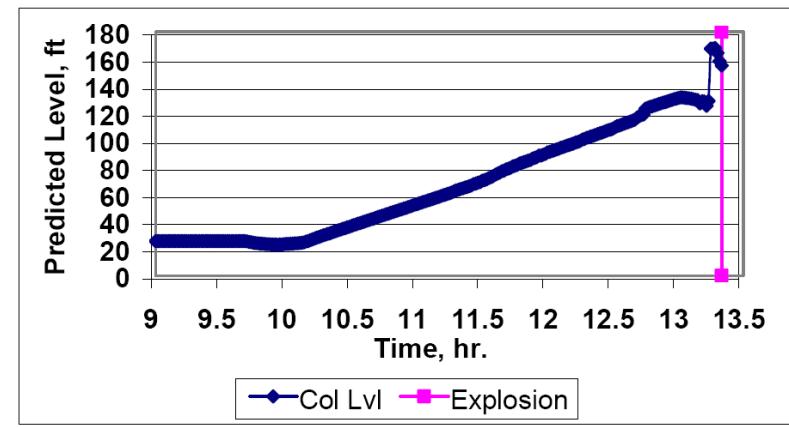


Figure 4. Predicted Column Liquid Level

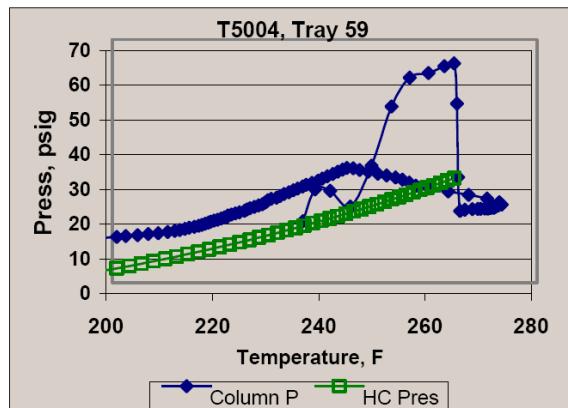


Figure 5. Observed Pressure Plotted Against Tray 59 Temperature Compared with Hydrocarbon Vapor Pressure Curve

To explain the observations between 13:12 and 13:20, we need additional information:

- 1) The water vapor pressure, P_{vw}
- 2) A flash fraction with water, x_v , at some zone in the column

In the spreadsheet model, we calculated the partial pressures of hydrocarbon, nitrogen, and water. The temperature for the top zone was taken to obtain the vapor pressure of hydrocarbon using the 15-component raffinate feed mixture in the SafeSite_{3G}TM model and the STRAPP model. For simplicity, the contribution of water was taken as negligible until the major pressure spike at 13:12. This allowed the partial pressure of nitrogen to be found as the difference between the indicated overhead pressure and the hydrocarbon vapor pressure up to time 13:12. After 13:12, the mass of nitrogen was assumed constant (or absent), and the vapor pressure of

FATAL ACCIDENT INVESTIGATION REPORT

BP Americas, Inc.
TXC Isom Potential Cause Assessment

BakerRisk Project No. 01-01093-002-05
August 24, 2005

water was found by difference. That is, the molecular weight of vapor, M_{vap} , was calculated as the molar average of the molecular weights of hydrocarbon, M_{HC} , nitrogen, M_{N2} , and water, M_w . The vapor density, ρ_{vap} , was found using the vapor mole weight, the indicated overhead pressure, and the temperature above the liquid (usually Tray 13). The vapor density times the vapor space volume gave the mass of vapor, m_{vap} . The mass of nitrogen, m_{N2} , mole weight of nitrogen, M_{Nw} , density of nitrogen, ρ_{N2} , and partial pressure of nitrogen, P_{N2} , were all proportional to the mass of vapor, m_{vap} , mole weight of vapor, M_{vap} , density of vapor, ρ_{vap} , and column pressure:

$$\frac{m_{N2}}{m_{vap}} = \frac{M_{N2}}{M_{vap}} = \frac{\rho_{N2}}{\rho_{vap}} = \frac{P_{N2}}{P_{col}}$$

Thus, the partial pressure of nitrogen was the mass ratio of nitrogen to total vapor times the column pressure, so the partial pressure of water can be found by difference.

Figure 6 shows the predicted mass of vapor and of nitrogen over time. The mass of hydrocarbon vapor increased as the surface temperature and vapor pressure of hydrocarbon increased. The mass of nitrogen should remain constant except when nitrogen was bled off at around 9:20 and when the PRVs open at 13:13.55. Figure 6 shows that the spreadsheet calculation satisfies this expectation up to 13:12.

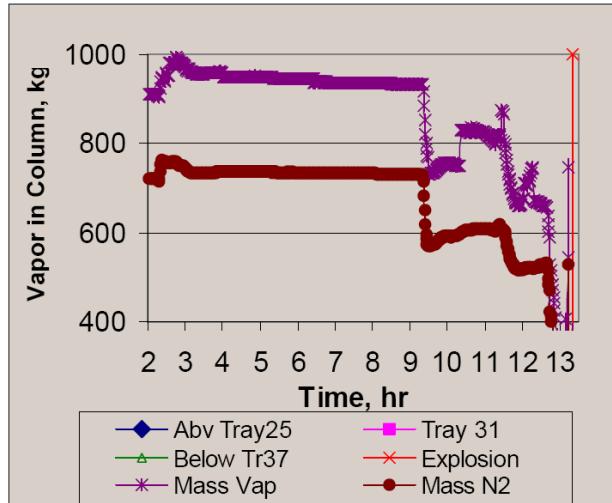


Figure 6. Calculated Masses of Vapor and Nitrogen in the Column Vapor Space

3.5 Stage-Wise Calculations Develop Compositions Capable of Producing Sudden Surge in Pressure and Vapor Fraction Using Observed Temperatures

In the absence of a rigorous stage-to-stage distillation column model, we can nonetheless indicate how water could be driven up the column and concentrated at a point higher in the column. The STRAPP model was used to calculate vapor composition from the raffinate feed

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

composition plus assumed water concentrations (5 and 10 mole%). The calculated vapor concentration was then taken as the feed for a Stage 2 calculation. This was repeated for a Stage 3 calculation. The pressure used was the steady overhead pressure indicated from 10:00 to 13:00 (22 psig or 36.7 psia).

The calculated results in Table 4 below indicate that the temperature profile for a 3-stage system at 36.7 psia would extend from around 230 to 159 °F (vapor generation to condensation). Vapor and liquid flows would reach equilibrium over the trays in that range as long as there was enough water to produce a concentration profile ranging from 0.05 mole fraction in the bottom to 0.668 mole fraction at the upper condensation point.

Table 4. Ideal Stage Calculations of Flooded Column Heated at the Bottom

Stage	Mole Fraction Water in Feed	Temp °F	x_v Mass Fraction of Vapor	K_e for Water	Vapor Mole Fraction Water
1	0.05	225	2E-6 (a)	4.7	0.248
		226	0.0104	4.7	0.241
		230	0.0619	4.9	0.210
2	0.210	181.2	2E-6 (a)	2.7	0.569
		182	0.0161	2.8	0.562
		184	0.0539	2.9	0.544
3	0.544	159	2E-6 (a)	1.2	0.650
		159.1	0.0518	1.2	0.655
		159.4	0.236	1.3	0.668

(a) Bubble point

If the initial concentration of water was higher, the temperature range for an ideal three-stage system would be lower, as shown in Figure 7. Figure 7 plots the vapor fraction against temperature from Table 3, and for similar data but with an initial mole fraction of water of 0.10.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

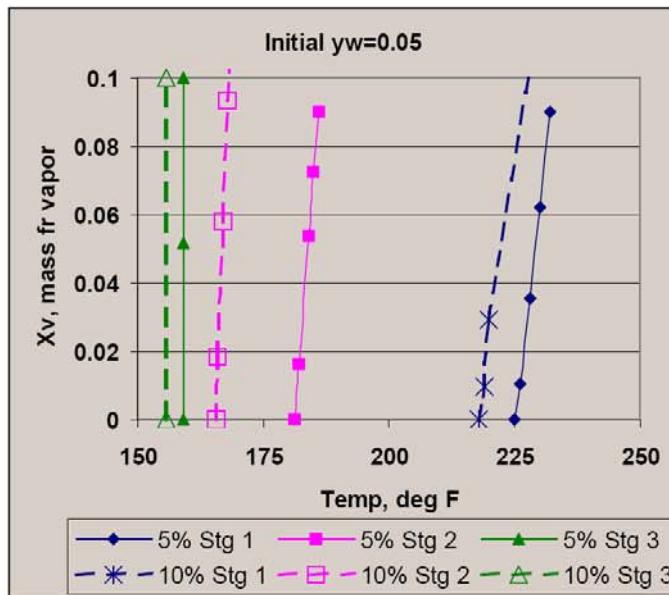


Figure 7. Calculated Flash Curves at Ideal Stages Developing in Raffinate Splitter

Figure 7 indicates that the flash curve is steep and becomes steeper as the water concentration increases. *That is, the higher the water concentration in a mixture, the more it acts like a pure component upon flashing.*

This point is further developed considering the flash fraction and vapor pressure of the ideal stage compositions. Table 5 and Table 6 list the predicted flash fraction and vapor pressure if the “ideal stage” water concentrations were on Tray 33. The data in Table 5 and Table 6 are plotted in Figures 8 and 9.

Figure 8 shows that a large and sudden vapor flash is predicted for the 5% Stage 3 and 10% Stage 2 compositions if located on Tray 33, beginning at 13:15. The temperature on Tray 33 exceeds 222 °F at that time. Figure 9 also indicates that light material containing a large fraction of water, if heated above 222 °F, would produce the peak pressures seen in Figure 1 of around 60 psig (74.7 psia).

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

Table 5. Predicted Flash Fraction at Observed Pressure and Temperatures

Time hr: min	P5002 psia	Tray 33 T5002, °F	x _V , Mass Fraction Vapor		
			5% Stage 2	5% Stage 3	10% Stage 2
13:12	35.36	152.30	0	0	0
13:13	45.124	163.35	0	0	0
13:14	66.229	194.27	0	0	0
13:15	77.872	222.82	0	0.836	0.258
13:16	77.073	226.11	0	0.919	0.358
13:17	75.056	227.03	0	0.972	0.4214
13:18	73.708	229.52	0	1	0.496
13:19	65.424	233.81	0.169	1	0.718
13:20	48.371	236.80	0.735	1	1

Table 6. Predicted Vapor Pressure at Observed Pressure and Temperatures

Time hr: min	P5002 psia	Tray 33 T5002, °F	Vapor Pressure, psia		
			5% Stage 2	5% Stage 3	10% Stage 2
13:12	35.36	152.30	23.76	32.87	31.2
13:13	45.124	163.35	28.2	39.38	37.14
13:14	66.229	194.27	44.07	63	58.42
13:15	77.872	222.82	63.95	93.3	85.18
13:16	77.073	226.11	66.6	97.4	88.76
13:17	75.056	227.03	67.36	98.5	89.78
13:18	73.708	229.52	69.43	101.75	92.59
13:19	65.424	233.81	73.13	107.5	95.57
13:20	48.371	236.80	75.8	111.65	101.165

FATAL ACCIDENT INVESTIGATION REPORT

BP Americas, Inc.
TXC Isom Potential Cause Assessment

BakerRisk Project No. 01-01093-002-05
August 24, 2005

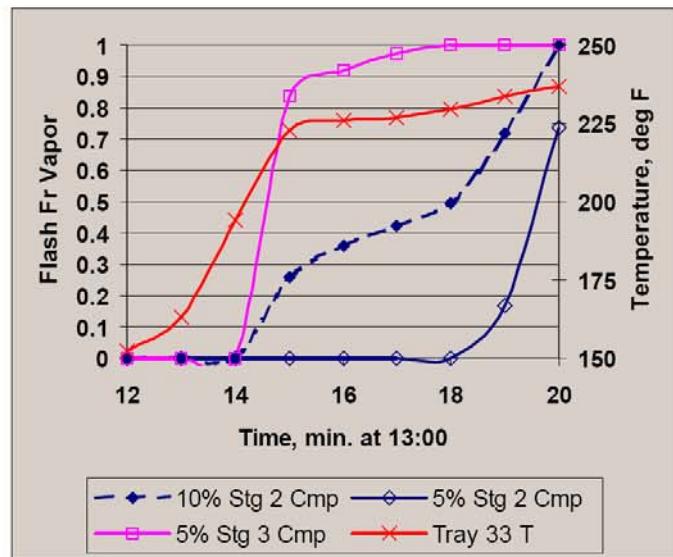


Figure 8. Mass Fraction of Flashed Vapor for Ideal Stage Compositions at Tray 33 Temperature and Column Pressure

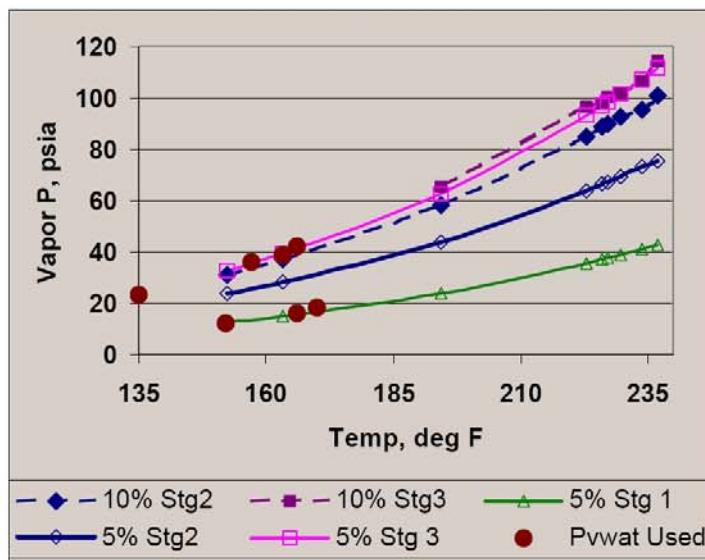


Figure 9. Vapor Pressure Curves for Ideal Stage Compositions

3.6 Postulated Flash Fraction

To evaluate the above theory, we put one of the vapor fraction curves from Table 4 into the spreadsheet, and predicted the column liquid level in the period 13:12 to 13:20. Figure 10 plots the partial pressure of water found by difference from the total indicated pressure after 13:12. Also plotted is an assumed flash fraction, x_v , using as a peak value the x_v found for 10% water, Stage 2 from Table 5 for the time 13:15. The values used in the figure and subsequent discussion are from a previous version of the analysis, but in any case illustrate the principle of water flash as a mechanism for liquid transport. The other x_v points are taken to follow the vapor pressure curve because the temperature measurements in the column are sparse. Further, in the time 13:16 to 13:20, the water vapor would likely move up and out the column so the flash fraction would drop along with the partial pressure of water. This also assumes that all of the nitrogen and vapor is discharged immediately after the PRVs open.

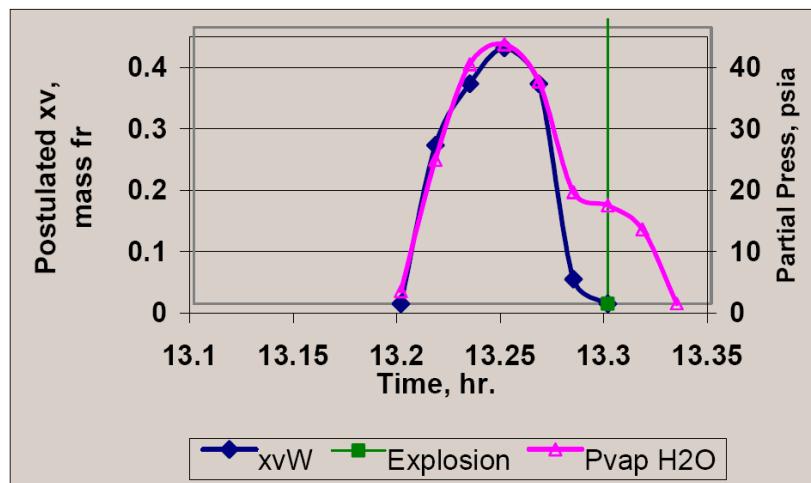


Figure 10. Water Vapor Pressure and Vapor Flash Fraction for 10% Water, Stage 2

We need to find how much “swell” will occur if a slice of liquid containing water flashes. Assuming a zone filled with liquid containing a concentration of water occurs with a vertical length of Δz_w , the mass in this zone, m_w , is:

$$m_w = \Delta z_w A_{col} \rho_{Liq}$$

When a portion of the liquid in this zone flashes to produce x_v mass fraction of vapor, the two-phase density applies, ρ_{2p} , and the volume of the zone increases to Δz_{2p} . The mass stays the same so:

$$m_w = \Delta z_{2p} A_{col} \rho_{2p}.$$

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

The two-phase density is given in terms of the liquid density, ρ_{Liq} and vapor density, ρ_{vap} , by:

$$\rho_{2p} = \frac{1}{\frac{x_v}{\rho_{vap}} + \frac{(1-x_v)}{\rho_{Liq}}}$$

Thus, the swell to Δz_{2p} is given by:

$$\Delta z_{2p} = \Delta z_w \frac{\rho_{Liq}}{\rho_{2p}}$$

We postulate water in a zone of length Δz_w , of 2 feet. With the flash curve in Table 5, the swell is added to the level without swell to produce the level plotted in Figure 11.

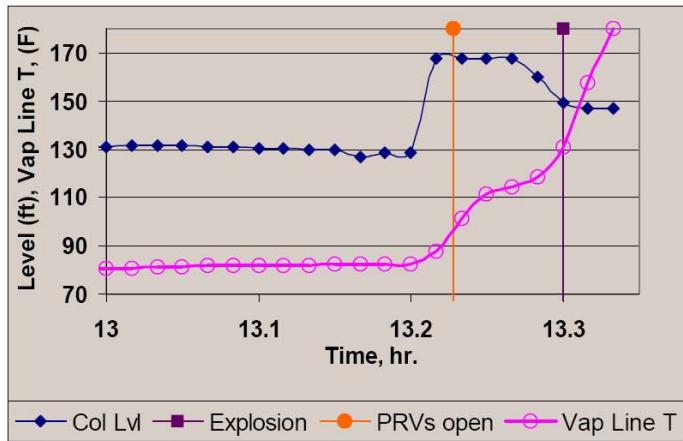


Figure 11. Column Level with Postulated Flash Fraction

In Figure 11 the level in the column is pushed to the top of the column for three minutes. The temperature in the vapor line is also shown. With this level pattern the discharge through the PRVs would be consistent with the vapor line temperatures. That is:

- Vapor discharges for less than 1 minute.
- Cold liquid discharges for three minutes.
- Hot two-phase material discharges for three minutes.

The postulated values for vapor fraction, taken from Table 5, are partially restated in Table 7. These are used in the spreadsheet to produce the levels plotted in Figure 11. The calculated partial pressures of water plotted in Figure 10 are also listed in Table 7 along with saturation temperatures interpolated from and plotted on Figure 9 as the brown circles. Two different compositions are needed, requiring that water be removed from the column in this scenario.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
TXC Isom Potential Cause Assessment*

*BakerRisk Project No. 01-01093-002-05
August 24, 2005*

Table 7. Postulated Variables and Corresponding Temperatures

Time hr: min (hr)	x _v	Δz _{2p} - Δz _w ft	P _{VW} psia	T _{sat} °F
13:12 (13.200)	0	0	2.07	
13:13 (13.217)	0	0	23.45	135
13:14 (13.233)	0	0	38.98	163.25
13:15 (13.250)	0.258	46.54	42.27	166
13:16 (13.267)	0.358	56.05	36.18	157
13:17 (13.283)	0.4214	48.26	18.16	170
13:18 (13.300)	0.1	11.29	16.01	166
13:19 (13.317)	0	0	12.13	152
13:20 (13.333)	0	0	0.0	

The saturation temperatures in Table 7 are in the range of observed values in the period after 13:12 for T5001 and T5002 (Tray 27 and feed Tray 33). They are below the temperatures for Tray 48 (T5007) and the feed temperature (T5005), shown in Figure 1.

The vapor discharge rate calculated over the period 13:12 to 13:20 is compared in Table 8 with calculated liquid and two-phase discharge rates. The yellow shaded portions indicate when each rate would be applicable according to the above postulated water-flashing scenario. The vapor rate includes material leaving both the column PRVs and a 1.5 inch bypass line around the reflux drum PRV that was reported to have been opened.

Table 8. Discharge Rates Through PRVs

Time	Vapor PRV F _{dis} , kg/s	Vapor 1.5" Line F _{dis} , kg/s	Discharged Vapor kg	Liquid PRV F _{dis} kg/s	Discharged Liquid kg/min	Two-Phase F _{dis} kg/s
13:12	0	0	0	0		0
13:13.55	33.46	0.90	379.5 in 11 s	202.1	3234 in 16 s	
13:14	37.82	1.07	0	221.4	13,284	
13:15	45.46	1.27	0	242.7	14,562	
13:16	44.83	1.25		241.00	14,460	
13:17	43.48	1.21		237.80		≈83.1
13:18	42.17	1.17		234.30		"
13:19	36.45	0.99		216.70		"
13:20	26.31	0.69		171		"

Next, we wish to find how the material discharged from the Raffinate Splitter distributes through the connecting piping and the Blowdown Vessel F20. Then we can estimate the hydraulic pressures in this system and the conditions leading to discharge out of F20. The discharged material passes through the 14-inch piping to Vessel F20 having the volume and cross-sectional areas summarized in Table 8. No outflow from F20 to the sewer is included here.

FATAL ACCIDENT INVESTIGATION REPORT

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August 24, 2005*

Table 9. Summary of Piping and Vessel F20 Holdup Volumes

Location	Length ft	Diameter ft	Area ft ²	Volume ft ³
Discharge line	885	1.094 (13.124")	0.9394	831.4
Discharge line w/two-phase, $x_{vap} = 0.035$	"	"	"	"
F20 bottom head	2.5	10	-	130.9
F20 cylinder	27 (T-T)	10	78.54	2120.6
F20 cone	10	Average 6.5	33.18	363.9
F20 stack	76.5	3	7.069	540.75
F20 below gas entrance (a)	14-0.547 (b)	10	78.54	1187.5

(a) Including bottom head

(b) Above tangent-tangent line

Table 10 provides an exercise to examine the implications of simply accumulating the discharged liquid in the transfer line and F20 vessel. Table 10 adds to the scenario outlined in Table 8 the liquid density for raffinate feed material evaluated at the vapor line temperatures, T5506. The liquid mass fraction of the two-phase discharge from 13:17 to 13:20 is taken as 0.965. Finding the cumulative mass discharged (the sum of column 4 entries in Table 10), and dividing by the liquid density gives the cumulative liquid volume discharged. Columns 6 and 7 are found by dividing the cumulative liquid volume discharged at each time by the volume of the transfer pipe and of the F20 vessel.

Table 10. Cumulative Discharge by Postulated Scenario

Time	F_{dis} kg/s	ρ_{Liq} kg/m ³	Discharged Liquid kg/min	Cumulative Discharged Liquid, m ³	Fraction Full Pipe	Fraction Full F20	Fraction Full F20 w/ Vapor in Pipe	ΔLevel in Col. ft
13:13.55	202.1	687.6	3234 in 16 s	4.70	0.200	0	0.0520	1.4
13:14	221.4	681.2	13,284	24.20	1.028	0.007	0.2678	7.0
13:15	242.7	676.3	14,562	45.74		0.246	0.5060	13.3
13:16	241.00	674.7	14,460	67.17		0.483	0.7432	19.6
13:17	≈83.1	672.9	4811	74.32		0.562	0.8223	
13:18	≈83.1	666.7	4811	81.53		0.642	0.9021	
13:19	60	653.2	3474	86.85		0.700	0.9610	
13:20	40	641.6	2316	90.46		0.740	1.0009	

Thus, if all the discharged liquid were to accumulate in the transfer piping and in F20, then F20 would be 75% full. However, at this point, the system would not be in hydraulic equilibrium. The height of the transfer piping would be approximately the column height of 168 ft plus the

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
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August 24, 2005*

elevation of the bottom of the column. The stack height of F20 is 116 ft plus the elevation of the bottom of F20. Assuming the Raffinate Splitter and F20 have about the same bottom elevation above ground, the transfer piping has potentially 52 ft. of hydraulic head, h , above F20 or p_{gh} of 15.2 psig. This pressure, plus the column pressure, would have been the driving force to empty the transfer piping.

If the pressure driving force emptied only the transfer piping, then a small amount of liquid would be discharged, as indicated by the bottom entry of column #8 in Table 9. However, this hypothetical point would also be hydraulically unstable, since the hydraulic head of a liquid-full F20 would be 29.2 psig. This is below the indicated column overhead pressure in the period 13:13 to 13:20 that ranges from 30.43 to 63.18 psig. Thus, a substantial fraction of the liquid in F20 above the inlet piping would be discharged. As a maximum, using the scenario outlined in Table 7 and Table 9, the amount discharged according to this scenario would have been 87,666 lb. (39,765 kg).

Table 9 also shows the change in liquid level in the Raffinate Splitter column by the listed discharge rate. In the first three minutes of all-liquid discharge, this change was 19.6 ft. Subtracting the 19.6 ft of liquid displaced as an assumed all-liquid discharge from the initial column level at 13:12 of 128.4 ft gives 108.8 ft. This point is between the feed Tray 31 and Tray 25, consistent with the assumption that any water zone was slightly above the feed tray.

FATAL ACCIDENT INVESTIGATION REPORT

*BP Americas, Inc.
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August 24, 2005*

4.0 SUMMARY

The analysis here provides postulated scenarios to address several observations. Temperature "waves" are seen to move up the column and to eventually establish a vertical temperature profile consistent with establishing a vapor/liquid equilibrium.

In a flooded column, vapor generated in the reboiler would condense in the cold liquid above at some point (call it the condensation point). A vapor/liquid flow would be established below.

Water in the raffinate feed or remaining from steam-out operations prior to startup might accumulate at high concentrations at the condensation point.

If accumulated water were gradually heated until it reached its saturation point, the water could flash to a high proportion of vapor over a small temperature range if vapor pressure exceeded hydrostatic plus ullage pressure. This could be a sudden event. By allowing for uncertainties in column temperatures and the exact location of a water-enriched zone, we assume the flashing of water began just before the pressure pulse. We postulate a flash curve similar to the curve of water partial pressure vs. time. With this assumption, a liquid swell could lift the column of cold liquid, compressing the vapor space and opening the PRVs. A liquid discharge is predicted to occur for 3 minutes, discharging 19.6 feet of liquid and filling the Blowdown Drum to 23.9 ft (disregarding holdup in the 14-inch connecting piping and flow into the sewer). The liquid level in the Raffinate Splitter is predicted to fall after 3 minutes, so two-phase discharge begins, and the temperature in the vapor line rises, consistent with observations. The two-phase discharge would provide the driving force to lift liquid out of the Blowdown Drum for three minutes.

Dispersion calculations from a release scenario involving two-phase discharge for three minutes produced vapor clouds consistent with observations (not shown here).

Appendix 15

Process Modeling

FATAL ACCIDENT INVESTIGATION REPORT



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Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas

Final technical report

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1.3	28 September 2005	Jesus Palacin-Linan	implementation of clarifications requested by BP

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FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report. Version 1.3



Executive summary	2
1 Introduction	3
2 Model scope	3
2.1 Single tray	3
2.2 Feed tray	4
2.3 Bottom tray and reboiler	4
2.4 Top tray	4
2.5 Overhead pipe model	4
2.6 Liquid/vapour mass and heat transfer	4
2.7 Physical properties	4
2.8 Model structure	5
3 Data provided	5
3.1 Estimated volumetric feed flows over time	5
3.2 Estimated feed temperature over time	5
3.3 Estimated volumetric flows of liquid withdraw from the reboiler over time	5
3.4 Estimated fuel volumetric flows over time in the reboiler	5
3.5 Estimated feed composition	5
3.6 Measured pressure profile	6
3.7 Initial conditions	6
4 Simulation results	6
4.1 Model set-up	6
4.2 Matching the observed pressure profile	6
4.3 Vapour fraction in trays	7
4.4 Influence of feed pre-heating	7
5 Conclusions	7
Appendix 1 Influence of initial water accumulation	17
Appendix 2 Influence of feed saturated in methane	18

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report. Version 1.3



Executive summary

A dynamic model of the events leading up to the pressure relief from the Texas City Raffinate Splitter column has been developed using the Process Systems Enterprise's proprietary software gPROMS. The model included a detailed analysis of the vapour/liquid flows through the column and the trays – in both filling and flooded mode of operation. Heat input from the reboiler and feed preheat was included.

The dynamic modelling results showed:

- The column overfills with liquid, and liquid enters the overhead vapour line.
- This overfilling of the overhead vapour line results in a high peak hydrostatic pressure observed at P5002 (Figure 3). The high hydrostatic head of liquid in the overhead line was sufficient to exceed the RV set pressure (the relief valves were located at the bottom of the overhead line).
- The liquid level reaches the overhead line by a combination of a very high liquid inventory in the vessel, and also by significant liquid level expansion by vaporisation (from reboiler heat) in the lower sections of the trays. The % vaporisation in the various trayed sections of the column at different times is shown in Figure 4.
- The simulation results are qualitatively consistent with the plant data (allowing for possible errors in the feed flow rate, feed composition and heat duty effectiveness). A summary of the simulation and plant pressure response during the incidents is shown in Figure 3.

1 Introduction

The main hypothesis considered as the cause of this grave incident supports that the liquid in the column spilled over the top of the column into the overhead pipe after the unit decompression, where it was ejected through the column relief valves to the blowdown system. The objective of this work is to ascertain whether the conditions given in the column during the day of the incident could provoke liquid spill over the column top. Due to the complexity of the different phenomena taking place simultaneously in the column, a rigorous dynamic mathematical model of the distillation column was developed to describe the functioning of the column under conditions far away from normal operation.

2 Model scope

The system under study operated at non-ordinary conditions during the day of the incident. The standard models used for the simulation of distillation columns (e.g. such as those embedded in Hysys® and similar tools) are unable to describe the behaviour of the system under those extreme conditions. Conventional standard models are only valid for normal operation of the distillation column and cannot describe the system behaviour with flooded or submerged trays. Consequently, a new dynamic model of a distillation column able to describe its behaviour under conditions far away from normal operation was developed. The model scope was intensely discussed to include everything that may have influenced during the incident. The model was implemented in PSE's proprietary software, gPROMS.

The main models developed to be combined into the column model are described in the following paragraphs.

2.1 Single tray

The tray model consists of a model of the downcomer and a model of the active tray area connected. Both downcomer and active tray area models include rigorous dynamic calculation of liquid and vapour species holdups along with the rigorous dynamic enthalpy balance. The complete tray can operate in two different modes :

- Normal operation: downcomer and active tray area are partially filled with liquid which is flowing driven by gravity. The vapour fills the space left by the liquid and flows through the valves between active tray areas due to pressure differences. The liquid flow between the downcomer and the active tray area is caused by the differential pressure between the downcomer bottom and the active tray bottom. The liquid flow from the active tray area into the downcomer of the tray below is calculated using the Francis weir equation.
- Flooded operation: the downcomer is full of liquid and the flow through it is determined by volumetric constraint. The active tray area contains liquid and vapour. The pressure in the tray corresponds to the hydrostatic pressure produced by the column of liquid above the tray. This pressure is transmitted to the active tray area through the downcomer. The liquid in the active tray area fills the space left by the gas at the specific pressure which corresponds to the hydrostatic pressure produced by the column of liquid above through all the flooded trays. The liquid flow between the downcomer and the active tray area is calculated based on that volumetric constraint and the pressure drop through the clearance.

The normal operation mode will switch to flooded operation when liquid level in the downcomer reaches the downcomer height, and it will switch back to normal operation when the liquid level on the active tray above is about being lower than the tray weir.

The vapour flow through the active tray area valves is calculated similarly in both modes using rigorous empirical correlations of vapour velocity through the valve with respect to differential pressure between the trays provided by BP.

The tray geometry is rigorously included so that the model can describe single pass and double pass trays of different dimensions.

2.2 Feed tray

The feed tray model is similar to the tray model described above but includes an additional liquid inlet in the active tray area.

2.3 Bottom tray and reboiler

The bottom tray is similar to the tray model described above but without outlet into the downcomer of the tray below (which does not exist). It includes a port for energy input to account for the reboiler heat input.

2.4 Top tray

The top tray was modelled as a tray without downcomer from the tray above. Furthermore, the vapour flow with the overhead pipe is calculated through volumetric constraint since the pressure drop in the overhead pipe is negligible.

2.5 Overhead pipe model

The long overhead pipe was modelled as being able to dynamically contain vapour and liquid. The pipe is connected to the top tray. The vapour is allowed to go in and out between the top tray and the pipe. The liquid expelled by the top tray accumulates at the bottom of the pipe and it is not allowed to go back into the top tray. The vapour fills the space left by the liquid and determines the pressure.

2.6 Liquid/vapour mass and heat transfer

A rate-based approach to calculate the mass and heat transfer between liquid and vapour in the active tray area was adopted.

2.7 Physical properties

The feed consists of a mixture of 35 light hydrocarbons. The components have been lumped into component categories whose physical properties have been assumed to be equal to a selected component, e.g. all the components including 5 carbons have been included in the category Pentanes and given the properties of n-pentane. This approach was assumed in order to limit the size of the model and is justified considering that the error introduced is negligible in comparison with the inaccuracies introduced by the rest of model inputs.

In addition to hydrocarbons, nitrogen and water must be included in the system since they may be present in the column during the operation. Nitrogen is used to pressurize and test the system for leaks before operation; it is present in large quantity at the beginning of the operation. The column was steamed before operation and, therefore some quantity of water may have accumulated on the trays or at the bottom of the column before the operation. Water is also present in the feed.

Methane was also added to the list since natural gas is used to pressurize the feed drum. Some methane could have dissolved in the feed if the resident time of the feed in the drum is long enough at some point during the operation. This dissolved methane could play an important role in the observed build up of pressure in the column and eventually liquid spilling over the top (Appendix 2).

The final list of components is shown in Table 1.

The liquid and vapour fugacities of the components in the mixture were calculated using the Redlich-Kwong-Soave equation of state. This model was considered sufficient to accurately describe the VLE behaviour of nitrogen and the light hydrocarbons used. Although the amount of water in the feed was taken into account, its concentration was considered too low to have an appreciable influence in the column VLE behaviour.

RKS EoS model could be less accurate in describing the properties of large quantity of water in the hydrocarbon mixture. Consequently, a predictive Soave-Redlich-Kwong (PSRK) group contribution method was used to ascertain the role of the initial amount of water, especially at the column bottom (Appendix 1).

Ideal mixture rules were used for the density and enthalpy calculations of the liquid and vapour mixtures.

2.8 Model structure

Figure 1 shows a schematic drawing of the units used in the model. The external units of the column were not included in the model since data measurements of temperature, volumetric rate and composition are available for all the streams connected to the column and used during the day of the incident.

3 Data provided

BP supplied measured data of the day of the incident to be used as model inputs and to compare with the results of the simulation.

3.1 Estimated volumetric feed flows over time

Table 2 shows the measured volumetric flows into the feed tray from 01:59 to 13:30 on the day of the incident. The data has been converted into a mass flow rate as required by the model, assuming a standard liquid density of this type of mixtures.

3.2 Estimated feed temperature over time

Figure 2 shows the feed temperature measured at the feed tray entrance. For most of the period, the fluid state of the feed is liquid. However, there is a period of a few minutes before the incident where the feed is partly vaporised due to higher levels of preheat.

3.3 Estimated volumetric flows of liquid withdraw from the reboiler over time

Table 3 shows the time variation of the measured volumetric flow rates withdrawn from the reboiler. Note that the measurement device was placed at the end of the line after heat exchanger with the feed line, and consequently the measurements are slightly delayed with respect to the real action of the pump. BP already corrected for this delay in the measured data supplied.

3.4 Estimated fuel volumetric flows over time in the reboiler

The fuel volumetric flow rate in the reboiler allow us to estimate the heat duty into the bottom of the column. Table 4 shows the calculated time variation of the heat duty.

3.5 Estimated feed composition

BP provided a table with 35 components and their overall mass fractions in the feed entering the drum placed upstream the column. The feed composition was estimated as explained in Section 2.7 based on the mass fractions provided, and specified in Table 1.

During the day of the incident, the liquid feed was detained for several hours in the feed drum (from 3:20 to 9:52). This could have favoured a significant dissolution of methane in that batch of feed that might have had an important contribution to the pressure build-up in the column and eventual liquid spillover the column top. In

order to account for this factor, the amount of methane dissolved in the feed was estimated through a flash calculation under the conditions specified for the feed drum (Table 1). Then that mixture is introduced during a period of time (3500 s) after the first pressure release down to atmospheric pressure. This period of time was estimated based on the amount of feed that accumulated in the feed drum assumed it was half filled.

3.6 Measured pressure profile

BP supplied pressure measurements over time at the bottom of the overhead pipe. Therefore, the pressure measurement includes the hydrostatic contribution of any liquid that may have spilled over the top of the column. The observed pressure profile is shown in Figure 3.

3.7 Initial conditions

The column was steamed, drained and then pressurized with nitrogen to check for leaks. Therefore, an unspecified amount of water could have remained in the column, especially at the bottom, and nitrogen will be the major species present in the gas phase during the early stages of that day operation. To facilitate the initialisation of the simulation calculation, a fixed temperature and pressure flash calculation was performed to obtain the vapour and liquid equilibrium compositions to include in the model as initial conditions (Table 5). In the model, at time 0 each tray is filled with a negligible amount of liquid, the rest of the space being filled with vapour in thermodynamic equilibrium with the liquid.

4 Simulation results

4.1 Model set-up

The dynamic model was set up with 14 trays. The actual column has 70 real trays, so the dynamic model was set up with a factor of 5 fewer trays. However, in all respects, the dynamic model maintained geometric similarity with the real column (even though fewer trays have been used). This compromise was selected to achieve quicker overall run times for the program and also complete additional case studies. The column bottom has the same height as in the real column but the area has been calculated to include the volume of the reboiler. The feed tray and the top tray have the same height and diameter as the real column. However, the tray heights in the column sections have been extended to compensate for the required extra volume to describe the real column. Given the uncertainty of the data, this model should be accurate enough to analyse qualitatively the incident.

4.2 Matching the observed pressure profile

In order to match the observed and predicted pressure profile, some factors have been varied, specifically:

1. Relief valve position: during the first pressure release at 9:43, the system pressure was decreased to atmospheric by opening a valve sealing the system. According to the pressure profile, once the atmospheric pressure was reached, the pressure stays around that value for 2000 s. Therefore, a relief valve seemed to be open for around that time period before being closed and the pressure starts to build up.
2. Feed flowrate and reboiler withdrawal have been varied similarly inside a range of $\pm 5\%$, (inside measurement error).
3. Heat input has been varied in a range down to a minimum value of -20% of the total heat input calculated for the fuel combustion (Table 4) to account for the burner efficiency and heat loss.

Factors 2 and 3 on the list above were modified by a multiplier, which was the same for all the values along the whole schedule. The values of the multipliers mentioned above that give an approximate fit of the pressure profile are specified in Table 6. Figure 3 shows the good agreement between the observed and simulated pressure profile at the bottom of the overhead pipe. It must be mentioned that we stopped the data reconciliation process

at a reasonable matching of the measured data due to time constraints, and that it should still be possible to obtain better agreement between predicted and observed behaviour.

4.3 Vapour fraction in trays

Figure 4 shows the vapour fraction in the different trays in the column at different time before, during and after the liquid spillover event. The feed is introduced in tray 7. The vapour fraction is maximum in the feed tray even though in terms of absolute liquid volume displaced by the vapour, it is very small in comparison with the absolute liquid volume displaced by the vapour produced in the trays below the feed tray (see Section 4.1 for clarification in the model tray dimensions). Furthermore, observe that the maximum vapour fraction in the feed tray is reached two minutes after the pressure peak at the bottom of the overhead pipe.

4.4 Influence of feed pre-heating

To investigate the impact of the sudden change in feed preheat close to the time of the incident, an additional simulation was carried out with the assumption that the feed inlet temperature did not increase, but stayed at 126 F. The pressure profiles obtained at the bottom of the overhead pipe are shown in Figure 5. The pressure peak is now slightly shifted to a later time (more than 100 s) and its magnitude is reduced.

Figure 6 shows a comparison between the vapour fractions in the trays at the time of the liquid spillover pressure peak obtained in each simulation case. In both cases the vapour fractions below the feed tray are very similar. The heated feed gives rise to a higher vapour fraction especially in the feed tray and quite moderately in the trays above the feed tray. Still, the majority of the vapour volume produced in all the trays is in the trays below the feed tray and is caused by the heat duty in the reboiler.

5 Conclusions

The causes of the liquid spillover are a combination of factors actuating dynamically, including:

- the excessive amount of liquid accumulated in the column,
- the continuous heat duty provided to the reboiler,
- the continuous increase of the pressure to excessive levels caused by the liquid accumulation and vapour formation,
- the gradual unit depressurisation which started at 12.41.

The heat duty caused the evaporation of the liquid in the trays below the feed tray pushing the liquid up the column. Simultaneously, the feed entering the column is filling the trays above the feed tray. Eventually, the liquid reaches the top of the column and spills into the overhead pipe. The influence of the feed preheat ramping is small and only affects the amount and timing of the liquid spilling over.

From the simulations, there is no evidence that water in the feed or in the column was definitely required to match the process data. It was possible to broadly match the process disturbances without the presence of water (see Appendix 1).

Also from the simulations, methane saturation from the feed drum has an impact on the pressure profile during the early stages of the pressure building-up process. However, methane was completely released to the atmosphere through the vent by the time the liquid spillover occurs, so it has no influence on event (see Appendix 2).

The discrepancies between the gPROMS model and the plant data are most likely due to inaccuracies in the measurement of feed flowrate and/or compositional errors. However, the magnitude of the discrepancies between the model and the plant data, are not considered significant enough to affect the general conclusions that the column pressure release was due to overfilling the column and lifting liquid into the column overhead line.

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report, Version 1.3



Quantitative analysis would require a data reconciliation process of previous operation with the column under special monitoring and controlled conditions.

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report. Version 1.3



Table 1 Feed composition (in mass fractions)

Components	Without methane	Saturated with methane
N ₂	0	0
H ₂ O	3.75E-05	3.87E-05
Methane	0	0.000450606
Pentane	0.3980	0.387201
Hexane	0.4845	0.491544
Heptane	0.1174	0.120766

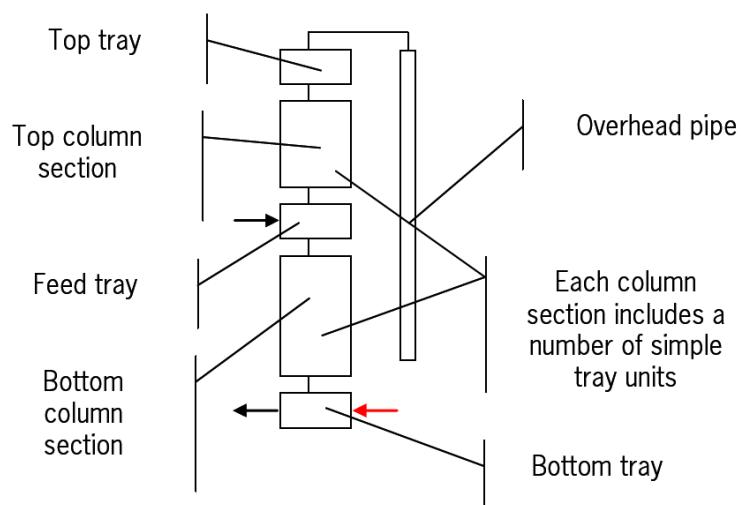


Figure 1 Model schematics (model units)

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
 Final technical report. Version 1.3



Table 2 Feed mass flowrate (liquid density assumed 41.2 lb/ft³ or 660 kg/m³)

time period (hours)	Time intervals (mins)	Feed flowrate (mbpd)	Time (sec)	mass flowrate (kg/s)
1.59 to 2.02.30	3.5	7	0	8.73
2.02.30 to 2.18	15.5	0	210	0.00
2.18 to 2.38	20	15.75	1140	19.63
2.38 to 2.45	7	15.4	2340	19.20
2.45 to 2.56	11	15.4	2760	19.20
2.56 to 3.08	12	15.4	3420	19.20
3.08 to 3.10	2	12.2	4140	15.21
3.10 to 3.20.30	10.5	10.4	4260	12.96
3.20.30 to 9.52	391.5	0	4890	0.00
9.52 to 9.56	4	6.7	28380	8.35
9.56 to 10.07	11	8.18	28620	10.20
10.07 to 12.30	143	20.8	29280	25.93
12.30 to 12.41	11	19.8	37860	24.68
12.41 to 13.00	19	19.6	38520	24.43
13.00 to 13.09	9	20.3	39660	25.31
13.09 - 13.11	2	21	40200	26.18
13.11 to 13.19	8	21	40320	26.18
13.19 to 13.21	2	19	40800	23.69
13.21 to 13.40	19	21	40920	26.18

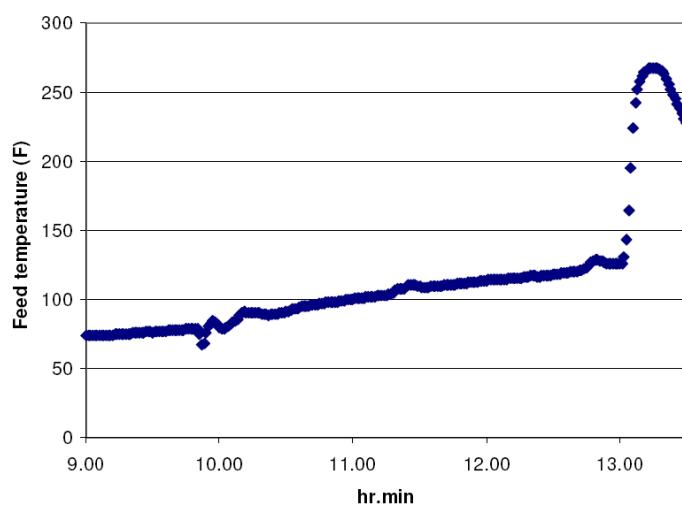


Figure 2 Feed temperature profile

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report. Version 1.3



Table 3 Mass flowrates of products extracted from bottom of the column (liquid density assumed 41.2 lb/ft³ or 660 kg/m³)

time period (hours)	Time intervals (mins)	Feed flowrate (mbpd)	Time (sec)	mass flowrate (kg/s)
1.59 to 9.43	464	0	0	0.00
9.43 to 9.46	3	-5	27840	-6.23
9.46 to 12.55	189	0	28020	0.00
12.55 - 13.00	5	-12.1	39360	-15.08
13.00 - 13.02.30	2.5	-24.8	39660	-30.92
13.02.30 - 13.05	2.5	-26.1	39810	-32.54
13.05 - 13.11	6	-28	39960	-34.90
13.11 - 13.12	1	-28.8	40320	-35.90
13.12 - 13.20	8	-28.25	40380	-35.22
13.20 - 13.22.30	2.5	-24.1	40860	-30.04
13.22.30 - 13.40	17.5	-21.6	41010	-26.93

Table 4 Estimated fired heat input based on the reboiler fuel flowrate (average calorific value assumed 857 BTU/ft³)

time period (hours)	Time intervals (mins)	Fuel flowrate (kscfh)	Time (sec)	Fired heat input* (J/s)
1.59 to 10.00	481	0	0	0
10 - 10.05	5	10	28860	2511248
10.05 - 10.17	12	33	29160	8287119
10.17 - 11.17	60	17	29880	4269122
11.17 - 11.21	4	30.5	33480	7659307
11.21 - 11.30	9	35	33720	8789368
11.30 - 11.49	19	27.9	34260	7006382
11.49 - 11.52	3	30.3	35400	7609082
11.52 - 12.43	51	31.8	35580	7985769
12.43 - 13.15	32	30.2	38640	7583969
13.15 - 13.19	4	24.08	40560	6047085
13.19 - 13.20	1	12	40800	3013498
13.20 - 13.40	20	0	40860	0

* fired heat input is multiplied by the efficiency in the model. Efficiency is one of the parameters varied to fit the observed pressure profile at the overhead pipe bottom.

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
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Table 5 Initial composition in the column (flash calculation performed at 73.4 F and 4 psig (296 K and 128903.8 Pa)

Components	Non-equilibrated mass fractions		Flash calculation at constant T and P using RKS EoS	
	liquid mass fraction	vapour mass fraction	liquid mass fraction	vapour mass fraction
N ₂	0	1	0.000285	0.49028
H ₂ O	3.754E-05	0	4.07E-05	1.74E-06
Methane	0	0	0	0
Pentane	0.39797	0	0.36936	0.35726
Hexane	0.48453	0	0.50379	0.14181
Heptane	0.11744	0	0.12652	0.010655

Table 6 Estimated multipliers to fit the observed pressure profile at the bottom of the overhead pipe

Factor	Multiplier	Schedule and previous values
Feed mass flowrate and reboiler withdrawal mass flowrate	0.97	The values of these factors over time are shown in Table 2 and 3.
Heat input	0.88	The values of these factors with the time are shown in Table 4.

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
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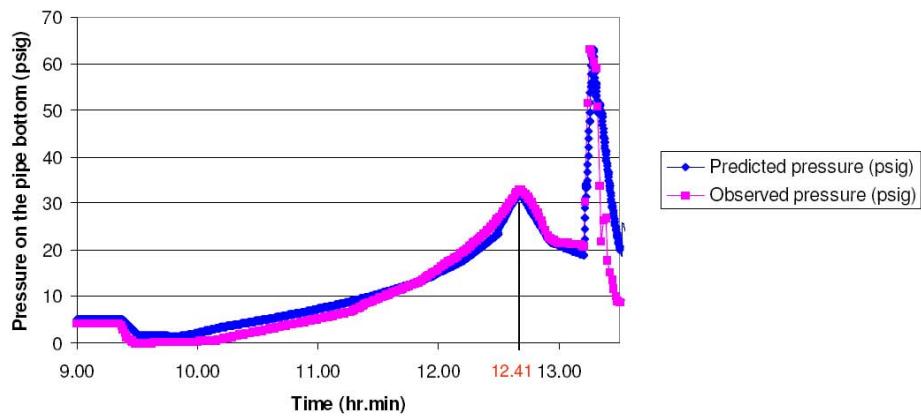


Figure 3 Comparison of the observed and simulated pressure profile at the bottom of the overhead pipe.

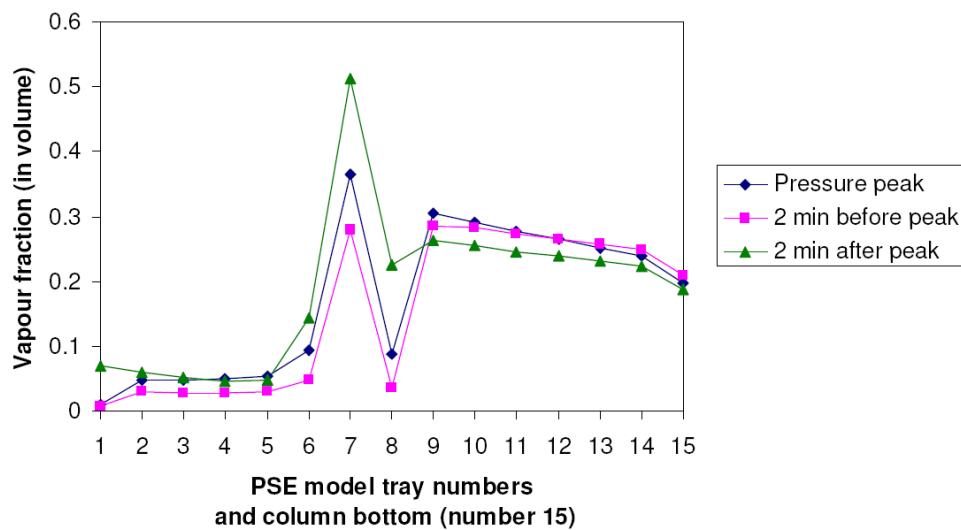


Figure 4 Tray vapour fraction profiles through the column at different times around the liquid spillover. The pressure peak at the bottom of the overhead pipe (Figure 3) is taken as indication of the liquid spillover. Although the high vapour fraction in the feed tray, this is very small in absolute terms in comparison with the vapour volume included in the trays below the feed tray. Top column corresponds to tray 1. Observe that the column consists of 14 trays and number 15 in the plot corresponds to the column bottom (see Section 4.1).

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report. Version 1.3

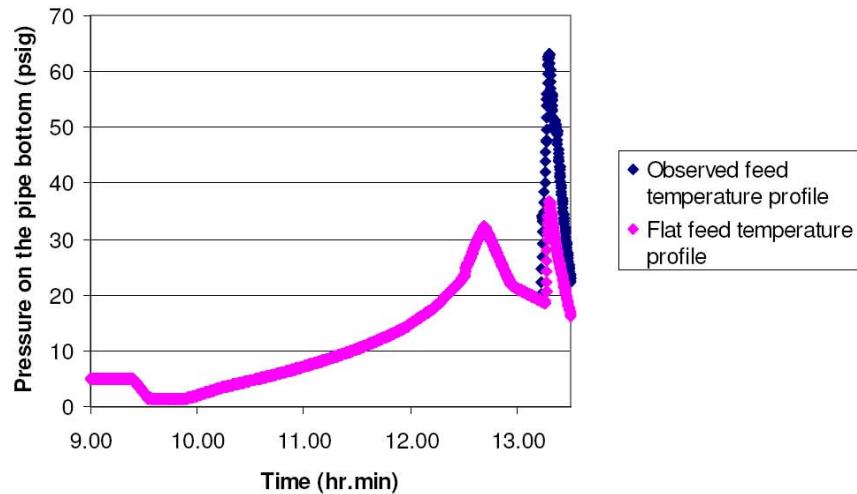


Figure 5 Comparison between the simulated pressure profile at the overhead pipe bottom obtained with the measured feed temperature profile as a model input and a flat temperature profile at 125.6 F. The feed temperature ramp accelerates the event and increases the amount of liquid spilling over the column top.

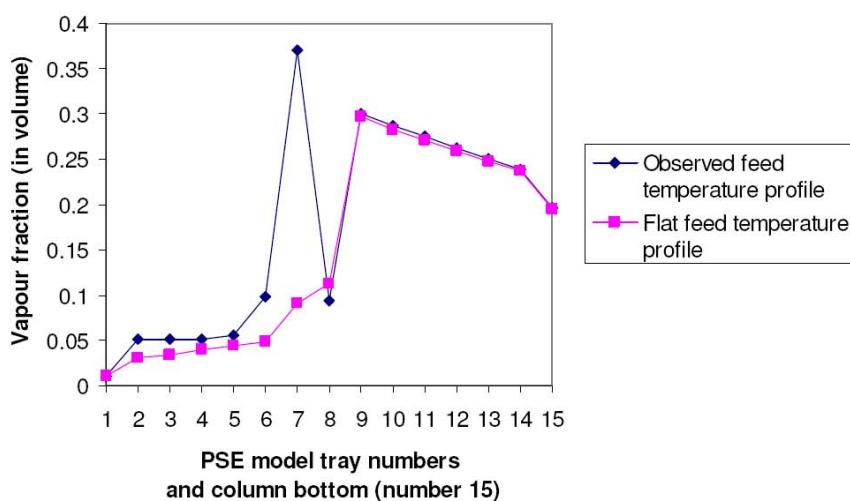


Figure 6 Predicted vapour fraction in the trays, assuming the observed feed temperature profile and a flat feed temperature profile at 125.6 F. The time coincides with the pressure peak on the overhead pipe bottom caused by liquid spillover. Top column corresponds to tray 1. Observe that the column consists of 14 trays and number 15 in the plot corresponds to the column bottom (see Section 4.1).

Appendix 1 Influence of initial water accumulation

Previously to operation, the column was steamed. Consequently, some amount of water could have accumulated in the column bottom. The vapour liquid equilibrium was modelled using predictive Soave-Redlich-Kwong (PSRK) group contribution method to calculate the fugacities of all components in the vapour and liquid phases. Table A.1 shows the composition of the fluid phases in the column bottom at the boiling point. Observe that the vapour is considerably rich in steam with respect to the overall water composition. The presence of water in the reboiler along with the hydrocarbons decreased the boiling point of the mixture by 7°C with respect to liquid without water.

When the reboiler is heated during operation, water and hydrocarbons will evaporate and go through the bottom tray after the liquid reaches the boiling point. The liquid evaporation rate is completely determined by the heat duty. Due to the large heat duty and high steam mass fraction, steam quickly flows up, is diluted throughout the entire column, and is released through the vent, which could be open at all times. Consequently, water/steam does not have appreciable influence on the liquid spillover since it has been almost completely released by the time the liquid spill over happens at the column top. Observe also that the initial total amount of water in the column (200 kg) is negligible with respect to the total amount of hydrocarbon fed by the time liquid spillover happens (more than 350,000 kg). The influence of water is restricted to the very early stages of the pressure build-up process and it is of very limited extent.

Table A.1 Composition of the fluid phases at the column bottom at the boiling point, assuming 0.2 m³ of water and the rest of the column bottom and reboiler (90.8 m³ – downcomer not taken into account) full of hydrocarbons in the same proportions as in the feed.

	Mass fractions			
	Overall	Vapour	Organic liquid	Water phase
NITROGEN	3.24E-04	6.90E-02	3.25E-04	6.42E-06
WATER	5.12E-03	4.11E-02	1.18E-03	0.99812
METHANE	1.34E-05	1.23E-03	1.35E-05	2.09E-07
PENTANE	0.39451	0.57082	0.39607	1.25E-03
HEXANE	0.48327	0.28853	0.48518	5.72E-04
HEPTANE	0.11676	2.93E-02	0.11722	4.96E-05
Pressure*	3.10E+05	Pa		
Boiling Point	350.342	K		

* Approximate pressure when the liquid in the column bottom starts boiling, according to the column model simulation

FATAL ACCIDENT INVESTIGATION REPORT

Model-based analysis of the events leading up to the March 2005 safety incident at BP Oil in Texas
Final technical report. Version 1.3



Appendix 2 Influence of feed saturated in methane

The pressure profile is used as a reference in all the simulations. Consequently, we tried to match approximately that profile for each simulation. The presence of methane in the feed in the concentration specified in Table 1 during 3500 sec after 09:00 am, influenced the pressure profile. In order to match the pressure profile, the vent valve must be open all the time and its flow coefficient adjusted. However, methane is almost completely released to the atmosphere well before the liquid spillover event. Consequently, it does not have an influence on the event.

Appendix 16

**Evaluation of the Size of and Mechanisms for the
Relief from the Raffinate Splitter**



BP TEXAS CITY ISOMERIZATION EXPLOSION
Packer Engineering Project Number 500082

Evaluation of the Size of and Mechanisms for the Relief from the Raffinate Splitter

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Executive Summary

On March 23, 2005 a hydrocarbon release, followed by subsequent explosions and fires occurred during start-up of the isomerization unit at BP's Texas City Refinery. The hydrocarbon release was from the blowdown (F-20) drum and the flows out the top of the blowdown stack are considered to be the primary source for the release. This report provides estimates of source terms for the flows from the isomerization unit raffinate splitter (E-1101) pressure relief valves through the blowdown drum (F-20) during the startup. Based on the PI data, the relief event occurred over a 6 minute period starting at approximately 13:14. This report analyzes aspects of the relief event and predicts the magnitude of the discharge from the blowdown drum. Three alternate relief event scenarios were analyzed and reported: 1) relief of the feed mixture, 2) relief with nitrogen present, and 3) relief with water present.

Summary of findings:

- 1) A two-phase relief from the blowdown requires either the presence of nitrogen or water.
- 2) A relief consisting solely of the feed mixture at 160F and 62 psig will be a sub cooled liquid (a liquid below its boiling point).
- 3) If water is present in the raffinate splitter, conditions for boiling are reduced so that boiling in the column can occur at lower temperatures with significant vaporization in the bottom of the column.
- 4) In the scenarios that generate a two-phase relief, the hydrocarbon vapor mixture discharge to the atmosphere is at a concentration above its lower flammability limit.
- 5) The blowdown drum (F-20) will be overwhelmed with liquid during the relief, based on alternate scenarios, approximately 5 minutes after the start of the relief event.
- 6) The liquid pool from the flow from the blowdown stack will rapidly spread, evaporate and contribute to the flammable vapor mass.
- 7) The total relief volume is approximately the quantity of liquid in the column above the feed. Temperature profiles and temperature acceleration profiles for the column support the conclusion that the origin of the relief event is at the feed.
- 8) Nitrogen from the reflux drum provides a credible source for a two-phase relief.

**Table of Contents**

Introduction	4
Composition, pressure and temperatures used for modeling the relief.....	5
Thermodynamic Limiting Conditions	5
Relief System Modeling	8
Scenario 1.....	8
Scenario 2.....	8
Scenario 3.....	10
Analysis of the Blowdown Drum	10
Consideration of Releases from the Sewer System	13
Mechanisms for Initiation of Relief Event from Raffinate Splitter	14
Source Term Approximation for Alternative Scenarios	23
Conclusions	24
Appendix.....	27
Figure 1 - Relief Timeline	5
Figure 2 - Relief Thermodynamic Condition	7
Figure 3 - Raffinate Splitter Temperature Timeline	14
Figure 4 - Thermodynamic conditions in The Raffinate Splitter-Hydrocarbon Only	15
Figure 5 - Thermodynamic Conditions in The Raffinate Splitter-with Water.....	16
Figure 6 - Raffinate Splitter Column Pressure	17
Figure 7 - Temperature Timeline showing Event Features	18
Figure 8 - Rate of Temperature Change in the Raffinate Splitter	19
Figure 9 - Rate of Temperature Change at Start of Relief Event	20
Figure 10 - Rate of Temperature Change at End of Relief Event	21
Figure 11 - Raffinate Splitter Temperature Profiles	22
Table 1 - Thermodynamic Equilibria for the pure Hydrocarbon Feed.....	6
Table 2 - Water Vapor Pressure.....	8
Table 3 - Effect of Nitrogen on Relief Flows	9
Table 4 – Molar Composition of Vapor for Relief with Nitrogen	9
Table 5 - Effect of Water on Relief Flows	10
Table 6 - Composition of Vapor for Relief with Water.....	10
Table 7 - Maximum Liquid Flows into the Sewer System	11
Table 8A - Blowdown Total Mass Flow out its Top	11
Table 8B - Blowdown Liquid Material Balance	12
Table 9 - Blowdown Fill Time and Overflow Volume.....	12
Table 10 - Relief System Volumes	13
Table 11 - Raffinate Splitter Relief Volume and Predicted Height.....	23
Table 12 - Approximate Pool Spread Radius (ft)	23
Table 13 - Source Term Liquid Evaporation	24



Introduction

On March 23, 2005 a hydrocarbon release, followed by subsequent explosions and fires occurred during start-up of the isomerization unit at BP's Texas City Refinery. The hydrocarbon release was from the blowdown (F-20) drum and the flows out the top of the blowdown stack are considered to be the primary source for the release. As part of the detailed analysis of the cause(s) of the incident calculations were performed to estimate the maximum flows through the relief system for various process scenarios. These values are used to examine the viability of alternate potential relief scenarios and to approximate the rate of production of a vapor cloud from first principles. Additionally, they are used to provide the source term for computer modeling relative to dispersion of the vapor cloud. This report analyzes possible scenarios and provides an estimate of the vapor and liquid releases through the relief system from the overhead manifold to the blowdown drum, flows out of the blowdown drum into the sewer system as far as the diversion box, and flows out of the BD drum top. The dispersion modeling is presented in a separate Packer Engineering report entitled "Computational Fluid Dynamics Modeling of the Vapor Cloud Dispersion and Correlation with Observed Physical Evidence".

During the March 23, 2005 relief event, the column overhead pressure (P5002) rose rapidly and shows a spike in pressure that exceeded the relief set pressure for approximately six minutes. At the start of the relief the pressure measurement rapidly climbs from 30 psig progressing rapidly through 51 psig to hold at a relatively constant condition for over 4 minutes until its rapid decrease from 59 psig to 34 psig. At the relatively constant peak condition the pressure measured at P5002 varied from a high of 63 psig to a low of 59 psig and the temperature measured in the overhead at T5506 varied from a high of 176 F to a low of 100 F. To provide an estimate of the source terms for the alternative scenarios analysis at a constant condition was performed. The highest temperature during the relief (160 F) and the average high pressure (62 psig) were chosen to represent the feed to the relief valve manifold at its elevation.

The column overhead pressure is measured on the overhead line's entrance manifold to the fin fan cooler (overhead condenser). This is approximately 148 feet below the top of the tower and 11.5 feet below the three relief valves. The temperature is measured in the overhead line approximately 80 feet below the top of the tower and 67.5 ft. above the relief valves. The indicated instrumentation readings at these locations are taken as representing the conditions for the feed into the relief manifold.

The relief conditions are shown in Figure 1. Times in this report are based solely on those reported by data from the PI system. Distributed Control System (DCS) data are approximately three minutes, forty-eight seconds (3:48) earlier and if used are converted to match the times reported by the PI system.

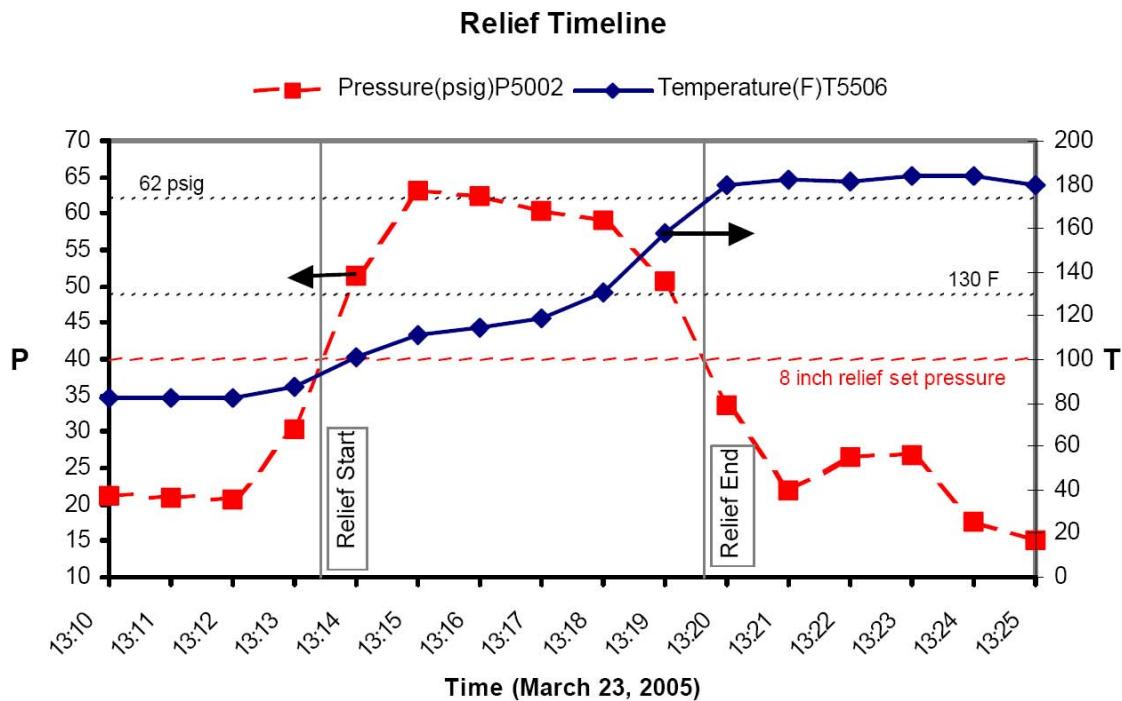


Figure 1 - Relief Timeline

Composition, pressure and temperatures used for modeling the relief.

The composition used for modeling was an estimate of the feed composition provided by Stuart Fraser of BP. Because very little product was withdrawn from the column the feed composition was used to represent the liquid mixture in the column. A reduced set of mixture components was obtained by adding the like species, e.g C5's, C6's etc. together according to carbon number and degree of saturation. This reduced mixture composition is shown in a table in the Appendix and was used for the calculations associated with this report.

Thermodynamic Limiting Conditions

It is noted that at the conditions for the relief (160 F, 62 psig), using an SRK equation of state model, if the relief is only the hydrocarbon feed, then it is predicted to be a substantially sub cooled liquid. At 62 psig the predicted bubble point is 307.4 F and the predicted dew point is 351.1 F. Thus, using 62 psig, if the release is only the feed, the relief is a liquid with about 147 degrees of sub cooling. Even at 20 psig, the normal operating pressure of the column, and a pressure below that measured at P5002, the predicted bubble point temperature is 240 F and the predicted dew point is approximately 287 F. Using 20 psig, the nominal operating pressure for the column, the relief would still be 60 degrees sub cooled. It is also noted that at 180 F, the temperature of the overhead after the relief event and the normal operating temperature on the top tray, the bubble point pressure is about -0.3 psig or slightly subatmospheric. Vacuum



pressures were not recorded. One can conclude that if the release is only the feed, then the thermodynamic phase condition for the release can only be as a sub cooled liquid and, furthermore, that the source of the vapor cloud can only be rapid evaporation.

The hydrocarbon feed temperature (T5005) changes in the startup varying from 125 F to 265 F in the 10 minute period from 13:01 to 13:11 just before the relief event due to its preheat by the bottom product in the preheat heat exchanger (C-1104). Under normal operations the pressure at the upper feed approximately equals the sum of the tower pressure + 2 inches liquid depth per tray times 25 trays or approximately 5 psig + 1 psig = 6 psig. Without any additional liquid in the column, at 125 F the feed will be sub cooled liquid with 76 degrees of sub cooling but at 265 F the feed will be a superheated vapor at 6 psig. The predicted dew point temperature at 5.9 psig is 258.5 F, the predicted bubble point is 204.1 F. The dew point pressure at 265 F is 8.3 psig. At 265 F the bubble point pressure is 32.4 psig. Fifty percent vaporization occurs at 265 F and 21.8 psig.

In order to evaluate alternative scenarios and conditions in the column, the following table shows thermodynamic equilibrium conditions for the feed:

Table 1 - Thermodynamic Equilibria for the pure Hydrocarbon Feed

Temperature (F)	Pressure (psig)	Bubble Pt condition	Dew Pt. condition	Phase Condition
160	62			Sub cooled Liquid
	62	307.4 F	351.1 F	
	5	201.1 F	255.8 F	
	-0.3 psig			
180	6	204.1 F	258.5F	
	15.5 psig		-1.9 psig	
230	19.8 psig		0.6 psig	
240	24.6 psig		3.5 psig	
250	29.82 psig		6.73 psig	
260	32.7 psig		8.6 psig	
265	35.6 psig		10.4 psig	
270	57.9 psig		25.8 psig	
302				

The relief pressure and temperature can be put on a thermodynamic phase diagram to indicate its relative position with respect to the curves representing the onset of boiling (the bubble point) and complete vaporization (the dew point). This is shown in Figure 2. The relief data (shown in red) plots the relief pressure as a function of temperature from 13:13 (before the relief) to 13:21 (after the relief). The lowest relief pressure is 40 psig. The light blue dotted line represents 50% vapor.

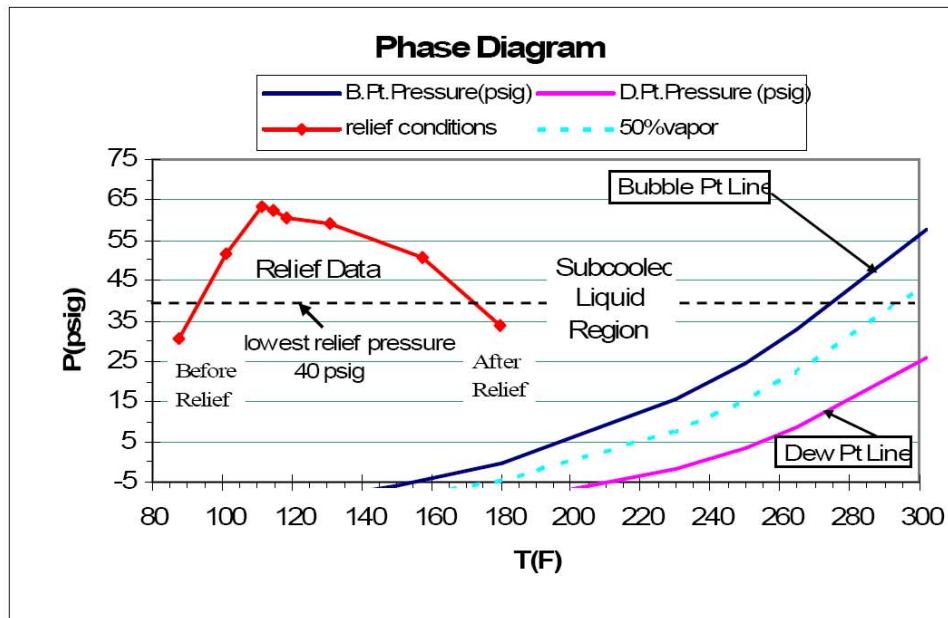


Figure 2 - Relief Thermodynamic Condition

There are two possible scenarios that generate a two-phase relief. The first is to consider the presence of nitrogen in the system. Nitrogen is essentially non-condensable under these conditions although at low concentrations the equation of state model predicts that it will entirely be absorbed in the liquid phase. The bubble point temperature for the feed with 1% Nitrogen is -47 F indicating that, if nitrogen is present, the relief will have two phases. The presence of nitrogen can have a large effect on the release and this will be discussed later.

The second possible way to generate a two-phase relief is to assume the presence of sufficient water in the column to have two liquid phases. Both 5 and 10 mole percent water concentrations were analyzed. The presence of water will create conditions for a potential liquid-liquid-vapor equilibrium in the column. An essentially pure aqueous phase will generate its own vapor pressure and effectively reduces the hydrocarbon pressure in the column.

When boiling occurs, both the aqueous and organic phases will boil at the same time. This effect can be seen by examining the relationship between the bubble point temperatures at 62 psig. Without water, 307 degrees F is needed to start boiling however, with water present, boiling will start at a temperature 30 degrees lower. Likewise, at a fixed temperature of 250 F, without water the pressure has to be lowered to 24 psig to start boiling whereas with water present boiling begins 18 psi higher at 42 psig. The vapor pressure of water at different column conditions is provided in Table 2. The temperature at the bottom of the column (T5114) showed a temperature of approximately 302F prior to the relief. At this temperature the water vapor pressure, 54.8 psig, is approximately the same as a column of hydrocarbon liquid 198 ft high.



For the raffinate splitter, which had a pressure of approximately 20 psig before the relief event, if one assumes that the liquid level is at tray 13, the water vapor pressure is approximately equivalent to the conditions at tray 70, about 120 feet below the liquid surface.

Table 2 - Water Vapor Pressure

T(F)	P(psig)
125	-12.77
180	-7.20
212	0.00
230	6.12
240	10.34
250	15.24
260	20.91
265	24.06
270	27.44
302	55.14

Relief System Modeling

The SimSci (Invensis) computer code, Visual Flow 4.1, was used to model the relief system from the raffinate splitter (E-1101) overhead to the F-20 blowdown drum, the blowdown drum itself, and the sewer system. The code is capable of modeling two-phase, compressible flow, and all liquid flow regimes and was used to predict the flow conditions for the relief system and piping networks. For this analysis the entire relief system was modeled including the pipe runs. The geometry was obtained from isometric drawings that were confirmed by field measurements. The specific relief valve types, sizes, and set pressures were specified. Maximum flows for three alternative relief scenarios were considered and the results are shown below. Details regarding the modeling for each scenario are given in the Appendix.

Scenario 1

In this scenario the feed is relieved through the system as a single phase liquid and enters the blowdown drum. It is assumed that the blowdown is at atmospheric pressure and that the relief is at 160 F and 62 psig. The relief is 100% liquid and has a flow of 24,777 lbmol/hr. This is equivalent to a flow of 2,452,923 million lb/hr or 7,651 gpm or 262,300 barrels/day.

Scenario 2

In this scenario the feed is mixed with nitrogen to provide a two phase relief. Three nitrogen concentrations in the resulting homogeneous mixture are evaluated: 1, 2, and 5 mole percent. The relief is maintained at 160 F and 62 psig. An alternative source for nitrogen is the reflux drum. During the relief event the 1.5 inch bypass line on the reflux drum may have been open. Assuming that any nitrogen in the system would be compressed to 62 psig during the relief event, a model of this vessel mixing its nitrogen with the hydrocarbon relief flow establishes an



order of magnitude for its contribution. For this case, the additional nitrogen slightly changes the molar and mass flows in the hydrocarbon relief. The model of the relief system piping was modified to include the mixing of the hydrocarbon relief at its relief pressure before the tee with a nitrogen stream at 62 psig emanating at F1102 and going through its 1.5 inch bypass line. The resulting two-phase flow represents the maximum flow to the blowdown drum as well as a credible source for the nitrogen. The fraction of nitrogen from this source provides a vapor flow representing approximately 3 mole % of the total release. The results for the above are shown in Table 3.

Table 3 - Effect of Nitrogen on Relief Flows

N2 %	Total Molar Flow (lbmol/hr)	Mass flow Lb/hr	Vapor Molar Flow	Liquid Molar Flow (lbmol/hr)	Fraction Vapor in relief	Volumetric Liquid flow (gpm)	Fraction vapor in Feed
Hydrocarbon Only 62 psig	24,777	2,452,923	0	24,777	0	7,650.9	0
1%, 62 psig	15,360	1,520,640	419.7	14,940.3	0.027	4,613.4	0.002
2%, 62 psig	12,620	1,249,380	639.8	11,980.2	0.051	3,699.4	0.013
5%, 62 psig	18,830	1,864,170	2037.0	16,793.0	0.108	5,185.0	0.049
Reflux drum N2	25,820	2,480,247	737.3	19,737.9	0.029	7,508.4	0.015

The calculated composition of the vapor emitted is over one-third nitrogen. The composition and temperature is relatively constant over the differing levels of nitrogen. Table 4 presents the composition data and includes Lower Flammability Limits (LFL) in air for pure compounds. Mixture Lower Flammability Limits were estimated using the Le Chatelier equation. These results are given in Table 4.

Table 4 – Molar Composition of Vapor for Relief with Nitrogen

Mol Percent Nitrogen	1% 62 psig	2% 62 psig	5% 62 psig	Reflux Drum N2	Pure Component LFL (F)
Temperature (F)	156.4	153.6	147.9	155.6	
Nitrogen	0.340	0.380	0.450	0.350	
C5's	0.140	0.130	0.110	0.140	0.014
C6's	0.360	0.340	0.295	0.350	0.012
C7's	0.135	0.125	0.120	0.130	0.012
C8's	0.020	0.020	0.020	0.025	0.010
Heavys	0.005	0.005	0.005	0.005	0.008
Mol. Wt.	66.9	64.7	60.4	66.3	
Density (lb/ft^3)	0.150	0.150	0.140	0.150	
Mixture LFL	0.019	0.020	0.022	0.020	

Pure component LFL for heavys is for decane.



Scenario 3

In this scenario the feed is mixed with water. Two hypothesized feed mixtures were studied: 5 and 10 mole percent water. At the inlet to the relief manifold the releases for the reliefs that contain water are initially all liquid at 160 F, 62 psig; however, at the blowdown the relief is a two-phase mixture for the 10% water case. Tables 5 and 6 show the effect of water on the relief. The results for the 2% nitrogen case are included for comparison.

Table 5 - Effect of Water on Relief Flows

Water mole%, Pressure	Total Molar Flow (lbmol/hr)	Mass flow lb/hr	Vapor Molar Flow	Liquid Molar Flow (lbmol/hr)	Fraction Vapor in relief	Volumetric Liquid flow (gpm)	Fraction vapor in Feed
Hydrocarbon only, 62 psig	24,777	2,452,923	0	24,777	0	7,650.9	0
5%, 62psig	27,254	2,698,215	0	21,130.0	0	5,185.5	0
10%, 62 psig	25,820	2,556,204	673.3	25,146.9	0.026	8,416.0	0
2%N2, 62 psig	12,620	1,249,380	639.8	11,980.2	0.051	3,699.4	0.013

Table 6 - Composition of Vapor for Relief with Water

Percent Water	10% 62 psig	2% Nitrogen 62 psig	Pure Component LFL (F)
Temperature (F)	154.5	153.6	
Water	0.420	0.380	
C5's	0.120	0.130	0.014
C6's	0.320	0.340	0.012
C7's	0.115	0.125	0.012
C8's	0.020	0.020	0.010
Heavys	0.005	0.005	0.008
Mol. Wt.	58.3	64.7	
Density (lb/ft^3)	0.130	0.150	
Mixture LFL	0.021	0.020	

Pure component LFL for heavys is for decane.

There is no predicted vapor with 5% Water

Both scenario 2 and 3 predict a vapor cloud to actually emanate from the blowdown which is consistent with expected behavior.

Analysis of the Blowdown Drum

The blowdown drum, F-20, and the sewer system were modeled to evaluate the maximum flow from the blowdown through the sewer system. The blowdown was modeled using the Visual Flow 4.1 code assuming three cases: with the bottom cylindrical section filled, with the

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 11 of 52

cylindrical section and the conical section filled, and with the entire stack filled. The model assumed static pressure due to the different heights of liquid in the blowdown. The effects on flow due to the restriction from the 10 feet diameter blowdown drum body to the 6-inch gooseneck, the restricted flow through the 6 inch gooseneck pipe followed by the 12-inch pipe to the diversion box were all considered. The results are shown in Table 7.

Table 7 - Maximum Liquid Flows into the Sewer System

Case	Height of liquid (feet)	Static Pressure (psig)	Maximum Liquid Flow (gpm)
Bottom Empty	0	0	1,763
Bottom full	27	7.5	2,888
Bottom & Cone full	37	10.3	3,199
Bottom, Cone and Stack full	113.5	31.5	5,001

Blowdown vapor flows were calculated for the alternative scenarios. These flows are shown in Table 8A. The total mass flow from the top is based on the assumption that, on average, the bottom section of the blowdown drum is full of liquid. Based on the outflows in Table 7 and the inflows previously calculated the approximate time to fill the blowdown stack can be estimated. The times were based on the outflow assuming the bottom section of the blowdown is full of liquid. A total volume of 3106 cubic feet is assumed for the blowdown drum, cone, and stack volume. The liquid material balance for the blowdown is given in Table 8B.

Table 8A - Blowdown Total Mass Flow out its Top

Case	Vapor Molar Flow (lbmol/hr)	Vapor Mass Flow (lb/sec)	Liquid Volumetric Flow (gpm)	Liquid Mass Flow (lb/sec)	Total Mass Flow from top (lb/sec)
All Liquid	0	0	4,763	424.5	424.5
1%N2	419.7	7.8	1,725	154.0	161.6
2% N2	639.8	11.9	811	72.6	84.2
5% N2	2,037	34.2	2,298	206.2	240.4
Reflux Drum N2	737.3	13.6	4,620	412.6	423.5
5% Water	0	0	5,528	447.7	461.3
10% Water	673.3	10.9	4,877	402.6	403.0

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 12 of 52

Table 8B - Blowdown Liquid Material Balance

Case	Total flow* (gpm)	Initial	Initial flows Out top	Bottom section full flows to sewer	Bottom section full flows out top	Completely	Completely	Approximate Time to fill blowdown drum
		flows to sewer				full	flows to sewer	
all liquid	7,650.9	1,763	5,888	2,888	4,763	5,001	2,650	293 4.9
1% N2	4,613.4	1,763	2,851	2,888	1,725	4,613	0	807 13.5
2% N2	3,699.4	1,763	1,937	2,888	811	3,699	0	1,718 28.6
5% N2	5,185.5	1,763	3,423	2,888	2,298	5,001	85	971 10.1
RefluxDrumN2	7,508.4	1,763	5,746	2,888	4,620	5,001	2,507	302 5.0
5% H2O	8,416.0	1,763	6,653	2,888	5,528	5,001	3,415	285 4.2
10% H2O	7,765.1	1,763	6,002	2,888	4,877	5,001	2,764	371 4.7

*Flows in gpm

The volumes of the equipment and relief system can be used for further calculations. Table 10 provides these volumes. The total volume assumes the blowdown and the reflux drum fill completely. For comparison purposes, the total volume of the Raffinate Splitter, E-1101, is 153,157 gallons.

A more refined calculation of the flow out the top of the blowdown stack can be performed by integrating the change in blowdown drum elevation as a function of time and accounting for the variation in flow from the blowdown to the sewer as the liquid elevation changes in the blowdown drum. However, because the pressure measurement, (P5002) was not located in the overhead before the relief valves, its reading only approximates the conditions in the relief header and reflects the compression of any gas (nitrogen) in the condenser (fin fan cooler) too. Therefore, a constant relief inflow into the blowdown drum was assumed for the entire six minute relief, see Table 8B. These detailed calculations are shown in the appendix. The calculations suggest that the liquid relief just barely overwhelms the stack and theoretically would appear to resemble a drinking fountain. The time to fill the blowdown drum for two cases is shown in Table 9.

Table 9 - Blowdown Fill Time and Overflow Volume

Case	Time to Fill relief line (min:sec)	Time to overwhelm blowdown (min:sec)	Duration of overfill (min:sec)	Total Volume of overfill (gallons)
All liquid	0:50	4:26	0:44	1,934
Reflux Drum N2	0:49	4:23	0:47	1,961

**Table 10 - Relief System Volumes**

System Element	Volume (cubic ft.)	Volume (gal)	Volume (barrels)
14 inch relief line	849.4	6,353.5	151.3
6 inch line from blowdown	6.4	47.9	1.1
12 inch sewer line to diversion box	147.4	1102.6	26.3
Reflux drum	949.2	7,100.0	169.0
Blowdown (to level of relief line)	2,314.6	17,313.2	412.2
Blowdown (bottom section only)	2,823.6	21,120.5	502.9
Blowdown (total)	3,106	23,232.9	553.2
Total Volume	5,058.4	37,836.8	900.9

Consideration of Releases from the Sewer System

The sewer system, represented on drawings B-4550-1117 and B-4550-P-3261, indicates that the gooseneck from the blowdown drains to a diversion box (Diversion Box #2) via a 12-inch line. Three lines (2-12 inch, 1-8 inch) then lead from the diversion box to a Fire Trap (Fire Trap#685) and a single 8-inch line leads from the diversion box to an Oily Water Separator. The Oily Water separator is then connected to a dry weather pump sump (#17) via an 8-inch line leading to a junction box and then a 12-inch line. The line exiting the fire trap enters a 36-inch sewer line. During the relief, prior to the explosion and fire, the diversion box and the dry weather sump High level alarms and High-High level alarms tripped, in some cases twice, indicating overflow from these boxes. Because the boxes overflowed into the sewer drain the backflow into the sewer system drains on the West side of the Isomerization Unit is not expected to be a significant contributor to the subsequent fire.

The 12-inch line from the blowdown drum is one of three lines going into the diversion box. Backflow into the second 12-inch line (which connects to other area drains in the NW corner of the ISOM) would require flow back over a 150 foot length and vertically up at least 4 feet to create a significant source from it. Backflow into the 8-inch line requires flow back at least 50 feet and vertically at least 3 feet to represent a significant additional source of hydrocarbon vapor.

The alternative flow path for the relief discharge in the sewer system is to go from the 12-inch line from the blowdown drum to the diversion box and into the lines designed to process flow from it. Specifically: From the diversion box the primary path will be through the 8-inch line to the Oily Water Separator, then to the Dry Weather Sump, and subsequently into the Fire Trap and the sewer. Once the 8-inch line is full (the High level alarm is reached) the relief flow will start to backup into the sewer system partially filling it until the 14-inch diversion box overflow is reached (the High-High level alarm). This requires filling the diversion box vertically 2'11.5" above the 8-inch line but still 1'8" below grade. Although the diversion box High-High alarm was reached, it cleared before the explosion indicating that the hydrocarbon liquid was contained in the sewer system. Hydrocarbon vapors from the liquid in the sewer will be reduced over time



because the liquid backed up in the sewer will go through the diversion box and from it into the Fire Trap from the Dry Weather Sump.

Before the explosion the Dry Weather sump High level alarmed three times over a three minute period and the High-High level alarm tripped once. These Dry Weather Sump alarms indicate that the sewer system had sufficient capacity to process the relief liquid discharge it received from the blowdown drum.

Mechanisms for Initiation of Relief Event from Raffinate Splitter

The temperature profile in the raffinate splitter provides a picture of the transient conditions and can provide some insight into the operation at the time of the relief. This is shown in Figure 3. The feed transient from 13:01 to 13:11 is clearly shown. The feed enters on tray 31 at an elevation of 117.6 feet. One can approximate the conditions in the column assuming that the liquid level is at tray 13 and then using this to approximate the temperature and pressure in the column. This is shown in figures 4 and 5. The feed temperature transient at tray 31 is shown on both figures. The entire feed tray timeline from 13:00 to 13:20 is shown by the horizontal line in both figures. After 13:00 high-end raffinate product is being withdrawn from the bottom of the splitter at the same time that feed is still being added but the flow out the bottom is at a higher rate. As a result, the liquid level will drop at the feed point (Tray 31) over the entire 20 minute period causing the pressure to drop approximately 1.7 psi. Taking this into account in the feed tray timelines will contribute a very slight negative slope to them (1.7 psi drop/141.4 deg F). Figure 4 shows the vapor –liquid vaporization curves for the hydrocarbon feed only while Figure 5 shows the effect of adding water as a second phase on the bubble point of the combined mixture.

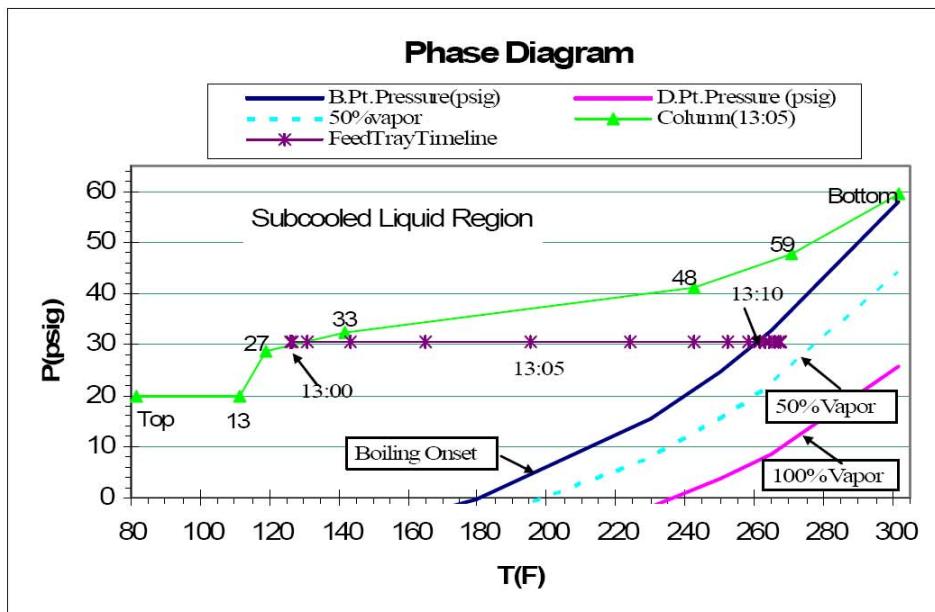




Figure 4 shows that at 13:10 the feed crosses the hydrocarbon boiling onset (bubble point) condition and becomes partially vaporized with increasing vapor until approximately 16.4 percent is vapor at 13:14. This represents a vapor feed flow of 35,811 gpm (492 lb/min).

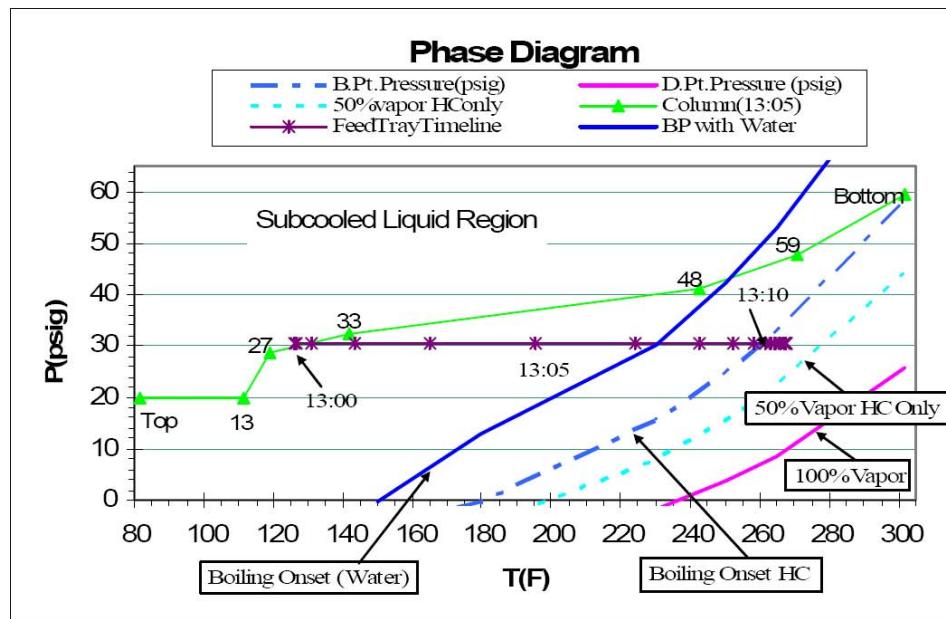


Figure 4 - Thermodynamic conditions in The Raffinate Splitter-Hydrocarbon Only

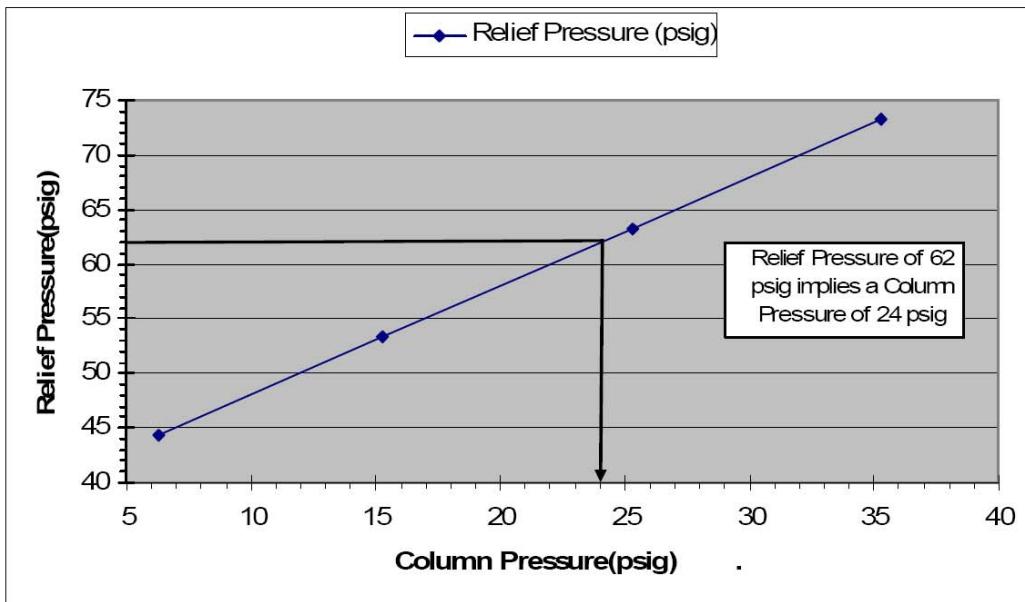


Figure 5 - Thermodynamic Conditions in The Raffinate Splitter-with Water

Figure 5 shows the effect of having water in the column and demonstrates the reduction in process conditions associated with having a second phase of water present. One can note that as long as there is a second (aqueous) phase present Figure 5 will represent the phase behavior. Instead of crossing the bubble point (boiling onset) condition at 13:10 the feed starts boiling shortly after 13:06. The figure predicts that boiling is occurring in the lower part of the column from the bottom to approximately tray 49. At tray 70, the predicted thermodynamic conditions are 286F and 53.5 psig. This corresponds to a density approximately 72 percent of the normally expected liquid density. One notes that the liquid level sensor reading (L5100) at tray 70 was approximately 78%.

The column pressure required to generate a 62 psig pressure reading at the relief valves can be calculated by modeling the pressure required to push liquid 3 feet up the splitter before the contraction to the 24-inch overhead line (approximately the reflux entry point at 182 ft). Figure 6 shows the relationship between the column pressure and the relief pressure. Regardless of flow, the column pressure at the 182 ft. elevation level that corresponds to 62 psig at the relief is approximately 24 psig. This pressure is only three psi greater than the pre-event column pressure; however, it is enough to flood the column on the top tray and to push the reflux up the overhead. This contributes to part of the relief flow from 13:17 to 3:20.

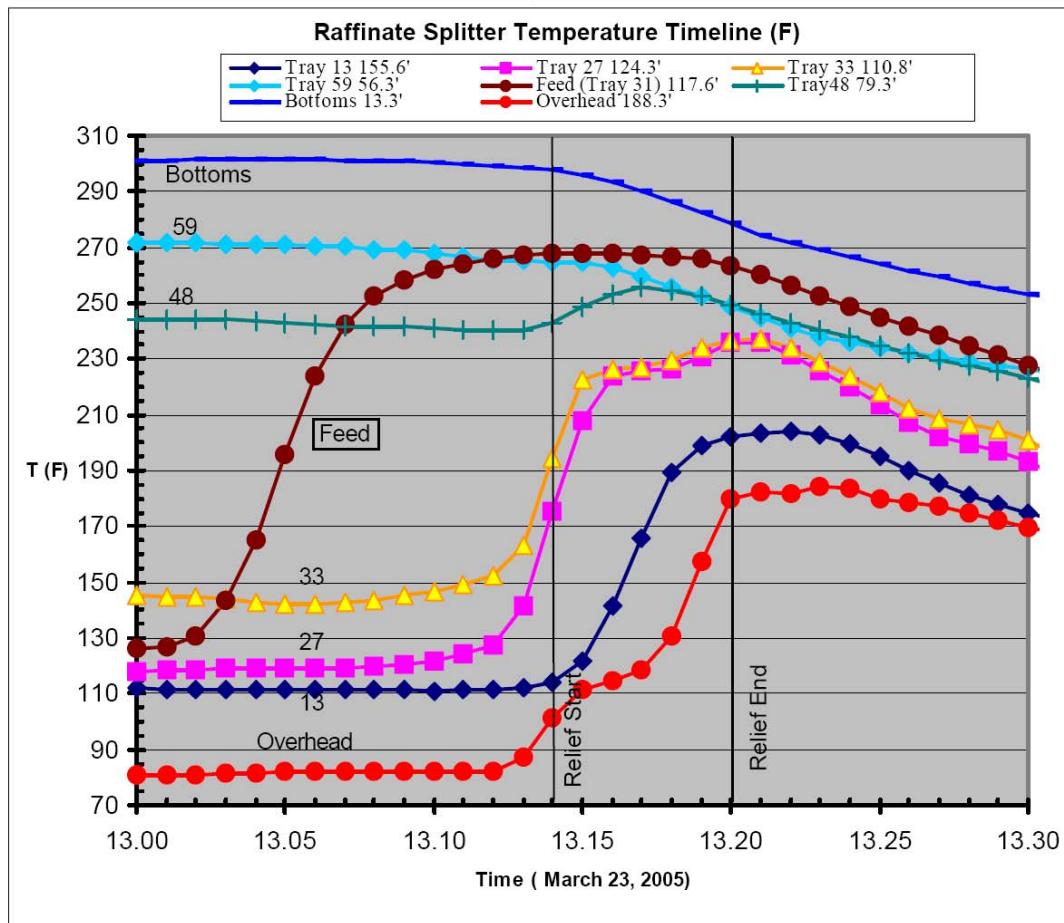


Figure 6 - Raffinate Splitter Column Pressure

As illustrated in Figure 7 the relief transient results in the column quickly returning to a profile more closely associated with normal operation with the overhead being near 180F and the bottoms approximately 270F. The geysering event begins after 13:12 when the temperatures throughout the column start to rapidly increase. The effect of the reflux is noted after 13:17. Figure 7 shows the temperature timeline and includes the significant relief events.

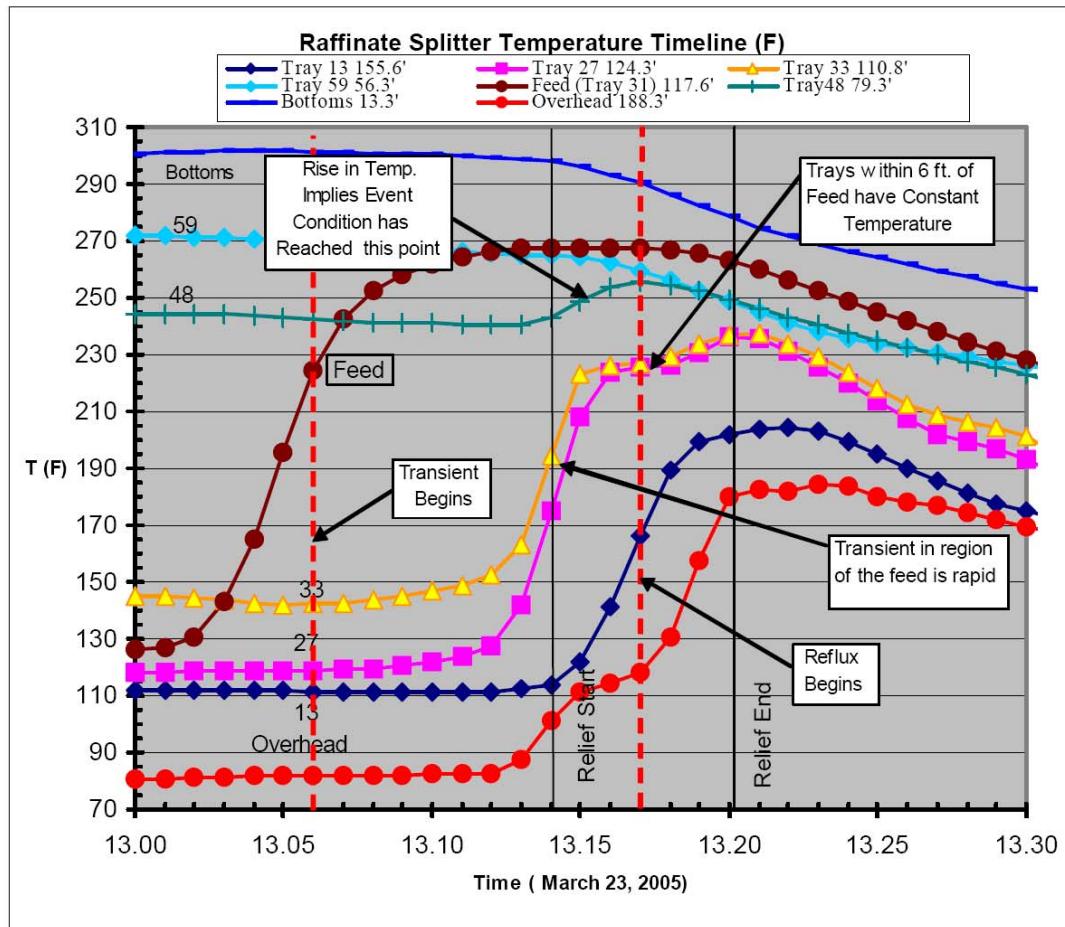


Figure 7 - Temperature Timeline showing Event Features

Analysis of the transient can be further understood by examining the derivatives of temperature throughout the column. Positive temperature derivatives indicate the rate of temperature rise (i.e. the temperature velocity). Derivatives for the entire column are shown in Figure 8. Derivatives for the conditions near the feed at the beginning of the relief event are shown in Figure 9. Derivatives for the later part of the event are shown in Figure 10. In Figure 8 of particular note are the two peaks in the Overhead (shown in red). The first peak rate occurred at 13:14 at the start of the relief and the second occurred at 13:19 near the end of the relief. The intermediate low point maybe associated with the start of the reflux into the column at 13:17. Figure 8 shows that the two trays surrounding the active feed at Tray 31 (Tray 27 and Tray 33) exhibit almost identical transient behavior consistent with an origin for the relief being at the feed. The transient for trays further away from the feed, Trays 48 and 13, occurs later.

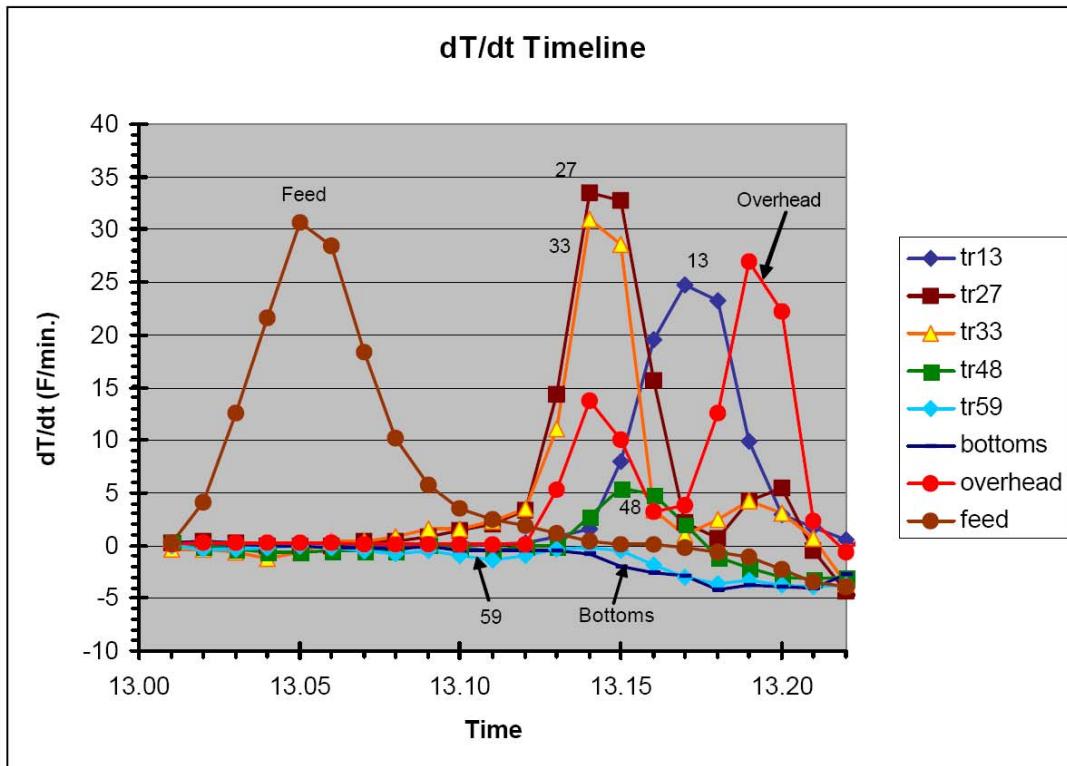


Figure 8 - Rate of Temperature Change in the Raffinate Splitter

Figure 9 reveals that the start of the relief event has its origin at about 13:06 just after the point when the feed temperature is going through its maximum rate. After this time, temperatures on trays both above and below the feed, Trays 27 and 33, start increasing at the same rate. The temperature on these trays track each other throughout the relief event and this graph shows that their derivatives do as well. At 13:12 the rate of temperature change on these trays accelerates and increases by an order of magnitude peaking at 13:14. The temperature gradient profiles in Figure 9 imply that the origin of the relief event is at the Feed on Tray 31.

Figure 10 shows the end of the transient and shows peaks in the temperature gradients at both Tray 13 and in the Overhead. The second peak in the overhead occurs after the reflux begins. The two peaks in the temperature gradient of the overhead may indicate that the relief occurred in two surges. After the relief event, at 13:21, the column temperature gradients diminish to near zero indicating steady operation.

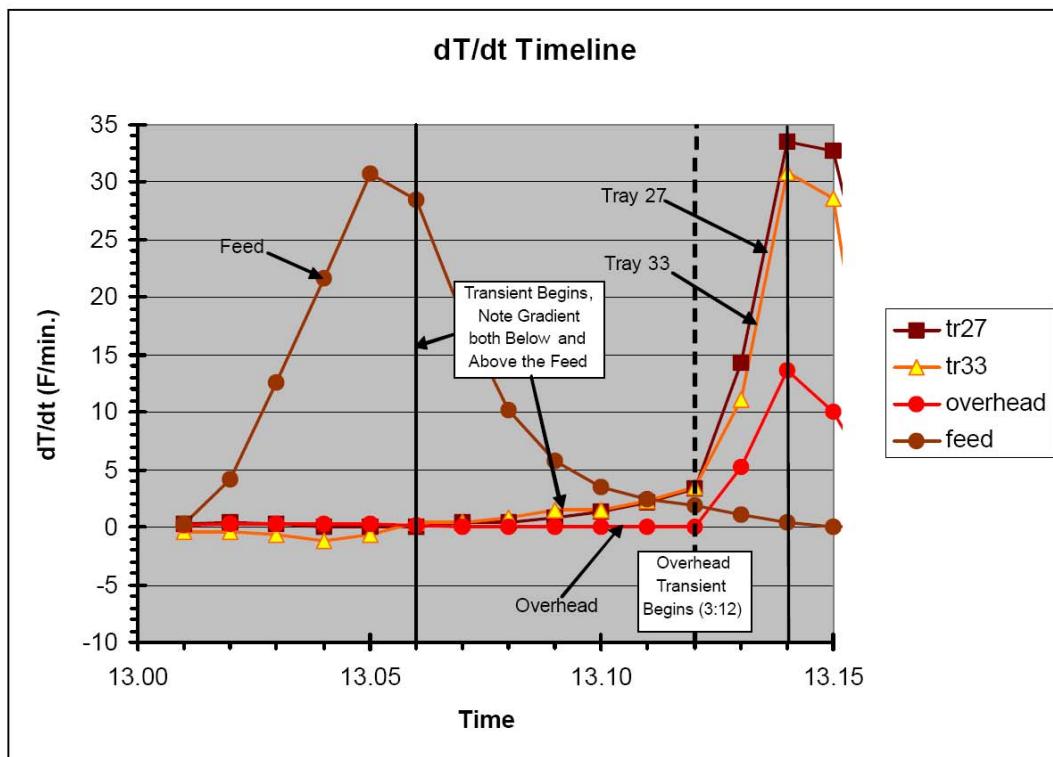


Figure 9 - Rate of Temperature Change at Start of Relief Event

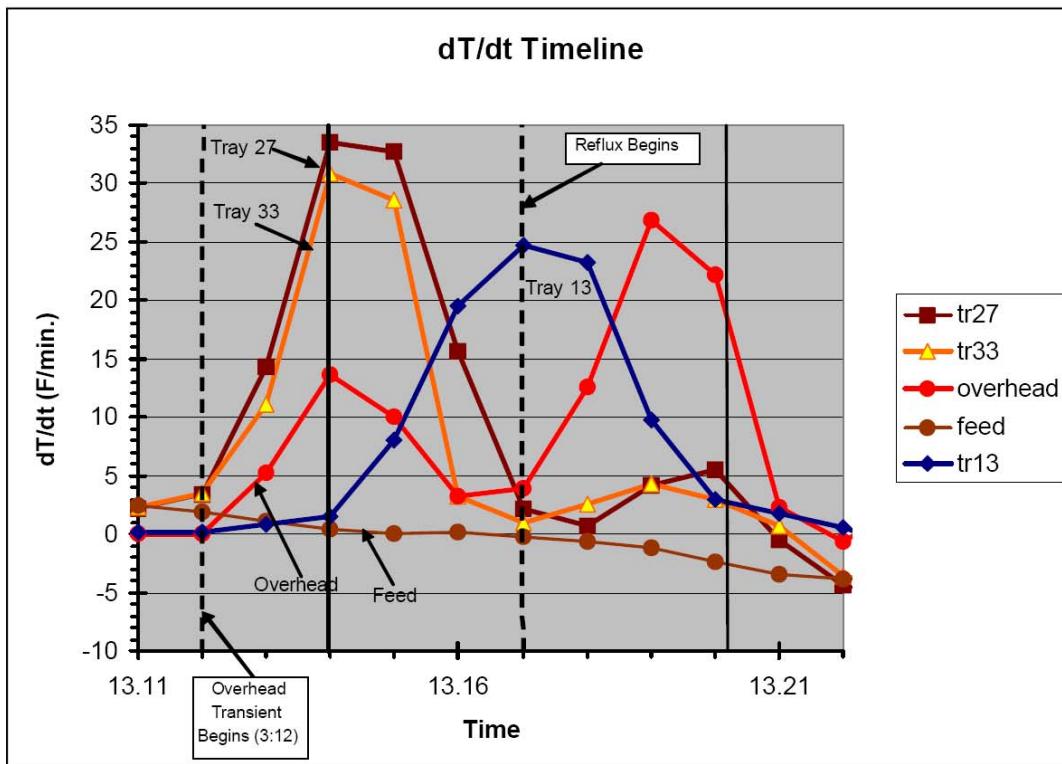


Figure 10 - Rate of Temperature Change at End of Relief Event

The temperature profiles in the column as a function of time are shown in Figure 11. They reveal a significant change in the region around the feed. One notes that from 13:12 to 13:15 the temperatures at both Trays 48 and 13 change by less than 10 degrees. The profile graphs shows that there is a bulge in the profile centered on the feed. At 13:17 the reflux begins and this steadies the profile in the upper section of the column. This graph also implies that the origin of the relief event is at the feed.

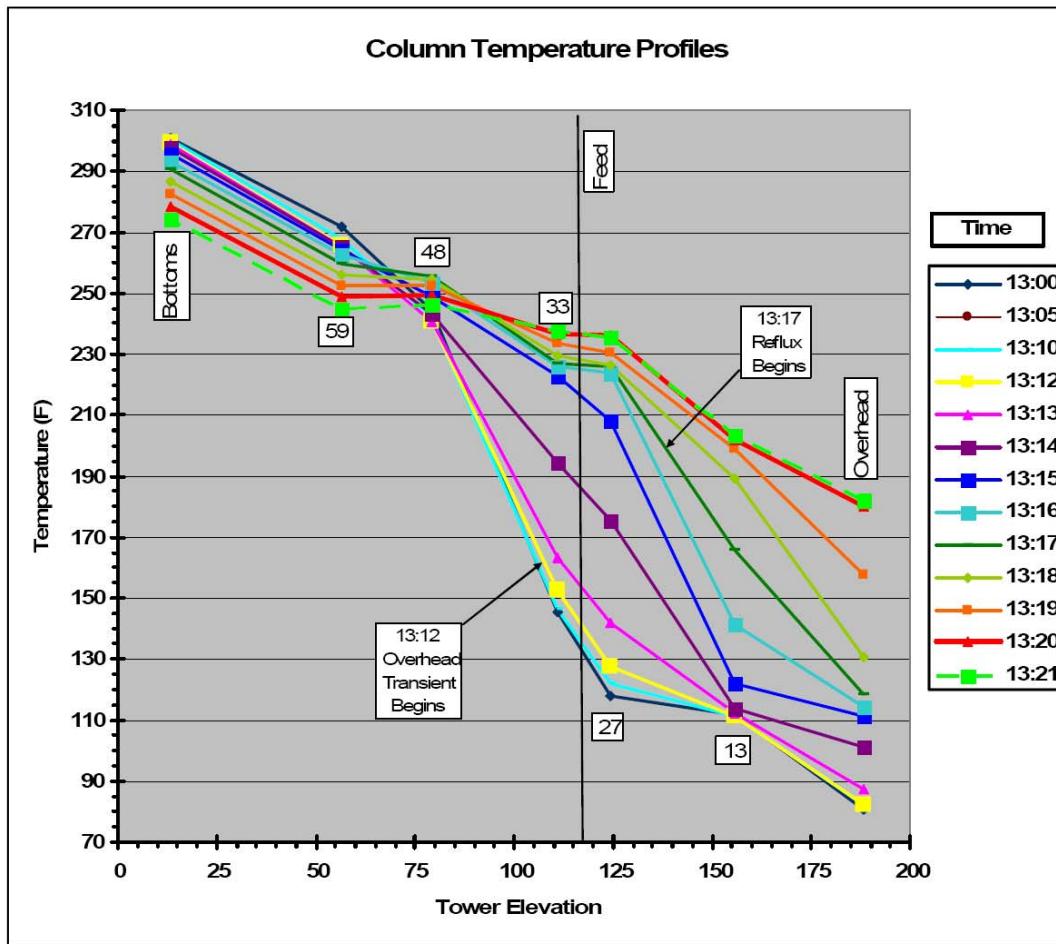


Figure 11 - Raffinate Splitter Temperature Profiles

Considering the individual scenarios evaluated in this report the approximate total quantity of the relief in the 6 minute period can be calculated and this can be translated into an equivalent height of liquid displaced in the raffinate splitter. Assuming that the liquid reaches a height of 155.6 feet (Tray 13) these calculations are shown in Table 11. The feed tray (tray 31) is at an elevation of 117.6 feet which is within 12 feet of the elevation predicted for four different scenarios. This calculation also supports the conclusion that the relief event origin is at the feed.

To provide 62 psig at the P5002 position the predicted pressure needed at the top of the column is 24 psig. Adding the equivalent pressure for the predicted height of the liquid relief (approximately 14 psi), the pressure required to balance the liquid above the feed is calculated to be approximately 38 psig. Thus a pressure at the feed greater than 38 psig is needed to send the liquid above it into the overhead.

**Table 11 - Raffinate Splitter Relief Volume and Predicted Height**

Scenario	Rate (lb/hr)	Volume (ft^3)	Equivalent Height* (ft)	Predicted Elevation
All Liquid	2,452,923	6,137.1	50.0	105.6
1% N2	1,520,640	3,700.6	30.1	125.4
2% N2	1,249,380	2,967.4	24.2	131.4
5% N2	1,864,170	4,159.5	33.9	121.7
Reflux Drum N2	2,480,247	6,022.8	49.1	106.5
5% Water	2,698,215	6,750.8	55.0	100.6
10% Water	2,556,204	6,228.7	50.8	104.8

* Height equivalent to the static pressure of the liquid

Source Term Approximation for Alternative Scenarios

A pool spread model will predict very large radii with these very large volumetric flows. The Wu and Schroy model for pool spread (see the CCPS Guidelines on CPQRA, 2000) predicts values considerably larger than those shown in the following table. A conservative (low area) estimate is to assume that the average pool thickness is 0.393 in (1 cm). Considering the liquid density, 40.0 lb/ft^3, and liquid viscosity, 0.25 cP, the hydrocarbon mixture will rapidly spread and evaporate. Table 12 provides an estimate of pool radius as a function of time for each scenario. The predicted radius is in feet consistent with the Fire Dynamics Simulator (FDS) code. For a 2% N2 relief, after 2 minutes a conservative pool radius is about 45.9 feet. These large pool diameters provide an extremely large area for evaporation. Obviously assuming a thicker pool would result in smaller pool dimensions; however, the low liquid viscosity will enable the liquid to spread more rapidly than water.

Table 12 - Approximate Pool Spread Radius (ft)

Assuming 0.393 in. (1 cm) Pool Thickness.

Min.	Sec.	all liquid	1% N2	2% N2	5% N2	Reflux DrumN2	5% H2O	10% H2O
1	60	78.6	47.3	32.4	54.6	77.4	84.7	79.5
2	120	111.2	66.9	45.9	77.2	109.5	119.8	112.5
3	180	136.1	81.9	56.2	94.6	134.1	146.7	137.8
4	240	157.2	94.6	64.9	109.2	154.8	169.4	159.1
5	300	175.8	105.8	72.5	122.1	173.1	189.4	177.9
6	360	192.5	115.9	79.5	133.7	189.6	207.4	194.8

Prediction of evaporation rate from the pool requires an estimate of the ambient conditions at the time of the relief and an energy balance on the pool. The ambient conditions were approximately 81F and 14.7 psia (0 psig). The conditions were a cloudless sky with strong insolation. The evaporation rate is based on using wind speed at 33 feet elevation (u) and the MacKay and Matsuga correlation based on experimental data. The vapor pressure of hexane is



Project Engineering Project 500082

August 11, 2005

Page 24 of 52

used to approximate the vapor pressure of the liquid at its discharge temperature of approximately 160F. Other properties are assumed to be at the molar average of the hydrocarbon mixture. Making these assumptions, the Kawamura and MacKay direct evaporation model (see Guidelines for CPQRA, 2000) predicts the effects of evaporation from solar radiation evaporative cooling, and heat transfer to the ground. At 6.6 ft/s wind speed the predicted evaporative flux is 0.0010 lbm/ft²-s and the mass transfer coefficient is 0.147 ft/s. The results are summarized in Table 13. The effect of the change of vapor pressure from ambient temperature, 81 F, to discharge temperature, 160 F is reduced due to the solar intensity.

Flux Prediction

Table 13 - Source Term Liquid Evaporation

Wind Speed at 33 ft elevation (ft/s)	Evaporative flux at 160 F discharge (lbm/ft ² s)	Evaporative flux at 81 F ambient (lbm/ft ² s)	Mass Transfer Coefficient (ft/s)
3.28	0.0204	0.0219	0.085
6.56	0.0219	0.0238	0.148
9.84	0.0243	0.0253	0.203
13.12	0.0258	0.0267	0.253
16.41	0.0267	0.0282	0.302

Conclusions

This report summarizes the current knowledge about the mechanisms to generate the relief from the Raffinate Splitter. Until more information is known, the presence of water in the column at the time of the relief remains unknown. Examination of the temperature and pressure data are consistent with the relief being generated by adding the feed to the column with a significant head of liquid above the feed combined with the feed being partially vaporized. Analysis of the overhead thermal velocities indicate that two accelerations occurred, the first before the reflux started and the second afterwards. The time history of the column profiles shows the largest change in the temperature profiles occurs near the feed and not below it further supporting the conclusion that the relief event origin is at the feed.

The maximum flows through the relief manifold and piping to the blowdown drum were calculated for three cases: for feed consisting of hydrocarbon alone, for feed consisting of hydrocarbon mixed with nitrogen, and for feed consisting of hydrocarbon mixed with water. Relief of the hydrocarbon feed would only be as a sub cooled liquid, whereas reliefs for the mixtures with nitrogen and with 10 mole percent water generated two-phase discharges into the blowdown drum. Rather than as a homogeneous mixture going through the relief valves a credible source of nitrogen is from the reflux drum as a second source to the 14-inch blowdown pipe. Consideration of this source permits nitrogen to be part of the relief and to generate a two-phase relief into the atmosphere. Flows from the blowdown drum were evaluated and the fraction that would enter the sewer and the fraction that would blow out the top were calculated



for each of the relief mixtures. The time to completely fill the blowdown drum was consistent for four different cases as approximately 5 minutes after the relief valves opened. The calculated maximum flows enabled a prediction of the total relief volume. This volume was consistent with a relief origin being due to the feed vaporization.

The effects of water in the column were examined in detail. If water were present, then the vaporization of the feed would occur at a lower temperature and vaporize earlier. With water present, the predicted column thermal footprint is consistent with vaporization occurring in the bottom of the column and also the column's liquid level reading. Additionally, the predicted time for feed vaporization is consistent with the onset of temperature acceleration both immediately below and above the feed location. All of these suggest that water was present in the column at the time of the relief; however, this remains to be proven by chemical analysis of the column inventory.

Modeling the relief flow enabled a prediction of the source term for a vapor cloud dispersion model and a complete consequence analysis. The predictions from this report were used as input conditions for a computational fluid dynamics (CFD) simulation using the Fire Dynamics Simulator (FDS) whose results are discussed in another Packer Engineering report entitled "Computational Fluid Dynamics Modeling of the Vapor Cloud Dispersion and Correlation with Observed Physical Evidence". The source term calculation predicts a conservative estimate of pool radius to be calculated; however, the liquid that flows out the top of the blowdown drum will evaporate very quickly resulting a liquid surface smaller than predicted.



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Appendix

Tables and Detailed Results

Table A - Molar compositions used for relief systems a approximate the hydrocarbon feed

	Reduced set Mol. Frac	Reduced set Molar flows (lbmol/hr)
H2O	0.0001	2.03E-01
i-Pentane	0.0163	2.50E+01
n-Pentane	0.0329	5.04E+01
2M-2-butene	0.0004	5.74E-01
Cyclopentane	0.0053	8.09E+00
22-Mbutane		
23-Mbutane		
2-Mpentane		
3-Mpentane		
n-Hexane	0.3288	5.05E+02
Mcyclopentan	0.0264	4.05E+01
Benzene	0.0011	1.67E+00
22-Mpentane		
Cyclohexane	0.0051	7.83E+00
24-Mpentane		
223-Mbutane		
11Mcycpentan	0.0017	2.54E+00
2-Mhexane		
1-tr3-MCC5	0.0035	5.41E+00
23-Mpentane		
3-Mhexane		
3-Epentane		
n-Heptane	0.3286	8.02E+02
Toluene	0.0023	3.57E+00
25-Mhexane		
24-Mhexane		
2244Mpentane		
NBP[0]256*		
NBP[0]263*		
NBP[0]270*		
NBP[0]278*		
nC8	0.1390	2.13E+02
NBP[0]286*		
NBP[0]293*		
NBP[0]301*		
NBP[0]308*		
NBP[0]316*		
NBP[0]322*		



nC9	0.0730	1.12E+02
NBP[0]330*		
NBP[0]338*		
NBP[0]346*		
NBP[0]353*		
NBP[0]360*		
NBP[0]368*		
nC10	0.0264	4.06E+01
NBP[0]375*		
NBP[0]383*		
NBP[0]390*		
NBP[0]398*		
nC11	0.0092	1.42E+01
Total	1.0000	1.53E+03

Relief Model Configurations

The basic relief configuration is a Vessel connected to a relief manifold with three relief valves to a discharge line. The exact configuration connections are shown below. The hydrocarbon feed concentrations were modified to include fixed fractions of either nitrogen or water with the same piping configuration.

Two modifications to this basic piping configuration were also evaluated. The first modification was to consider the case where the relief flow was mixed with a pure nitrogen stream emanating from the relief bypass from the reflux drum. The relief flow and pressure for the hydrocarbon feed only case was mixed with a nitrogen stream at 62 psig to estimate the maximum nitrogen addition from this source. The piping configuration from the reflux drum was included in a piping network and mixed in the first East direction leg of the 14-inch blowdown line. The resulting network was evaluated.

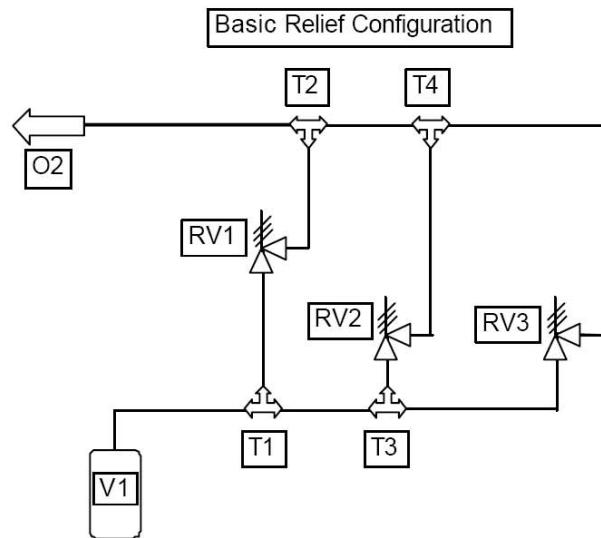
The second configuration was to include a section of the raffinate splitter and the entire overhead in the analysis. The flow for the hydrocarbon relief was modeled from a point at the 182 ft. level in the up direction in the raffinate splitter. It was found that it required a pressure of approximately 24 psig to generate a pressure of 62 psig at the relief valve location.

The detailed piping configurations for these cases are given in the tables below.
The basic configuration is on the following three pages.

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 29 of 52



FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 30 of 52

Connection		*RV1<->T2*		Diameter (in) Inlet	Outlet	Length (ft)	K-Value	L/D Ratio	Direction	DP Corr.
Name	Type	Device	Diameter (in) Inlet							
RV1<->T2:P1	Pipe		10.00	10.00	8.68	0.00	0.00	West		BBMHV
RV1<->T2:E1	Elbow		10.00	10.00	0.00	0.20	14.00	West -> Down		BBMHV
RV1<->T2:P2	Pipe		10.00	10.00	7.62	0.00	0.00	Down		BBMHV
Connection	*T1<->RV1*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.	
Name	Type	Device								
T1<->RV1:P1	Pipe		10.00	10.00	3.22	0.00	0.00	Up		BBMHV
Connection	*T2<->T4*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.	
Name	Type	Device								
T2<->T4:P1	Pipe		14.00	14.00	2.03	0.00	0.00	North		BBMHV
Connection	*RV2<->T4*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.	
Name	Type	Device								
RV2<->T4:P1	Pipe		6.00	6.00	8.68	0.00	0.00	West		BBMHV
RV2<->T4:E1	Elbow		6.00	6.00	0.00	0.21	14.00	West -> Down		BBMHV
RV2<->T4:P2	Pipe		6.00	6.00	7.26	0.00	0.00	Down		BBMHV
Connection	*T3<->T1*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.	
Name	Type	Device								
T3<->T1:P1	Pipe		24.00	24.00	1.98	0.00	0.00	North		BBMHV
Connection	*T3<->RV3*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.	
Name	Type	Device								
T3<->RV3:P1	Pipe		24.00	24.00	2.03	0.00	0.00	North		BBMHV
T3<->RV3:E1	Elbow		24.00	24.00	0.00	0.17	14.00	North -> Up		
T3<->RV3:X1	Expander		24.00	10.00	0.00	6.40	399.75	Up		
T3<->RV3:P2	Pipe		10.00	10.00	3.22	0.00	0.00	Up		BBMHV

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 31 of 52

Connection	*RV3<->T4*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.
Name	Device Type								
RV3<->T4:P1	Pipe	10.00	10.00	8.68	0.00	0.00	West	BBMHV	
RV3<->T4:E1	Elbow	10.00	10.00	0.00	0.20	14.00	West -> Down	BBMHV	
RV3<->T4:P2	Pipe	10.00	10.00	7.62	0.00	0.00	Down	BBMHV	
RV3<->T4:E2	Elbow	10.00	10.00	0.00	0.20	14.00	Down -> South	BBMHV	
RV3<->T4:X1	Expander	10.00	14.01	0.00	0.17	10.82	South	BBMHV	
RV3<->T4:P3	Pipe	14.00	14.00	2.03	0.00	0.00	South	BBMHV	
Connection	*T3<->RV2*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.
Name	Device Type								
T3<->RV2:P1	Pipe	6.00	6.00	2.86	0.00	0.00	Up	BBMHV	
Connection	*V1<->T1*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.
Name	Device Type								
V1<->T1:P1	Pipe	24.00	24.00	2.00	0.00	0.00	North	BBMHV	
Connection	*T2<->O2*		Diameter (in) Inlet	Outlet	(ft)	K-Value	L/D Ratio	Direction	DP Corr.
Name	Device Type								
T2<->O2:P1	Pipe	14.00	14.00	12.40	0.00	0.00	South	BBMHV	
T2<->O2:E1	Elbow	14.00	14.00	0.00	0.18	14.00	South -> Down	BBMHV	
T2<->O2:P2	Pipe	14.00	14.00	16.50	0.00	0.00	Down	BBMHV	
T2<->O2:E2	Elbow	14.00	14.00	0.00	0.18	14.00	Down -> North	BBMHV	
T2<->O2:P3	Pipe	14.00	14.00	45.50	0.00	0.00	North	BBMHV	
T2<->O2:E3	Elbow	14.00	14.00	0.00	0.18	14.00	North -> East	BBMHV	
T2<->O2:P4	Pipe	14.00	14.00	56.50	0.00	0.00	East	BBMHV	
T2<->O2:E4	Elbow	14.00	14.00	0.00	0.18	14.00	East -> North	BBMHV	
T2<->O2:P5	Pipe	14.00	14.00	61.75	0.00	0.00	North	BBMHV	
T2<->O2:E5	Elbow	14.00	14.00	0.00	0.18	14.00	North -> West	BBMHV	
T2<->O2:P6	Pipe	14.00	14.00	4.75	0.00	0.00	West	BBMHV	
T2<->O2:E6	Elbow	14.00	14.00	0.00	0.18	14.00	West -> North	BBMHV	
T2<->O2:P7	Pipe	14.00	14.00	205.00	0.00	0.00	North	BBMHV	
T2<->O2:E7	Elbow	14.00	14.00	0.00	0.18	14.00	North -> West	BBMHV	
T2<->O2:P8	Pipe	14.00	14.00	74.00	0.00	0.00	West	BBMHV	
T2<->O2:E8	Elbow	14.00	14.00	0.00	0.18	14.00	West -> North	BBMHV	
T2<->O2:P9	Pipe	14.00	14.00	46.00	0.00	0.00	North	BBMHV	
T2<->O2:E9	Elbow	14.00	14.00	0.00	0.18	14.00	North -> West	BBMHV	
T2<->O2:P10	Pipe	14.00	14.00	23.75	0.00	0.00	West	BBMHV	
T2<->O2:E10	Elbow	14.00	14.00	0.00	0.18	14.00	West -> Down	BBMHV	
T2<->O2:P11	Pipe	14.00	14.00	5.00	0.00	0.00	Down	BBMHV	

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082

August 11, 2005

Page 32 of 52

T2<->O2:E11	Elbow	14.00	14.00	0.00	0.18	14.00	Down -> West	
T2<->O2:P12	Pipe	14.00	14.00	193.50	0.00	0.00	West	BBMHV
T2<->O2:E12	Elbow	14.00	14.00	0.00	0.18	14.00	West -> South	
T2<->O2:P13	Pipe	14.00	14.00	27.50	0.00	0.00	South	BBMHV
T2<->O2:E13	Elbow	14.00	14.00	0.00	0.18	14.00	South -> Down	
T2<->O2:P14	Pipe	14.00	14.00	5.75	0.00	0.00	Down	BBMHV
T2<->O2:E14	Elbow	14.00	14.00	0.00	0.18	14.00	Down -> West	
T2<->O2:P15	Pipe	14.00	14.00	7.70	0.00	0.00	West	BBMHV
File Name:	bpa.flr			Converged Solution:			True	

Hydrocarbon Only ReliefAt 62.3 psig

Name O2

STREAM DATA:

Temp (Deg F)	160.36	
Pres (psig)	0	
Rate (lbmol/hr)	24777	
Enthalpy (Btu/lbmol)	-377.94	
Mw	99.077	
	Vapor	Liquid
Rate (lbmol/hr)	0	24777
Mw	0	99.077
Z	0	0.006255
Density (lb/ft^3)	0	39.938
Enthalpy (Btu/lbmol)	0	-377.94
Viscosity (cP)	0	0.25258
Component Fractions		
NITROGEN	0	0
WATER	0	9.999E-005
2-METHYL-BUTANE	0	0.016498
N-PENTANE	0	0.033397
2-METHYL-2-BUTE	0	0.00039996
CYCLOPENTANE	0	0.0053995
N-HEXANE	0	0.32847
METHYLCYCLOPENT	0	0.026397
BENZENE	0	0.0010999
CYCLOHEXANE	0	0.0050995
ETHYLCYCLOPENTA	0	0.0051995
N-HEPTANE	0	0.32827
TOLUENE	0	0.0022998
N-OCTANE	0	0.13889
N-NONANE	0	0.072893
N-DECANE	0	0.026397
N-UNDECANE	0	0.0091991



Maximum Hydrocarbon Flow from the Column

Name V1

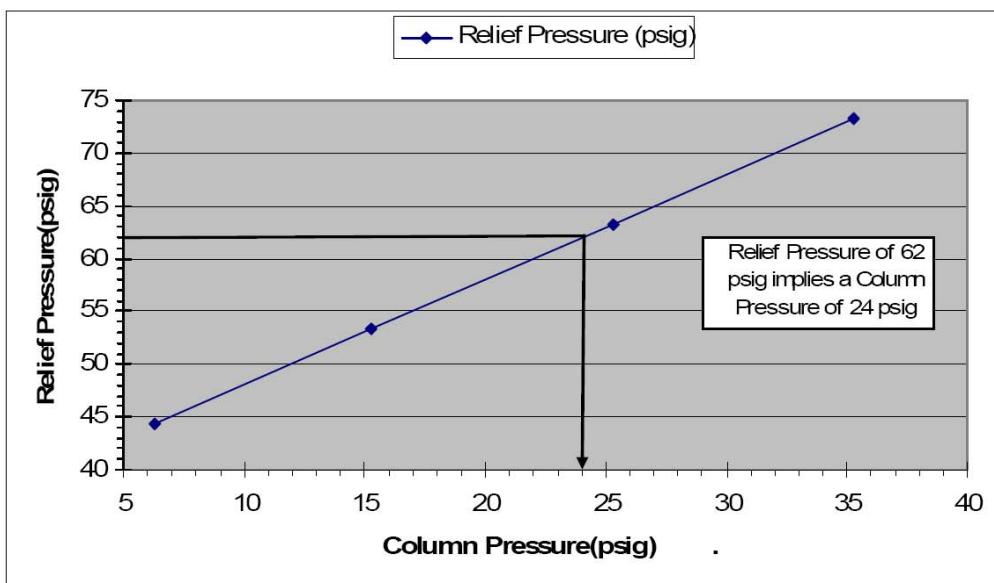
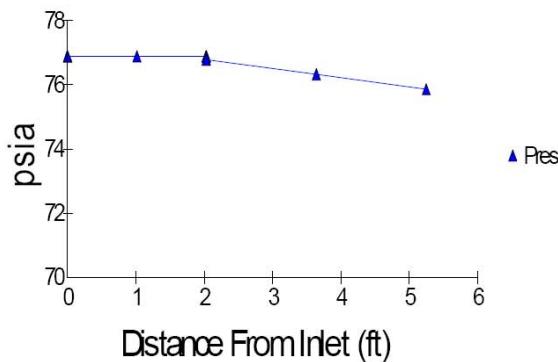
STREAM DATA:

Temp (Deg F)	160
Pres (psig)	24.3
Rate (lbmol/hr)	24777
Enthalpy (Btu/lbmol)	-392.16
Mw	99.077

	Vapor	Liquid
Rate (lbmol/hr)	0	24777
Mw	0	99.077
Z	0	0.01659
Density (lb/ft^3)	0	39.975
Enthalpy (Btu/lbmol)	0	-392.16
Viscosity (cP)	0	0.25287
Component Fractions		
NITROGEN	0	0
WATER	0	9.999E-005
2-METHYL-BUTANE	0	0.016498
N-PENTANE	0	0.033397
2-METHYL-2-BUTE	0	0.00039996
CYCLOPENTANE	0	0.0053995
N-HEXANE	0	0.32847
METHYLCYCLOPENT	0	0.026397
BENZENE	0	0.0010999
CYCLOHEXANE	0	0.0050995
ETHYLCYCLOPENTA	0	0.0051995
N-HEPTANE	0	0.32827
TOLUENE	0	0.0022998
N-OCTANE	0	0.13889
N-NONANE	0	0.072893
N-DECANE	0	0.026397
N-UNDECANE	0	0.0091991



T3<>RV3: Pressure vs. Length



1% Nitrogen ReliefAt 62.3 psigName O₂

STREAM DATA:

Temp (Deg F)	156.39	
Pres (psig)	0	
Rate (lbmol/hr)	15360	
Enthalpy (Btu/lbmol)	-324.68	
Mw	9	8.363
	Vapor	Liquid
Rate (lbmol/hr)	419.74	14940
Mw	66.871	99.247
Z	0.98133	0.0062848
Density (lb/ft ³)	0.15152	40.087
Enthalpy (Btu/lbmol)	9741.7	-607.49
Viscosity (cP)	0.0090877	0.25692
Component Fractions		
NITROGEN	0.34192	0.00067264
WATER	0.00044646	9.0246E-005
2-METHYL-BUTANE	0.049679	0.015359
N-PENTANE	0.082545	0.031704
2-METHYL-2-BUTE	0.00095066	0.00038445
CYCLOPENTANE	0.010162	0.0052651
N-HEXANE	0.32513	0.32514
METHYLCYCLOPENT	0.024453	0.026141
BENZENE	0.00098553	0.001103
CYCLOHEXANE	0.0039354	0.0051317
ETHYLCYCLOPENTA	0.0018271	0.0052937
N-HEPTANE	0.12943	0.33043
TOLUENE	0.00079051	0.0023419
N-OCTANE	0.022277	0.14071
N-NONANE	0.0046921	0.074082
N-DECANE	0.00067861	0.026809
N-UNDECANE	9.5956E-005	0.0093511

2% Nitrogen ReliefAt 62.3 psigName O₂

STREAM DATA:

Temp (Deg F)	153.61	
Pres (psig)	0	
Rate (lbmol/hr)	12620	
Enthalpy (Btu/lbmol)	-257.19	
Mw	97.649	
	Vapor	Liquid
Rate (lbmol/hr)	639.83	11980
Mw	64.663	99.41
Z	0.98299	0.0063082
Density (lb/ft ³)	0.14694	40.195
Enthalpy (Btu/lbmol)	9358.3	-770.73
Viscosity (cP)	0.0093222	0.26074
Component Fractions		
NITROGEN	0.3804	0.00074573
WATER	0.00040002	8.3945E-005
2-METHYL-BUTANE	0.045278	0.014537
N-PENTANE	0.076226	0.03047
2-METHYL-2-BUTE	0.00088708	0.00037386
CYCLOPENTANE	0.0095792	0.0051751
N-HEXANE	0.30753	0.32257
METHYLCYCLOPENT	0.023126	0.025935
BENZENE	0.00094319	0.001108
CYCLOHEXANE	0.0037747	0.0051692
ETHYLCYCLOPENTA	0.0017564	0.0053823
N-HEPTANE	0.12306	0.33221
TOLUENE	0.00075979	0.0023815
N-OCTANE	0.021132	0.1422
N-NONANE	0.0044271	0.07506
N-DECANE	0.00063479	0.027136
N-UNDECANE	8.9148E-005	0.0094731



5% Nitrogen Relief

At 62.3 psig

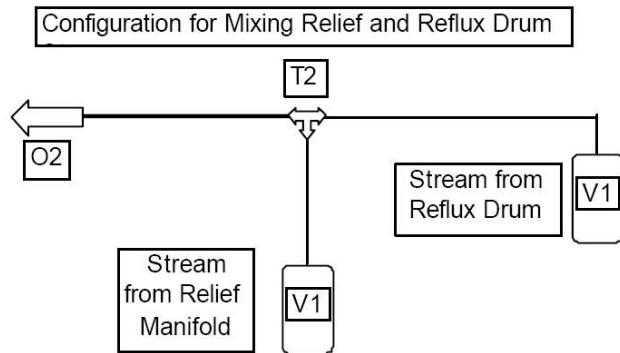
Name O₂

STREAM DATA:

Temp (Deg F)	147.87	
Pres (psig)	0	
Rate (lbmol/hr)	18830	
Enthalpy (Btu/lbmol)	-54.204	
Mw	95.519	
	Vapor	Liquid
Rate (lbmol/hr)	2037	16793
Mw	60.384	99.781
Z	0.98602	0.0063598
Density (lb/ft ³)	0.13808	40.418
Enthalpy (Btu/lbmol)	8626.3	-1107.1
Viscosity (cP)	0.0098211	0.26906
Component Fractions		
NITROGEN	0.4549	0.00088613
WATER	0.00032186	7.3089E-005
2-METHYL-BUTANE	0.037305	0.012967
N-PENTANE	0.064118	0.02788
2-METHYL-2-BUTE	0.00077195	0.00035488
CYCLOPENTANE	0.0081979	0.0048364
N-HEXANE	0.27296	0.31651
METHYLCYCLOPENT	0.020674	0.025637
BENZENE	0.00086743	0.0011282
CYCLOHEXANE	0.0034205	0.0051916
ETHYLCYCLOPENTA	0.0016027	0.0055242
N-HEPTANE	0.11068	0.33597
TOLUENE	0.00067595	0.0023849
N-OCTANE	0.018947	0.1456
N-NONANE	0.0039231	0.07723
N-DECANE	0.00055674	0.028077
N-UNDECANE	7.6508E-005	0.009746



The changes to simulate the additional flows from the reflux drum include the following additional piping:



FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 40 of 52

Connection		*T2<->O2*		Diameter (in)	Length (ft)	K-Value	L/D Ratio	Direction	DP Corr.
Name	Device Type	Inlet	Outlet						
T2<->O2:P1	Pipe	14.00	14.00	56.50	0.00	0.00	East	BBMHV	
T2<->O2:E1	Elbow	14.00	14.00	0.00	0.18	14.00	East -> North	BBMHV	
T2<->O2:P2	Pipe	14.00	14.00	61.75	0.00	0.00	North	BBMHV	
T2<->O2:E2	Elbow	14.00	14.00	0.00	0.18	14.00	North -> West	BBMHV	
T2<->O2:P3	Pipe	14.00	14.00	4.75	0.00	0.00	West	BBMHV	
T2<->O2:E3	Elbow	14.00	14.00	0.00	0.18	14.00	West -> North	BBMHV	
T2<->O2:P4	Pipe	14.00	14.00	205.00	0.00	0.00	North	BBMHV	
T2<->O2:E4	Elbow	14.00	14.00	0.00	0.18	14.00	North -> West	BBMHV	
T2<->O2:P5	Pipe	14.00	14.00	74.00	0.00	0.00	West	BBMHV	
T2<->O2:E5	Elbow	14.00	14.00	0.00	0.18	14.00	West -> North	BBMHV	
T2<->O2:P6	Pipe	14.00	14.00	46.00	0.00	0.00	North	BBMHV	
T2<->O2:E6	Elbow	14.00	14.00	0.00	0.18	14.00	North -> West	BBMHV	
T2<->O2:P7	Pipe	14.00	14.00	23.75	0.00	0.00	West	BBMHV	
T2<->O2:E7	Elbow	14.00	14.00	0.00	0.18	14.00	West -> Down	BBMHV	
T2<->O2:P8	Pipe	14.00	14.00	5.00	0.00	0.00	Down	BBMHV	
T2<->O2:E8	Elbow	14.00	14.00	0.00	0.18	14.00	Down -> West	BBMHV	
T2<->O2:P9	Pipe	14.00	14.00	193.50	0.00	0.00	West	BBMHV	
T2<->O2:E9	Elbow	14.00	14.00	0.00	0.18	14.00	West -> South	BBMHV	
T2<->O2:P10	Pipe	14.00	14.00	27.50	0.00	0.00	South	BBMHV	
T2<->O2:E10	Elbow	14.00	14.00	0.00	0.18	14.00	South -> Down	BBMHV	
T2<->O2:P11	Pipe	14.00	14.00	5.75	0.00	0.00	Down	BBMHV	
T2<->O2:E14	Elbow	14.00	14.00	0.00	0.18	14.00	Down -> West	BBMHV	
T2<->O2:P15	Pipe	14.00	14.00	7.70	0.00	0.00	West	BBMHV	
Connection	*V1<->T2*		Diameter (in)	Length (ft)	K-Value	L/D Ratio	Direction	DP Corr.	
Name	Device Type	Inlet							
V1<->T2:P1	Pipe	14.00	14.00	2.00	0.00	0.00	West	BBMHV	

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 41 of 52

Connection	*V1<->T2*							
	Name	Device Type	Diameter (in)	Outlet	(ft)	K-Value	L/D Ratio	Direction
V1<->T2:P1	Pipe	3.00	3.00	5.45	0.00	0.00	Up	BBMHV
V1<->T2:E1	Elbow	3.00	3.00	0.00	0.25	14.00	Up -> East	
V1<->T2:X1	Expander	3.00	1.50	0.00	2.93	182.82	East	
V1<->T2:P2	Pipe	1.50	1.50	0.25	0.00	0.00	East	BBMHV
V1<->T2:V1	Valve(Gate)	1.50	1.50	0.00	0.17	0.00	East	
V1<->T2:P3	Pipe	1.50	1.50	0.25	0.00	0.00	East	BBMHV
V1<->T2:E2	Elbow	1.50	1.50	0.00	0.29	14.00	East -> Up	
V1<->T2:P4	Pipe	1.50	1.50	1.50	0.00	0.00	Up	BBMHV
V1<->T2:E3	Elbow	1.50	1.50	0.00	0.29	14.00	Up -> North	
V1<->T2:P5	Pipe	1.50	1.50	0.50	0.00	0.00	North	BBMHV
V1<->T2:V2	Valve(Gate)	1.50	1.50	0.00	0.17	0.00	North	
V1<->T2:P6	Pipe	1.50	1.50	0.50	0.00	0.00	North	BBMHV
V1<->T2:E4	Elbow	1.50	1.50	0.00	0.29	14.00	North -> West	
V1<->T2:P7	Pipe	1.50	1.50	0.50	0.00	0.00	West	BBMHV
V1<->T2:V3	Valve	1.50	1.50	0.00	0.17	0.00	West	
V1<->T2:P8	Pipe	1.50	1.50	0.50	0.00	0.00	West	BBMHV
V1<->T2:E5	Elbow	1.50	1.50	0.00	0.29	14.00	West -> North	
V1<->T2:X2	Expander	1.50	3.00	0.00	0.52	32.65	North	
V1<->T2:P9	Pipe	3.00	3.00	3.79	0.00	0.00	North	BBMHV
V1<->T2:E6	Elbow	3.00	3.00	0.00	0.25	14.00	North -> Down	
V1<->T2:P10	Pipe	3.00	3.00	2.82	0.00	0.00	Down	BBMHV
V1<->T2:E7	Elbow	3.00	3.00	0.00	0.25	14.00	Down -> North	
V1<->T2:X3	Expander	3.00	5.01	0.00	0.40	24.72	North	
V1<->T2:P11	Pipe	5.00	5.00	14.69	0.00	0.00	North	BBMHV
V1<->T2:E8	Elbow	5.00	5.00	0.00	0.21	14.00	North	
V1<->T2:P12	Pipe	5.00	5.00	6.71	0.00	0.00	Down	BBMHV
V1<->T2:V4	Valve(Gate)	5.01	5.01	0.00	0.21	0.00	Down	
V1<->T2:P13	Pipe	6.00	6.00	0.25	0.00	0.00	Down	BBMHV
File Name:	bpaN21half1.net	Converged Solution:					True	

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 42 of 52

The predicted pressure at the relief valves required the additional piping from the Raffinate Splitter to the first Tee. This modified piping is shown below

Connection	*V1<->T1*								
	Name	Device Type	Diameter		(in)	(ft)	K-Value	L/D Ratio	Direction
			Inlet	Outlet					
V1<->T1:P1	Pipe	150.00	150.00	3.00	0.00	0.00	Up		BBMHV
V1<->T1:X1	Expander	150.00	24.00	0.00	578.13	36,132.90	Up		BBMHV
V1<->T1:P2	Pipe	24.00	24.00	2.00	0.00	0.00	Up		BBMHV
V1<->T1:E1	Elbow	24.00	24.00	0.00	0.17	14.00	Up -> West		
V1<->T1:P3	Pipe	24.00	24.00	10.30	0.00	0.00	West		BBMHV
V1<->T1:E2	Elbow	24.00	24.00	0.00	0.17	14.00	West -> Down		
V1<->T1:P4	Pipe	24.00	24.00	142.50	0.00	0.00	Down		BBMHV
V1<->T1:E3	Elbow	24.00	24.00	0.00	0.17	14.00	Down -> North		
V1<->T1:P1	Pipe	24.00	24.00	2.96	0.00	0.00	North		BBMHV

Predicted flows for Mixing 1.5 Nitrogen Stream with Hydrocarbon Relief

Name O2

STREAM DATA:

Temp (Deg F)	155.6	
Pres (psig)	0	
Rate (lbmol/hr)	25053	
Enthalpy (Btu/lbmol)	-348.92	
Mw	98.294	
	Vapor	Liquid
Rate (lbmol/hr)	737.34	24316
Mw	66.304	99.264
Z	0.98175	0.00629
Density (lb/ft^3)	0.15037	40.113
Enthalpy (Btu/lbmol)	9641.5	-651.87
Viscosity (cP)	0.0091445	0.25787
Component Fractions		
NITROGEN	0.35151	0.00069092
WATER	0.00043433	8.8717E-005
2-METHYL-BUTANE	0.049042	0.015324
N-PENTANE	0.081266	0.031566
2-METHYL-2-BUTE	0.0009274	0.00037943
CYCLOPENTANE	0.0099215	0.0052011
N-HEXANE	0.32063	0.32498
METHYLCYCLOPENT	0.02415	0.026166
BENZENE	0.00096219	0.0010916
CYCLOHEXANE	0.0038425	0.0050797
ETHYLCYCLOPENTA	0.0017817	0.0052441
N-HEPTANE	0.12749	0.33063
TOLUENE	0.00077085	0.00232
N-OCTANE	0.021908	0.14086
N-NONANE	0.0046025	0.074136
N-DECANE	0.00066545	0.026878
N-UNDECANE	9.3849E-005	0.0093708



5% Water Relief

At 62.3 psig

Name O2

STREAM DATA:

Temp (Deg F)	160.36
Pres (psig)	0
Rate (lbmol/hr)	27254
Enthalpy (Btu/lbmol)	-624.69
Mw	95.027
	Vapor Liquid
Rate (lbmol/hr)	0 27254
Mw	0 95.027
Z	0 0.0060112
Density (lb/ft^3)	0 40.116
Enthalpy (Btu/lbmol)	0 -624.69
Viscosity (cP)	0 0.25877
Component Fractions	
NITROGEN	0 0
WATER	0 0.050005
2-METHYL-BUTANE	0 0.015602
N-PENTANE	0 0.031803
2-METHYL-2-BUTENE	0 0.00040004
CYCLOPENTANE	0 0.0052005
N-HEXANE	0 0.31183
METHYLCYCLOPENT	0 0.025103
BENZENE	0 0.0011001
CYCLOHEXANE	0 0.0050005
ETHYLCYCLOPENTA	0 0.0051005
N-HEPTANE	0 0.31163
TOLUENE	0 0.0022002
N-OCTANE	0 0.13191
N-NONANE	0 0.069307
N-DECANE	0 0.025103
N-UNDECANE	0 0.0087009

10% Water ReliefAt 62.3 psig

Name O2

STREAM DATA:

Temp (Deg F)	154.52
Pres (psig)	0
Rate (lbmol/hr)	25820
Enthalpy (Btu/lbmol)	-879.43
Mw	90.973
	Vapor Liquid
Rate (lbmol/hr)	673.31 25147
Mw	58.303 91.848
Z	0.97433 0.0058445
Density (lb/ft^3)	0.13346 40.475
Enthalpy (Btu/lbmol)	9309 -1152.2
Viscosity (cP)	0.0078799 0.27134

Component Fractions

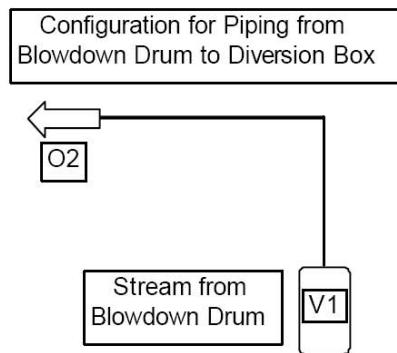
NITROGEN	0	0
WATER	0.41624	0.091532
2-METHYL-BUTANE	0.044652	0.014001
N-PENTANE	0.074181	0.029022
2-METHYL-2-BUTE	0.00093248	0.00038574
CYCLOPENTANE	0.0090157	0.0048925
N-HEXANE	0.28873	0.29537
METHYLCYCLOPENT	0.021294	0.023867
BENZENE	0.00092201	0.0011048
CYCLOHEXANE	0.0035044	0.0048347
ETHYLCYCLOPENTA	0.0016273	0.0049876
N-HEPTANE	0.1139	0.29985
TOLUENE	0.00066955	0.0021383
N-OCTANE	0.019553	0.12772
N-NONANE	0.0040998	0.067349
N-DECANE	0.00059397	0.024421
N-UNDECANE	8.3771E-005	0.00852

FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 46 of 52

Modeling the blowdown and sewer used the following piping network



Connection Name	*V1<->O1*		Length	K-Value	L/D Ratio	Direction	DP Corr.
	Device Type	Diameter (in)					
V1<->O1:P1	Pipe	120	120	3	0	0 Down	BBMHV
V1<->O1:X1	Expander	120	6	0	46797.3	2924830 Down	
V1<->O1:P2	Pipe	6	6	5.86	0	0 Down	BBMHV
V1<->O1:E1	Elbow	6	6	0	0.21	14 Down -> East	
V1<->O1:P3	Pipe	6	6	5.33	0	0 East	BBMHV
V1<->O1:E2	Elbow	6	6	0	0.21	14 East -> Up	
V1<->O1:P4	Pipe	6	6	7.33	0	0 Up	BBMHV
V1<->O1:E3	Elbow	6	6	0	0.21	14 Up -> South	
V1<->O1:P5	Pipe	6	6	4.16	0	0 South	BBMHV
V1<->O1:E4	Elbow	6	6	0	0.21	14 South -> Down	
V1<->O1:P6	Pipe	6	6	10	0	0 Down	BBMHV
V1<->O1:X1	Expander	6	12	0	0.54764	34.2276 Down	
V1<->O1:P7	Pipe	12	12	5	0	0 Down	BBMHV
V1<->O1:E5	Elbow	12	12	0	0.18	14 Down -> West	
V1<->O1:P8	Pipe	12	12	29.16	0	0 West	BBMHV
V1<->O1:E6	Elbow	12	12	0	0.18	14 West -> South	
V1<->O1:P8	Pipe	12	12	155.5	0	0 South	BBMHV
File Name:	blowdn.net		Converged Solution:		True		



Blowdown Drum Sewer Flow for Bottom Section Filled (22.2 psia)

Name O1

STREAM DATA:

Temp (Deg F)	160.07
Pres (psig)	0
Rate (lbmol/hr)	9350.2
Enthalpy (Btu/lbmol)	-394.53
Mw	99.077
	Vapor Liquid
Rate (lbmol/hr)	0 9350.2
Mw	0 99.077
Z	0 0.0062565
Density (lb/ft^3)	0 39.948
Enthalpy (Btu/lbmol)	0 -394.53
Viscosity (cP)	0 0.25281
Component Fractions	
NITROGEN	0 0
WATER	0 9.999E-005
2-METHYL-BUTANE	0 0.016498
N-PENTANE	0 0.033397
2-METHYL-2-BUTE	0 0.00039996
CYCLOPENTANE	0 0.0053995
N-HEXANE	0 0.32847
METHYLCYCLOPENT	0 0.026397
BENZENE	0 0.0010999
CYCLOHEXANE	0 0.0050995
ETHYLCYCLOPENTA	0 0.0051995
N-HEPTANE	0 0.32827
TOLUENE	0 0.0022998
N-OCTANE	0 0.13889
N-NONANE	0 0.072893
N-DECANE	0 0.026397
N-UNDECANE	0 0.0091991



Blowdown Drum Sewer Section Flow with Drum Completely Filled (46.2 psia)

Name O1

STREAM DATA:

Temp (Deg F)	160.19
Pres (psig)	0
Rate (lbmol/hr)	16194
Enthalpy (Btu/lbmol)	-388.13
Mw	99.077
	Vapor Liquid
Rate (lbmol/hr)	0 16194
Mw	0 99.077
Z	0 0.0062559
Density (lb/ft^3)	0 39.944
Enthalpy (Btu/lbmol)	0 -388.13
Viscosity (cP)	0 0.25272
Component Fractions	
NITROGEN	0 0
WATER	0 9.999E-005
2-METHYL-BUTANE	0 0.016498
N-PENTANE	0 0.033397
2-METHYL-2-BUTE	0 0.00039996
CYCLOPENTANE	0 0.0053995
N-HEXANE	0 0.32847
METHYLCYCLOPENT	0 0.026397
BENZENE	0 0.0010999
CYCLOHEXANE	0 0.0050995
ETHYLCYCLOPENTA	0 0.0051995
N-HEPTANE	0 0.32827
TOLUENE	0 0.0022998
N-OCTANE	0 0.13889
N-NONANE	0 0.072893
N-DECANE	0 0.026397
N-UNDECANE	0 0.0091991

**Source Term Model**

(spreadsheet adapted from the CCPS Guidelines for CPQRA Supplement)

Pool Evaporation using Kawamura and MacKay

Direct Evaporation
Model

Input Data:

Geometry:

Diameter of pool:	10	m	32.8	ft
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Physical Properties of Liquid:

Molecular weight of liquid:	99	99		
Heat of vaporization of liquid:	29	kJ/mol	28.55	btu/mol
Vapor pressure of liquid at ambient:	0.22	bar abs	3.19	psia
Kinematic viscosity of liquid in air:	3.90016E-07	m ² /s	4.1939E-06	ft ² /s

Physical Properties of Air:

Diffusivity:	7.10E-06	m ² /s	7.64e-05	ft ² /s
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Heat Transfer Properties:

Solar input:	0.642	kJ/m ² s	211.5191	btu/ft ² -hr
Heat transfer coefficient of liquid:	0.0431	kJ/m ² s K	7.8889	btu/ft ² -hr-F
Heat transfer coefficient of ground:	0.0453	kJ/m ² s K	8.2916	btu/ft ² -hr-F

Ambient temperature:	300.3	K	81.1	F
Wind speed at 10 meters:	2	m/s	6.56	ft/s

Calculated Results:

Pool area:	78.54	m ²	844.9	ft ²
Schmidt number:	0.05		0.05	
Mass transfer coefficient:	0.044891964	m/s	0.147265	ft/s
Overall ground heat transfer coefficient:	0.0221	kJ/m ² s K	4.0451	btu/ft ² -hr-F

Evaporation Rates:

Mass transfer:	3.08	kg/s	6.780754	lbm/s
Solar radiation:	0.17	kg/s	0.37948	lbm/s

Beta:	0.071		0.071	
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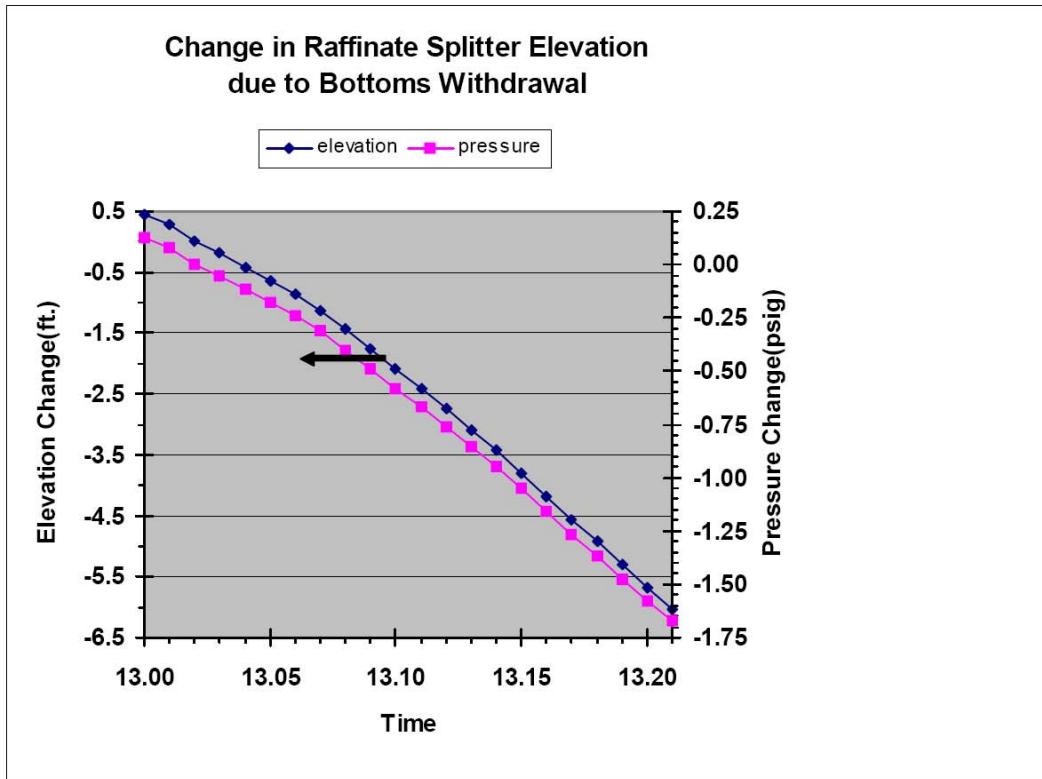
Net evaporation rate:	0.364	kg/s	0.803529	lb/s
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Evaporation flux	0.004640712	kg/(m ² s)	3.42235	lb/ft ² -hr
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Material Balance for the Raffinate Splitter after 13:00

The material balance on the splitter accounts for the feed flow measured with F5000, the heavy raffinate flow from the bottom measured with F5015, and the stabilized isomerate flow measured by F5016. The net volumetric flow into the column is translated into approximate equivalent elevation change assuming no column internals. Equivalent pressure change is then calculated assuming 0.2778 psi/ft. The resulting change in elevation and pressure over the relief timeframe (from 13:00 to 13:21) is plotted in the accompanying figure.



Blowdown Drum Material Balance Integration

The rate of flow from the blowdown drum to the diversion box is used with the maximum flow from the relief through the manifold to the blowdown to estimate the accumulation in the blowdown drum and to estimate the rate of elevation rise in the drum to ultimately predict the time needed to overflow the blowdown drum.

The procedure is as follows. First, the static pressure head in the blowdown drum is used to estimate the maximum flow in the line from the blowdown to the diversion box. Second, this flow is subtracted from the maximum flow to the blowdown from the relief header to estimate the net flow into the blowdown. Third, the net flow into the blowdown drum is calculated. Fourth, this net flow is translated into a rate of elevation change in the blowdown drum. Fifth, the elevation in the blowdown is recalculated. Sixth, the new elevation is used to predict a static



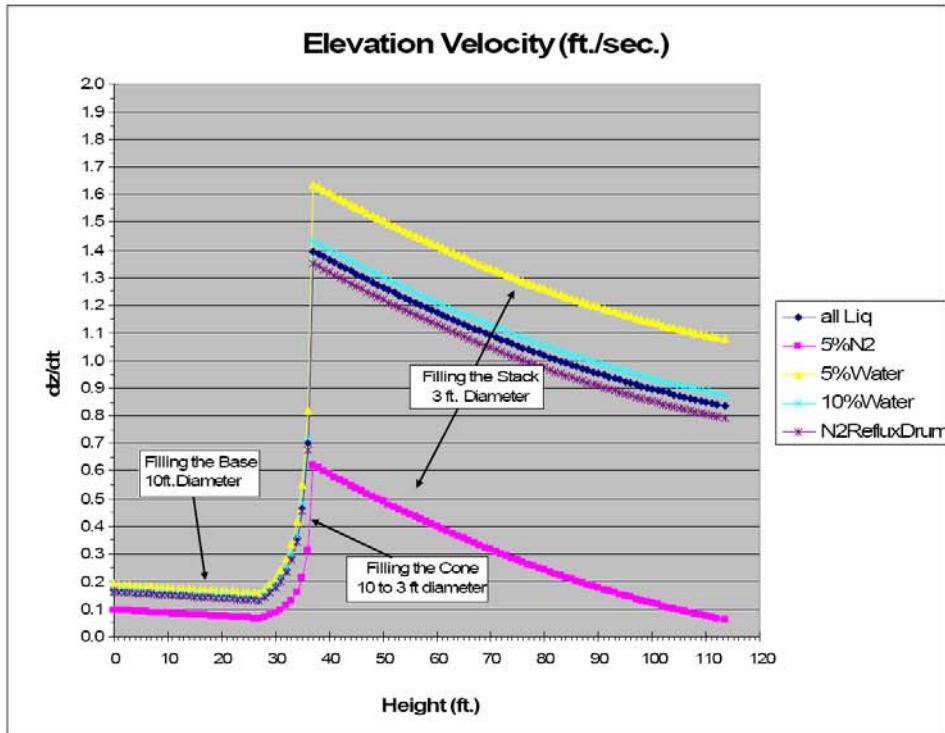
pressure and the procedure is repeated starting with the first step until the blowdown stack is overwhelmed at 113.5 feet.

The accompanying figure shows the rate of elevation change as a function of height. One notes that the graph shows a constant rate that diminishes in the two cylindrical sections, the 10 foot diameter drum and the 3 foot diameter stack, connected by the rapid acceleration section for the conical section of the blowdown. For three of the cases, all liquid, Reflux Drum N2, and 10% Water, the elevation rise is approximately the same.

The time to fill the blowdown drum by performing the numerical integration is shown in the next figure. Approximately two and a half minutes are needed to fill the drum, the conical section is then filled in the next 40 seconds, followed by the time to fill the stack, approximately 70 seconds. The total time to fill the drum, conical section and stack is approximately 260 seconds, roughly 4 minutes and 20 seconds from the time the drum starts to fill.

These approximate figures can be used to estimate the time of the overfill. By subtracting off the time to fill the 14" relief line (6355 gal.), from the 6 minute relief, only about 45 seconds are left for the overfill. A total volume balance on the relief is shown in the table below.

Case	Total Volume of relief (gal)	Overfill Volume (gal)	Volume to sewer (gal)
All liquid	45,905	1,934	43,971
Reflux Drum N2	46,591	1,961	44,630



FATAL ACCIDENT INVESTIGATION REPORT



Project Engineering Project 500082
August 11, 2005
Page 52 of 52

