



U.S. DEPARTMENT OF
ENERGY

PNNL-25077

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Hydrotreater/Distillation Column Hazard Analysis Report

Rev. 2

April 2016



Pacific Northwest
NATIONAL LABORATORY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <<http://www.ntis.gov/about/form.aspx>>
Online ordering: <http://www.ntis.gov>



This document was printed on recycled paper.

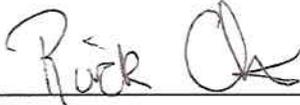
(8/2010)

Hydrotreater/Distillation Column Hazard Analysis Report

Revision Number	Effective Date	Description of Change
0	11/2012	Initial issue.
1	12/14/2015	Update to reflect changes in procedures; clarification of HTDC processes; clarification of controls; BLEVE and PVB calculations updated.
2	4/8/2016	Update to remove pressure interlocks as critical controls (see HTDC-2016-023 and HTDC-2016-026); clarification that attached drawings are subject to change.

Hydrotreater/Distillation Column Hazard Analysis Report

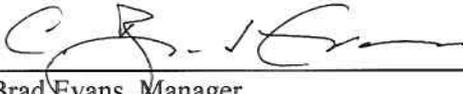
Prepared by: Peter Lowry
Katie Wagner

Concurred by: 
Rick Orth, Technical Group Manager
Chemical and Biological Process Development Group

4-8-16
Date


Bob Gruel, Capability Manager
Hydrotreater and Distillation Column Project

4/12/16
Date

Approved by: 
Brad Evans, Manager
Nuclear Operations Division

4/14/16
Date

This page intentionally left blank

Executive Summary

This project Hazard and Risk Analysis Report contains the results of several hazard analyses and risk assessments. An initial assessment was conducted in 2012, which included a multi-step approach ranging from design reviews to a formal What-If hazard analysis. A second What-If hazard analysis was completed during February 2013 to evaluate the operation of the hydrotreater/distillation column processes to be installed in a process enclosure within the Process Development Laboratory West (PDL-West) facility located on the PNNL campus. The qualitative analysis included participation of project and operations personnel and applicable subject matter experts. The analysis identified potential hazardous scenarios, each based on an initiating event coupled with a postulated upset condition. The unmitigated consequences of each hazardous scenario were generally characterized as a process upset; the exposure of personnel to steam, vapors or hazardous material; a spray or spill of hazardous material; the creation of a flammable atmosphere; or an energetic release from a pressure boundary.

In response to independent review comments received by PNNL from PNSO, two supplemental hazard analyses were conducted and quantitative risk assessments performed for the Distillation Column and Hydrotreater units in June 2014 and April 2015, respectively (see Appendices D and E). As described below, selected hazardous scenarios received increased attention:

- For scenarios involving a release of hazardous material or energy, controls were identified in the What-If analysis table that either prevent the occurrence or mitigate the effects of the release.
- For scenarios with significant consequences that could impact personnel outside the enclosure, “critical controls” were identified in the What-If analysis table that either prevent the occurrence or mitigate the effects of the release.
- For events requiring critical controls (highly energetic releases and potential deflagrations), quantitative analyses were performed to determine the potential magnitude of the scenario, including the potential to affect the environment outside of the PDL-West facility.

Only for the conservative unmitigated analysis involving a Boiling Liquid Expanding Vapor Explosion (BLEVE) of the reactor vessel (R-130) could a significant overpressure (greater than 21 kPa) challenging PDL-West facility structure occur. Calculations determined that there were no cases in which overpressures were sufficient to result in greater than minor damage (7 kPa) at any of the normally occupied facilities outside of the PDL-West facility.

The following critical controls prevent these high-energy scenarios from occurring:

- Vessel and piping design, including pressure relief valves
- Hydrogen utility (supply) design
- Reactor and distillation column temperature and pressure controls
- Enclosure design and ventilation system
- Hydrogen and flammable vapor monitors and selected interlocks
- Safe Operating Procedures

Hydrotreater/Distillation Column Hazard Analysis Report

The analysis concludes that with the identified hazard controls in place, the risks posed from operation of the hydrotreater and distillation columns are adequately mitigated, and these systems can be operated safely, consistent with PNNL control of other laboratory operations.

This page intentionally left blank

Table of Contents

1.0	INTRODUCTION	1
1.1	PURPOSE	1
1.2	SCOPE	1
2.0	FACILITY AND PROCESS DESCRIPTION	3
2.1	SITE AND FACILITY LAYOUT.....	3
2.2	HYDROTREATER/DISTILLATION COLUMN PROCESSES	5
2.2.1	<i>Hydrotreater Operations Outline</i>	<i>10</i>
2.2.2	<i>Distillation Operations Outline</i>	<i>11</i>
3.0	HAZARD ASSESSMENT	13
3.1	HAZARD IDENTIFICATION	13
3.2	WHAT-IF ANALYSIS.....	16
3.3	ANALYSIS RESULTS	17
3.4	EVALUATION OF HIGH HAZARD SCENARIOS.....	65
3.4.1	<i>Boiling Liquid Expanding Vapor Explosion (BLEVE)</i>	<i>65</i>
3.4.1.1	BLEVE Consequence Methodology	65
3.4.1.2	BLEVE Results.....	68
3.4.2	<i>Pressure Vessel Burst Scenarios</i>	<i>71</i>
3.4.2.1	PVB Consequence Methodology	71
3.4.2.2	PVB Results.....	72
3.4.3	<i>Deflagration Scenarios.....</i>	<i>73</i>
3.4.3.1	Deflagration Consequence Methodology	74
3.4.3.2	Deflagration Results.....	74
3.4.4	<i>Calculation Summary.....</i>	<i>76</i>
4.0	HAZARD CONTROLS	78
4.1	CRITICAL CONTROLS	78
4.1.1	<i>Vessel and Piping Design.....</i>	<i>79</i>
4.1.2	<i>Reactor and Distillation Column Temperature Critical Controls</i>	<i>80</i>
4.1.3	<i>Enclosure Design and Ventilation.....</i>	<i>81</i>
4.1.4	<i>Hydrogen Monitors</i>	<i>81</i>
4.1.5	<i>Flammable Vapor Monitors</i>	<i>81</i>
4.1.6	<i>Safe Operating Procedures (SOPs).....</i>	<i>81</i>
4.2	OTHER CONTROLS (NON-CRITICAL).....	82
4.2.1	<i>Flame Detectors</i>	<i>82</i>
4.2.2	<i>Fire Suppression System.....</i>	<i>82</i>
4.2.3	<i>Temperature and Pressure Controls/Alarms Prompting Operator Response</i>	<i>82</i>
4.2.4	<i>Check Valves</i>	<i>83</i>
4.2.5	<i>Facility Configuration.....</i>	<i>83</i>
4.3	SAFETY MANAGEMENT PROGRAMS	83
4.3.1	<i>Worker Safety and Health</i>	<i>83</i>
4.3.2	<i>Fire Protection Program.....</i>	<i>83</i>
4.3.3	<i>Training and Qualification.....</i>	<i>84</i>
4.3.4	<i>Maintenance and Testing Program</i>	<i>84</i>
4.3.4.1	Initial Testing	84
4.3.4.2	Maintenance.....	85
5.0	CONCLUSION	86
6.0	REFERENCES	87
	Appendix A : Attendees	88
	Appendix B : Key Design Information Reviewed	90

Hydrotreater/Distillation Column Hazard Analysis Report

Appendix C : November 2012 Hydrotreater / Distillation Column Project Hazard and Risk Analysis Report	93
Appendix D : Supplemental Hazard Analysis and Risk Assessment – Distillation Column	95
Appendix E : Supplemental Hazard Analysis and Risk Assessment - Hydrotreater	97

This page intentionally left blank

1.0 Introduction

The hydrotreater/distillation column project consists of catalytic hydrotreatment (hydrotreater) and distillation processes to produce a range of desired petroleum products from fast pyrolysis bio-oil feedstock. The hydrotreater and distillation processes are being installed in a portion of the Process Development Laboratory West (PDL-West) facility located on the PNNL Campus.

1.1 Purpose

As part of the PNNL Integrated Safety Management process, the hazards associated with performing work within PNNL-managed facilities are identified and appropriate controls applied. The hazards associated with the hydrotreater/distillation column processes have been reviewed during design review meetings as part of the overall design process. In addition, facilitated hazard analysis sessions and quantitative risk assessments were performed. The purpose of this report is to document the hazards and controls associated with the process-related system components forming the hydrotreater/distillation column processes contained within the PDL-West facility and the potential interactions of these hazards with respect to supporting systems and the facility as evaluated during What-If hazard analysis sessions held in February 2013 and supplemental hazard analyses and risk assessments performed in 2014 and 2015 (Appendices D and E).

1.2 Scope

The What-If hazard analysis used for the hydrotreater/distillation column project is consistent with the methodology found in the American Institute of Chemical Engineers (AIChE) *Guidelines for Hazard Evaluation Procedures – With Worked Examples, 2nd Edition* [AIChE, 1992], and in *Chemical Process Hazards Analysis* [DOE-HDBK-1100-2004].

The scope of this assessment did not include evaluating those hazards that were considered normal and incidental to the operation of the PDL-West facility unless those hazards were judged to have the potential to challenge the safe operation of the hydrotreater/distillation column processes. These incidental hazards are adequately addressed through the Integrated Operations System (IOPS) and existing PNNL work controls.

Examination of the spectrum of potential upset conditions that could expose members of the public, onsite workers, facility workers, and the environment to hazardous materials and conditions is incorporated into this report. The hazard evaluation postulated scenarios involving both single-point/event failures and common-cause initiators. The upset conditions with the potential to result in highly energetic releases or potential deflagrations were evaluated using quantitative analysis to determine the potential magnitude of the scenario, including the potential to affect the environment outside of the PDL-West facility.

Section 2, *Facility and Process Description*, provides a brief description of the design and information to enable an understanding of the hazards associated with the hydrotreater/distillation column processes.

Section 3, *Hazard Assessment*, provides a summary of the What-If methodology used, description of the hazardous scenarios considered, and the results of the analysis.

Hydrotreater/Distillation Column Hazard Analysis Report

Section 4, *Hazard Controls*, describes the “critical controls” for the high consequence hazards and PNNL Safety Management Programs which support performing work safely. The critical controls are those required to prevent or mitigate significant consequences associated with the hydrotreater and distillation column process hazards. Other non-critical controls were included to further reduce hazardous event frequencies.

Appendices A and B contain the meeting participant information and design information reviewed during the hazards analysis meetings. The design documents in Appendix B are historical and subject to change. See the Hydrotreater/Distillation Column SharePoint site for current design documents.

Appendix C contains the November 2012 Hydrotreater / Distillation Column Project Hazard and Risk Analysis Report which described a number of appropriate controls that were, or are being, put in place to ensure the safe operation of the hydrotreater and distillation processes. The 2012 report will be retained as a static part of this hazard analysis; it will not be revised.

Appendices D and E contains the July 2014 and April 2015 Supplemental Hazard Analysis and Risk Assessment for the Distillation Column and Hydrotreater units. These reports were generated in response to independent review comments received by PNNL from the U.S. Department of Energy Pacific Northwest Site Office (PNSO) with regard to the *Hydrotreater/Distillation Column Hazard Analysis Report* issued in April 2013.

2.0 Facility and Process Description

2.1 Site and Facility Layout

The hydrotreater/distillation column processes will be conducted in the PDL-West high bay work area in a dedicated process enclosure. The PDL-West building is located on the PNNL site in north Richland as shown in Figure 2-1.

Approximate distances from the hydrotreater/distillation column process enclosure to key landmarks are shown in Table 2-1.

Table 2-1. Distance from PDL-West to Surrounding Landmarks

Landmark	Direction	Distance from Process Enclosure	
		feet	meters
Process Development Laboratory East*	East	116	35
5 th Street	South	120	37
Innovation Boulevard	West	140	43
Chemical Engineering Laboratory	East	175	53
Technical Support Warehouse	North	290	88
4 th Street	South	420	128
Research Technology Laboratory	South East	730	222
George Washington Way	East	790	241
Atmospheric Measurement Laboratory	Northwest	825	251
Inhalation Laboratory	Northeast	880	268
KinderCare	West-Southwest	1120	341

*Nearest normally occupied Facility outside PDL-West, endpoint for the evaluation of impacts in Section 3.4.

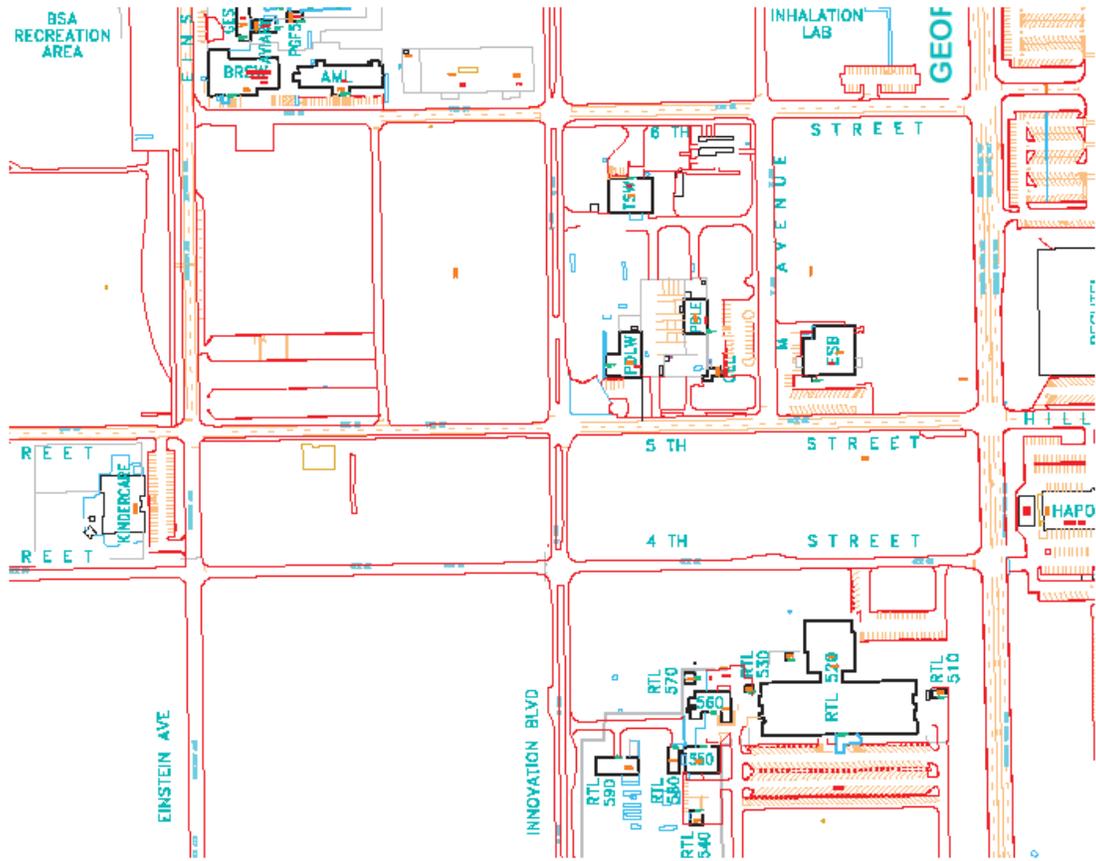


Figure 2-1. Location of PDL-West (PDLW)

2.2 Hydrotreater/Distillation Column Processes

The hydrotreater/distillation column project consists of catalytic hydrotreatment (hydrotreater) and distillation processes to produce a range of desired petroleum products derived from fast pyrolysis bio-oil feedstock. Figure 2-2 depicts the process flow diagram for the hydrotreater and distillation processes. The planned operation duration and frequency are 1 week (five, 24-hour continuous operation days per month). The hydrotreater/distillation systems are located in a dedicated enclosure as shown in Figure 2-3. Figure 2-4 shows the major hydrotreater process equipment; Figure 2-5 shows the major distillation process equipment.

Hydrogen is supplied to the hydrotreater by a high pressure compressor, storage bottles (or tube trailer), and a distribution system. This system will also supply hydrogen to other research projects located near PDL-West. High and low pressure nitrogen will be supplied via a distribution system that is dedicated to the hydrotreater/distillation processes.

During hydrotreatment, deoxygenation of bio-oil takes place to produce hydrocarbon products that are similar to gasoline, diesel and jet fuel blendstock. Hydrotreatment is accomplished by adding hydrogen as feed along with the bio-oil in the presence of a catalyst. The process is typically operated at temperatures up to approximately 400°C and pressures up to approximately 135 atm. Distillation is then used to obtain the specific gasoline, diesel and jet fuel cuts from the hydrotreated product.

The hydrotreater consists of a down-flow trickle, fixed bed reactor with gas and liquid feed systems, liquid/gas product separation and recovery, and an instrumentation/control system. The system is designed for a 2.5 liter per hour bio-oil feed capacity at 400°C and 135 atm with hydrogen feed at 5 m³/h. In addition, the distillation column will be used to fractionate the hydrocarbon product into gasoline, diesel, jet fuel, and cycle oil products. The distillation column can be, but is not planned to be, operated concurrent with the hydrotreater and is designed with a throughput of 7.5–15 liters of feed per hour. Both the hydrotreater and the distillation column are skid mounted with power distribution systems, transformers, outlets, wiring, panels, cooling, heating, control, and other ancillary process systems.

To support the hazards analysis, the key process steps for the hydrotreater/distillation operations were outlined and reviewed for in Section 2.2.1 and 2.2.2.

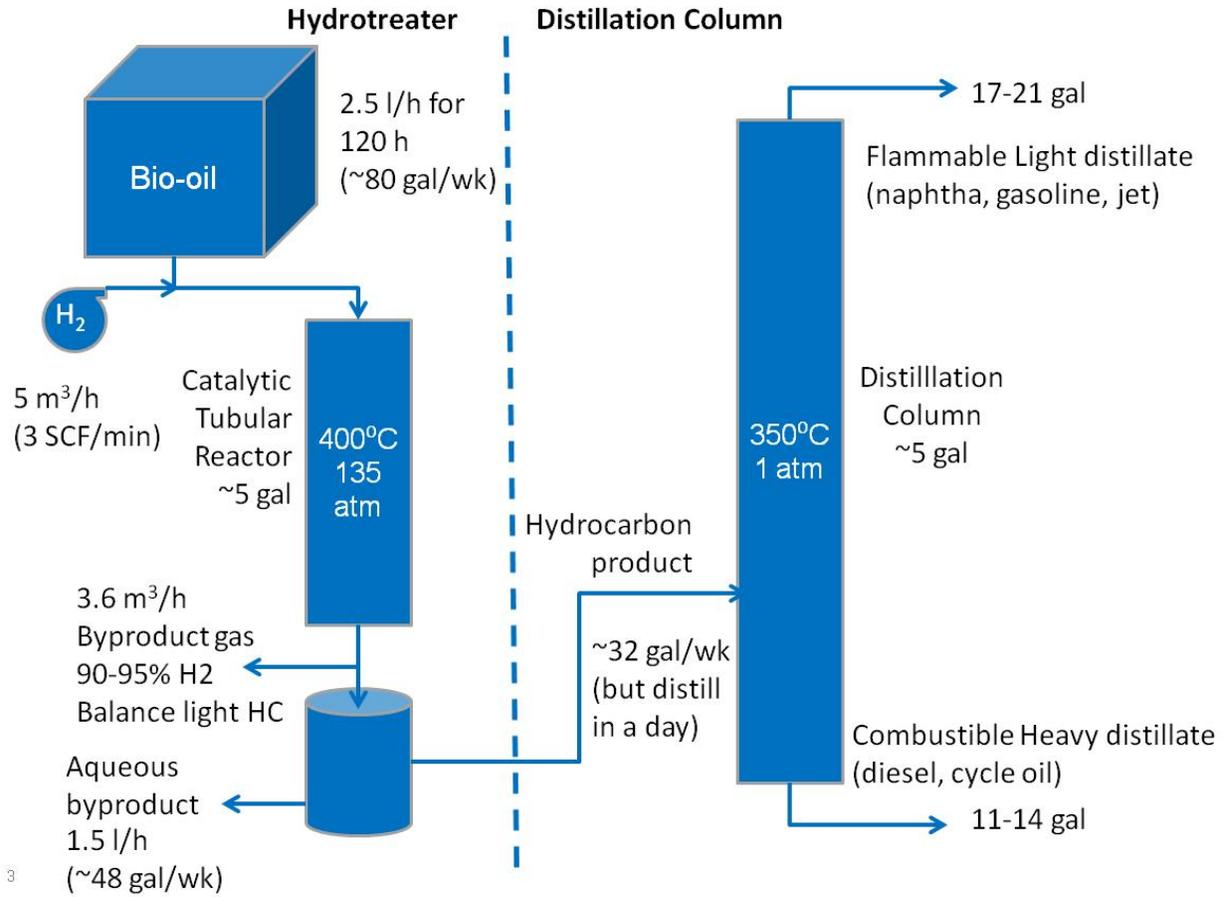
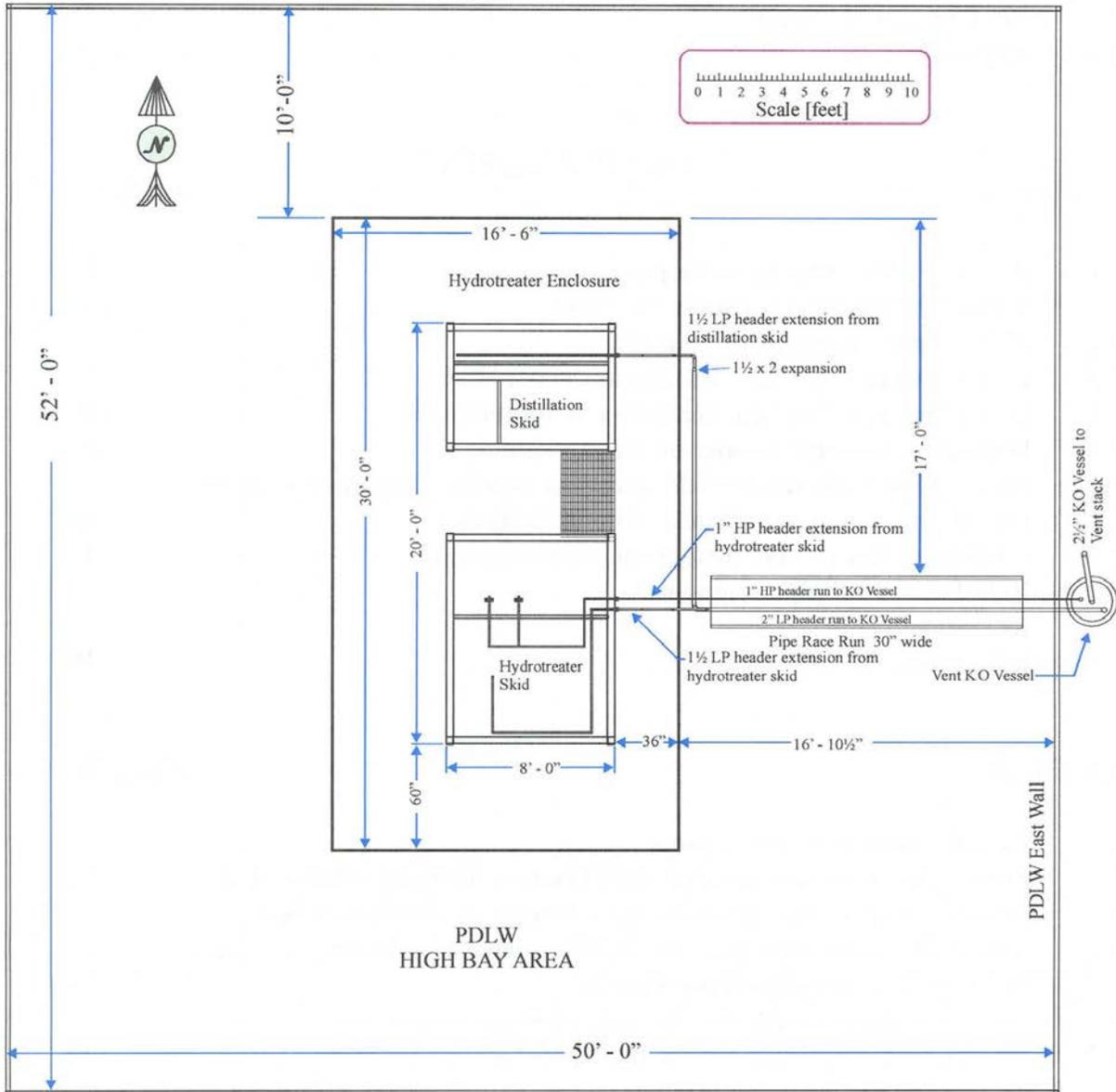


Figure 2-2. Hydrotreater/Distillation Process Flow Diagram

Hydrotreater/Distillation Column Hazard Analysis Report



**Figure 2-3. Location of Hydrotreater/Distillation Enclosure within PDL-West
(from CTI-12-631)**

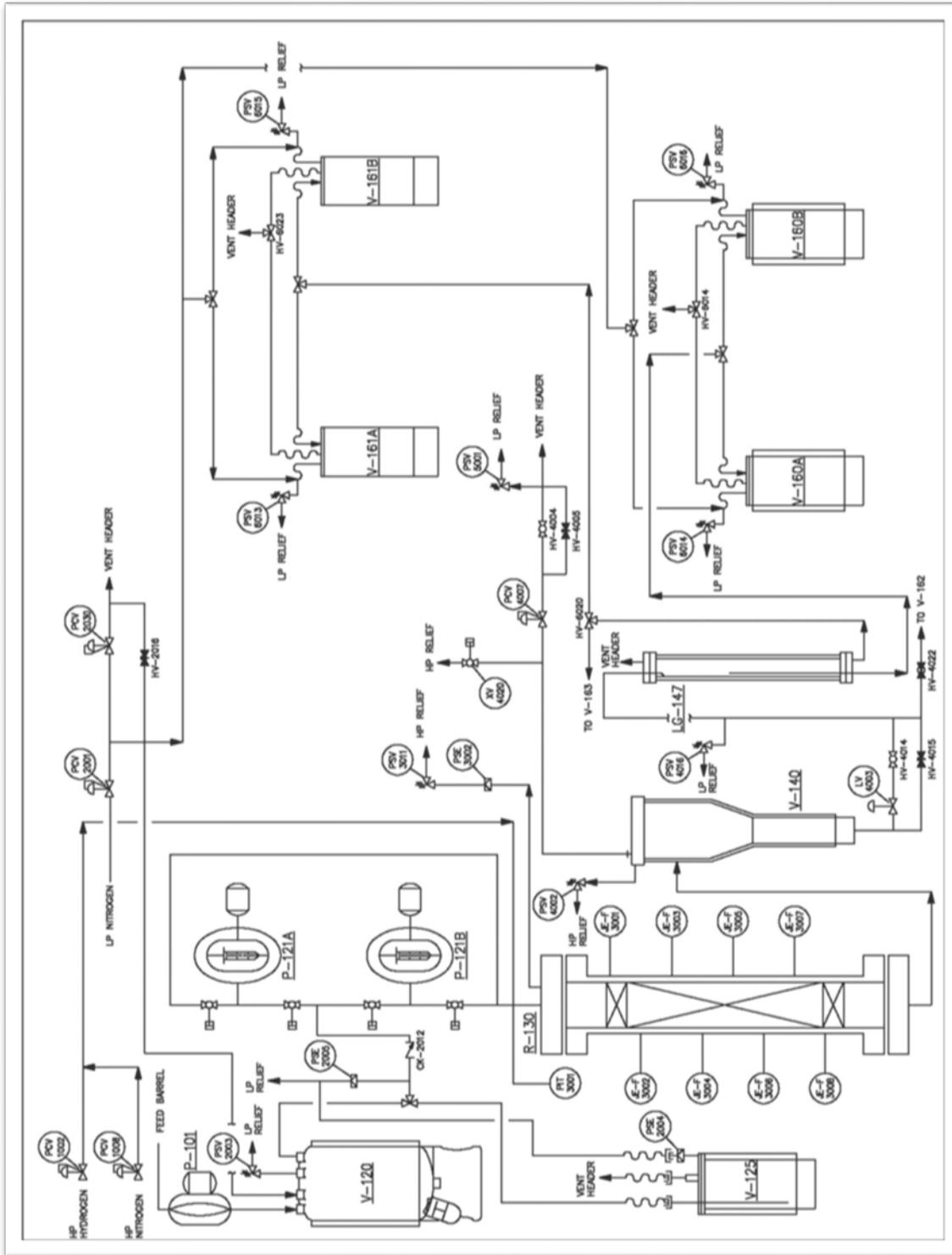


Figure 2-4. Hydrotreater Process Major Components

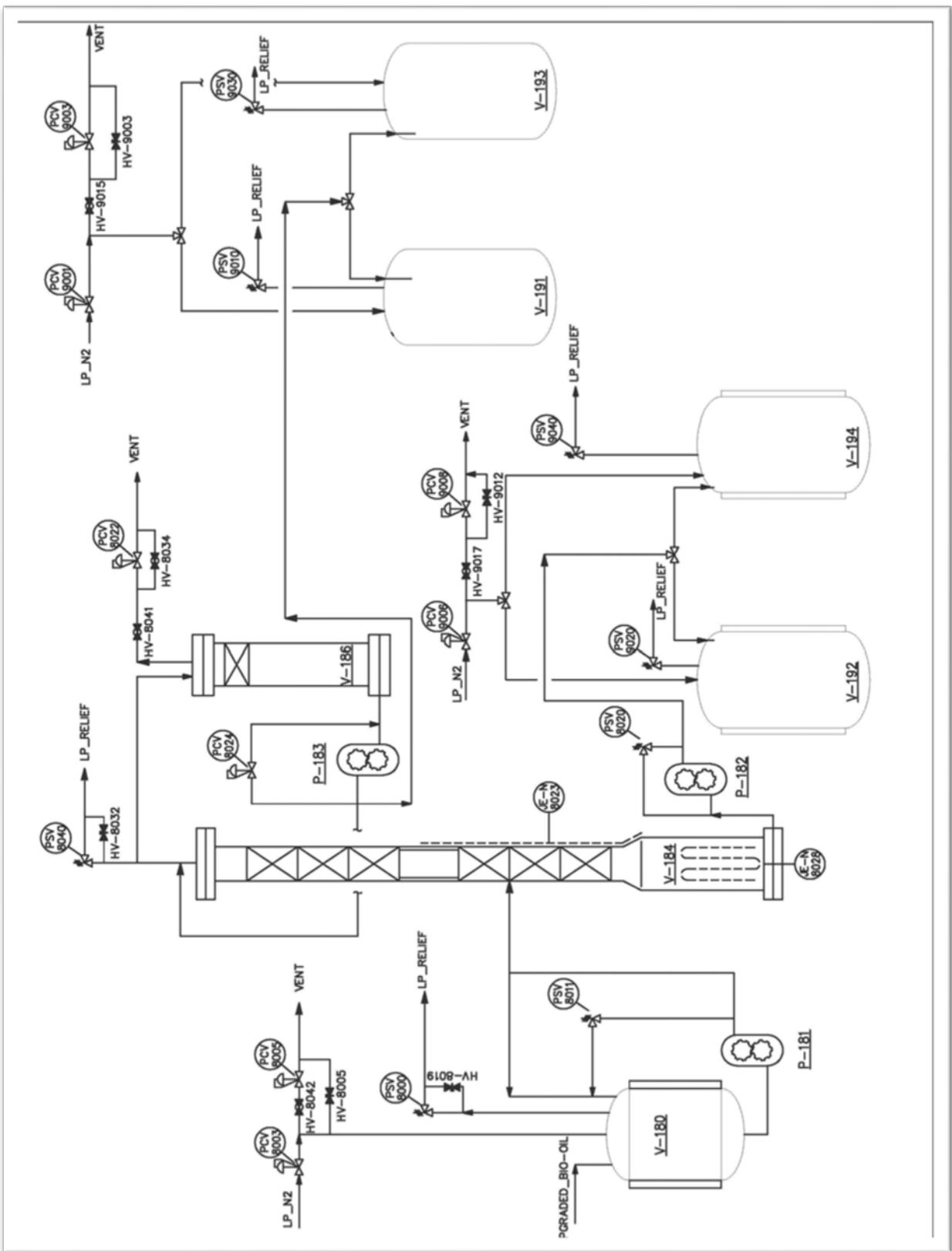


Figure 2-5. Distillation Process Major Components

2.2.1 Hydrotreater Operations Outline

Prestart Operations

- 1) Install reactor
- 2) Chain out inter-skid area prior to working on upper head.
- 3) Load catalyst
- 4) Seal reactor
- 5) Pre-op valve position check for entire system
- 6) Connect bio-oil tank
- 7) Pressure check system
- 8) Put valves to flow positions
- 9) Transfer bio-oil to feed tank

Startup/Sulfiding

- 1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment
- 2) Initiate purge of electrical cabinets and furnace.
- 3) Put sulfiding tank in place
- 4) Direct product valves to slop tank
- 5) Fill pumps with sulfiding solution
- 6) Pressurize reactor to operating pressure
- 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow
- 8) Bring reactor to sulfiding temperature
- 9) Begin sulfiding flow
- 10) Ramp temperature through sulfiding procedure
- 11) Block out and remove sulfiding tank

Bio-oil feeding

- 1) Adjust hydrogen flow and temperature to operating conditions
- 2) Fill pumps with bio-oil from feed tank
- 3) Start bio-oil supply drum recirculation/take-up loop
- 4) Direct product valves to L/L separator and A or B product tanks
- 5) Start bio-oil feed at ~30% of target flowrate
- 6) Allow system to equilibrate
- 7) Gradually bring reactor to target flowrate

Operation

- 1) Monitor feed and product levels
- 2) When product drums are at 85 to 90% full, switch to other product tanks
- 3) Download water vessel to product container
- 4) Download oil vessel to product container or transfer to still skid feed tank

Transfer to still feed tank

- 1) Pad oil product container
- 2) Depad still feed tank
- 3) Connect transfer line
- 4) Open transfer valves
- 5) When empty, close transfer valves
- 6) Pad still tank
- 7) Depad product container
- 8) Remove transfer line

Shutdown

- 1) Stop oil feed and turn off reactor heaters.
- 2) Continue product vessel monitoring per “operation” section
- 3) Empty pumps back to bio-oil feed tank
- 4) Reduce gas flow once product collection has diminished
- 5) Allow reactor to cool

Flush

- 1) Reactor should be around 150C or lower for this procedure
- 2) Load acetone into pumps via transfer tank
- 3) Direct product valves to slop tank
- 4) Inject acetone into reactor
- 5) Shut down feed system and allow reactor to cool below 100C
- 6) Halt gas flow and depressurize reactor
- 7) Flush with N₂
- 8) Verify that all systems are off

Refit

- 1) Depressurize and verify zero energy state on all hydrotreater subsystems
- 2) Chain out inter-skid area prior to working on upper head
- 3) Open upper reactor head.
- 4) Remove catalyst

2.2.2 Distillation Operations Outline

Prestart Operations

- 1) Seal process tanks
- 2) Pre-op valve position check for entire system
- 3) Pressure check system (purge and pad all subsystems)
- 4) Transfer feed to tank via hydrotreater skid or transfer tank using tank pads
- 5) Alternately, feed can be loaded into one of the bottoms product tanks and padded over
- 6) Put valves to flow positions, including bottoms and distillate product tanks
- 7) Prime feed pump and turn to auto control

Hydrotreater/Distillation Column Hazard Analysis Report

Startup

- 1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment
- 2) Initiate purge of electrical cabinets and furnace
- 3) Turn on coolant to HX and to bottoms pump
- 4) Turn on nitrogen purge to heatup setpoint and set system backpressure
- 5) Engage feed pump and set backpressure loop
- 6) Fill still bottom to submerge heater elements via feed control badger and/or bypass.
- 7) Turn on still heater and external jacket heater
- 8) As liquid level drops in still, set feed badger to maintain liquid height in still

Reflux

- 1) Observe reflux in sight glass via level sensor
- 2) Once distillate reaches 8 inches, engage reflux pump (P-183) and set backpressure loop
- 3) Prime reflux pump
- 4) Set reflux badger to target kg/hr
- 5) Set product badger to target liquid level in sight glass
- 6) Reduce nitrogen flow to target setpoint and adjust system backpressure

Full operation

- 1) Set feed rate badger to target feed rate
- 2) Turn on and prime bottoms level control pump to target setpoint
- 3) Monitor liquid level on bottoms and distillate tanks, and switch to alternate tank when full
- 4) Monitor feed tank level

Shutdown

- 1) Turn off still heater and jacket.
- 2) Halt feed pump and set feed badger to zero
- 3) Close reflux badger.
- 4) Set reflux level control to zero to drain reflux glass into distillate product
- 5) Turn off reflux pump after low level indicator
- 6) Set bottoms level control to zero
- 7) Turn off bottoms level pump after low level indicator
- 8) Turn on nitrogen sweep to low level

3.0 HAZARD ASSESSMENT

A series of facilitated hazards analysis sessions were conducted in February 2013. These hazard analysis sessions built upon the previous hazards analysis documented in the November 2012 Hydrotreater / Distillation Column Project Hazard and Risk Analysis Report. The scope of the February assessment was focused on the operations and hazards associated with the process-related system components forming the hydrotreater/distillation column processes located within the PDL-West facility and the potential interactions of these hazards with respect to supporting systems and the facility. The PNNL team assembled for the hazards analysis sessions included Engineering (F&O and Project); R&D operations and engineering; Fire Protection; Pressure Systems; Environmental, Safety and Health; and hazard and safety analysts. PNSO observers also attended. Appendix A lists the attendees at the hazards analysis sessions. (Note: not all attendees listed were present for the entire duration; however, a core team representing design, operations, fire protection, pressure systems, and hazard and safety analysis was always present.)

The following sections provide a brief description of hazard evaluations performed and results of the evaluations.

3.1 Hazard Identification

The first step of the hazard analysis process was to identify the form, quantities, and characteristics of hazards, including chemicals associated with the major process components (Hazard Identification). This allowed the screening of hazards considered as normal laboratory practices or activities incidental to the operation of the facility to be addressed through IOPS and existing PNNL work controls. For the hydrotreater/distillation column processes, significant hazards requiring further evaluation via the hazards analysis process included high pressure processes and the presence of flammable and combustible liquids and gases. Table 3-1 identifies the product of the hazard identification process.

Regulatory provisions of 40 CFR 355, 29 CFR 1910.119, and 40 CFR 68 provide guidance relative to screening chemical hazards based on quantities and the potential consequences they represent to workers and the public. As shown in Table 3-2, these threshold values are many times greater in magnitude than those of the process chemicals and products common to the hydrotreater/distillation column processes.

Table 3-1. Hydrotreater Hazard Identification Checklist

Component	Inventory	Vessel Volume Liter ⁽¹⁾	Operating Pressure psig
Supply Drum	Bio-Oil	55 gal	Atm
V-120	Bio-Oil (filtered)	72	10
V-125	Di-tert-butyl disulfide / Acetone	20	10
R-130	Treated Bio-Oil Hydrogen	26	2100
V-140/LG-142	Treated Bio-Oil Hydrogen	6	2100
LG-147	Treated Bio-Oil	4 ⁽²⁾	Atm
V-160A/B	Treated Bio-Oil	20	10
V-161A/B	Process Water	20	10
V-162	Slop Bio-oil	38 ⁽³⁾	10
V-163	Process Water	38 ⁽³⁾	10
V-180	Treated Bio-Oil Light Product (recycle) Bottoms Product (recycle)	140 ⁽⁴⁾	10
V-184	Treated Bio-Oil Light Product (recycle) Bottoms Product (recycle)	16 ⁽⁴⁾	15
V-191 (V-193)	Light Distillates (e.g. naphtha, gasoline, jet)	72	10
V-192 (V-194)	Bottoms Product (e.g., diesel, cycle oil)	72	10
1/4"-T035-316	High Pressure (3000 psi) Hydrogen	-	2500
1/4"-T035-316 1/2"-T035-316	Low Pressure (100 psi) Nitrogen	-	100
1/4"-T035-316	High Pressure (3000 psi) Nitrogen	-	2500

(1) From CTI 12-631, unless otherwise noted.

(2) Project Drawing-782-4-140

(3) Project Drawing-782-4-160

(4) Project Drawing-782-4-180

Table 3-2. Comparison of Chemicals to Screening Thresholds

Material	40 CFR 355	29 CFR 1910.119	40 CFR 68
Bio-Oil	Not Listed	Not Listed	Not Listed
Treated Bio-Oil ^(a)	Not Listed	Not Listed	Not Listed
Light Distillate -naphtha -gasoline -jet fuel	Not Listed	10,000 lbs (flammable liquids)	Not Listed
Bottoms Product -diesel -cycle oil	Not Listed	Not Listed (combustible liquids)	Not Listed
Nitrogen (Compressed Gas)	Not Listed	Not Listed	Not Listed
Hydrogen (Gas)	Not Listed	10,000 lbs (flammable gas)	10,000 lbs (flammable gas)
Acetone	Not Listed	Not Listed	Not Listed
Di-tert-butyl disulfide	Not Listed	Not Listed	Not Listed
Hydrogen Sulfide ^(b)	100/500 lbs ^(c)	1500 lbs	10,000 lbs

(a) Assumed to be bio-diesel, <http://www.apexoil.com/msdsbio.pdf>

(b) Byproduct of hydrotreatment and sulfiding process

(c) Reportable quantity/planning threshold quantity

3.2 What-If Analysis

The What-If analysis technique is a structured brainstorming method of determining potential undesired events (what things can go wrong). The answers to these what-if questions form the basis for making judgments regarding the acceptability of the controls that prevent or mitigate hazardous conditions and determining a recommended course of action for events requiring further consideration. The What-If concept encourages the team to think of potential upsets or deviations based on initiating questions generally beginning with “What if...”.

As noted in Section 3.0, facilitated hazards analysis sessions were held in February 2013 following incorporation of design changes resulting from review comments and actions from the hazards analysis documented in the November 2012 Hydrotreater / Distillation Column Project Hazard and Risk Analysis Report. The What-If sessions were held in two blocks of time; a four-day session covering the hydrotreater process and supporting systems followed by a two-day session to cover the distillation column process and interface with PDL-West facility systems. Involvement by the participants was outstanding, particularly the operations team which had recently returned from the Factory Acceptance Testing held at the vendor’s facilities.

The What-If analysis was structured around the process steps of hydrotreater and distillation operations as outlined in Sections 2.1.1 and 2.1.2. The scope of the hazards analysis focused on the process systems and potential for adverse interactions to the process from upsets in the supporting utilities. For the hydrotreater and distillation column processes, a selected operator presented the key process steps in his/her area of expertise followed by a series of What-If questions posed for each step. The What-If team leveraged the operators’ recent test experience to gain insight on the operation of the systems under postulated off-normal or upset conditions. The process and utility drawings reviewed included redline drawings from the factory acceptance test, as appropriate, to reflect the most current state of the design and are identified in Appendix B, “Key Design Information Reviewed.”¹

As part of the What-If analysis, a qualitative likelihood was assigned to all unmitigated hazardous scenarios. This reflected the team’s estimation regarding the likelihood of an initiating event coupled with a postulated upset condition, absent of the preventive or mitigative effects of hazard controls (i.e., unmitigated). The basis for the likelihood of a given hazardous scenario was the number and types of operational failures needed to result in the identified potential upset condition (Table 3-3).

Each hazardous scenario was further defined by qualitative evaluations of the potential unmitigated consequences such as: process upset; exposure of personnel to steam, vapors or asphyxiant; spray or spill of flammable material; creation of a flammable atmosphere; or energetic release events from a vessel pressure boundary (boiling liquid expanding vapor explosion [BLEVE] or pressure vessel burst [PVB]). It was clarified that the unmitigated consequences identified during the analysis were not sure to occur even under the failures postulated; rather the consequences identified represent the bounding case outcomes in most instances, rather than a less significant expected outcome.

¹ These design documents are historical and subject to change. See the Hydrotreater/Distillation Column SharePoint site for current design documents.

Table 3-3. Likelihoods Used for the Hydrotreater/Distillation Column What-If Analysis

Likelihood	Qualitative Evaluation Criteria
Likely	Failure of a single process control, failure of active components or support systems (e.g., power), or administrative steps
Unlikely	Conditions involving failure of two or more of the above, mechanical failures of active systems (e.g., pump/motor failures)
Very Unlikely	Multiple failures (more than 2), failures of robust passive systems
Extremely Unlikely	Many concurrent, independent failures

3.3 Analysis Results

The results of the What-If analysis are provided in Table 3-4. For all releases of hazardous material or energy, controls were identified to prevent the occurrence or mitigate the effects of the release (Table 3-4). Footnotes have been added to Table 3-4 to provide addendum information pertinent to the analysis.

Approximately 66 highly energetic releases (33) BLEVE and PVB and (33) potential deflagrations were identified. For these events, additional analysis was performed (Section 3.3) to determine the potential magnitude of the impacts from the event to receptor locations within and outside of the PDL-West building for bounding scenarios of each type. The critical controls credited to mitigate the likelihood or consequences of these events are identified in the hazard analysis tables and summarized in Chapter 4.0.

One action affecting control selection was identified during the What-If analysis for scenarios H.2-17 and H.6-1. This action replaces the “T” upstream of HV-2009/2006 with HV-2018, a 3 way valve (e.g., Swagelock© SS-H83PS8) to provide positive isolation from potential reactor backpressure during pump flushing operations.

No other control-affecting actions were identified or required to assure adequate protection against the release of hazardous material or energy during the What-If analysis sessions. In some cases, the What-If team identified suggestions to improve the design and operational processes. These suggestions were captured for consideration by project management.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations						
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
H.1-1	1	What if we drop or impact the reactor?	Damage reactor thermocouple from dropping reactor or running it into object results in loss of thermocouple functionality	Likely	Process upset. During sulfiding or operating steps. (also see heater/thermocouple events in subsequent process steps)	Lift Procedure and engineered lift points on vessel. Pressure Test Procedure on startup. Instrument test Procedure Interlocks on thermocouple.
H.1-2	1	What if we impact another piece of equipment or piping?	Damage to furnace or furnace door due to impact (for instance reactor vessel) results in short circuit of heater or damage to furnace door and it might not shut properly.	Likely	Short circuit of heater leads to high temperature in reactor during sulfiding operations and potential energetic event due to pressure boundary failure. (see subsequent events e.g., H.2-3, H.2-20) Loss of purge operations, during sulfiding or operating steps, leads to potential ignitions of flammable gases in reactor furnace- requires concurrent failure in pressure boundary. (see subsequent events e.g., H.2-3)	Lift Procedure and engineered lift points on vessel. Heater circuits are fused (protection against short circuit) Pressure indication (alarm) on furnace Z purge.
H.1-3	3	What if you improperly load the column?	Failure to properly prepare the column before adding catalyst. (Forgetting the screen would result in the catalyst running down exit hole and plugging up the 90 degree bend.)	Likely	Process upset during sulfiding or operating steps. Plugging the reactor flow path and/or plug filter (F-4019) downstream of separator with pressurization of the reactor.	Pressure Test Procedure. High Pressure Nitrogen Supply set @ 3000 psi. High Pressure Nitrogen System set @ 2500 psi.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations						
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
H.1-4	3 What if you use the wrong catalyst?	Failure to select the right catalyst (matched to sulfiding agent and bio-oil, operating conditions).	Likely	Process upset during sulfiding or operating steps. Potential plugging of the reactor flowpath (due to heavy oils) with pressurization of the reactor. If left for long period potential complete blockage See H.4-6	Startup operating procedure – gradual start up. Pre-testing/qualification (benchtop) of new catalyst-sulfiding combinations for use with bio-oils.	Pyrophoric catalysts are not currently proposed.
H.1-5	3 What if you introduce wrong material?	Introduction of wrong catalyst results in failure to produce quality product.	Unlikely	Process upset during sulfiding or operating steps. Potential plugging of the reactor flowpath (due to heavy oils) with pressurization of the reactor. If left for long period potential complete blockage See H.4-6	Startup operating procedure – gradual start up. Pressure monitoring.	
H.1-6	3 What if you don't put enough catalyst into reactor?	Failure to add sufficient catalyst results in failure to produce quality product.	Likely	Process upset during sulfiding or operating steps. Potential plugging of the reactor flowpath (due to heavy oils) with pressurization of the reactor. If left for long period potential complete blockage See H.4-6	Startup operating procedure – gradual start up. Procedural- Keep track of volume of catalyst added. Pressure monitoring.	Cannot overfill with catalyst and still close reactor head.
H.1-7	4 What if there is failure to properly reassemble reactor seals/flanges/piping connections?	Failure to properly reassemble reactor components (e.g., forget to install VCR nickel gaskets).	Likely	Exposure of personnel. Release of nitrogen into enclosure during pressure testing.	Assembly Procedures. Pressure Test Procedure. Low pressure alarms.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations								
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.								
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments		
H.1-8	4	What if there is failure to properly reassemble reactor seals, flanges, piping connections?	Failure to properly re-assemble reactor components (e.g., forget to install VCR nickel gaskets) results in subsequent leak at operating temperature and pressure.	Unlikely	Flammable atmosphere, during subsequent operations. Leak of hydrogen/bio-oil or sulfiding agent /steam into enclosure.	Pressure Test Procedure. (detection of no pressure on system components) Hydrogen monitors on skid and in enclosure. Enclosure Design – Class 1 Division 2. Enclosure Ventilation System. Flammable vapor monitor on skid. Low pressure alarm - R-130.	C C C C C	High pressure spray of (jet flame) of combustible liquid and potential creation of flammable atmosphere may be mitigated by steam.
H1-9	5	What if valve is left open?	Failure to close valve (vent valve) results in inability to pressurize system	Likely	Process Upset. Fail pressure test (vent valve) release of nitrogen into vent system.	Valve lineup procedure. Pressure Test Procedure.		
H.1-10	5	What if valve is left open?	Failure to close valve (drain valve) resulting in nitrogen released into enclosure	Very Unlikely	Exposure of personnel. Creation of oxygen deficient atmosphere with personnel present.	Valve lineup procedure. Pressure Test Procedure. Enclosure Ventilation System - operable when system is pressurized.		
H.1-11	5	What if valve is left open?	Failure to close process valve results in pressurization portions of system not designed for high pressure.	Likely	Energetic event - over pressurization of low pressure system (LG-147/Vent line).	Valve lineup procedure. Pressure Relief valves on low pressure system components.	C	Relief valves have been sized for this scenario. This would require two valves to be misaligned.
H.1-12	5	What if fail to pressure check part of system due to valve misalignment?	Inadequate pressure check, combined with pre-existing leak or failure to re-assemble properly results in leak at operating temperature and pressure.	Unlikely	Flammable atmosphere, during subsequent operations Release of hydrogen/bio-oil or sulfiding agent/steam into enclosure.	Pressure Test Procedure. (detection of no pressure on system components) Hydrogen monitors on skid and in enclosure. Enclosure Design – Class 1 Division 2. Enclosure Ventilation System. Flammable vapor monitor on skid. Low pressure alarm - R-130.	C C C C C	High pressure spray of (jet flame) of combustible liquid and potential creation of flammable atmosphere may be mitigated by steam.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations							
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments	
H.1-13	6	What if failed to connect return line to drum?	Failure to connect return line to feed drum results in release of Bio-oil.	Likely	Spray/Spill. Spill of Bio-Oil into enclosure. Cleanup.	Procedural check. Secondary containment on the drum.	
H.1-14	7	What if fail to do the pressure test?	Failure to perform pressure check, combined with pre-existing leak or failure to re-assemble properly results in leak at operating temperature and pressure.	Likely	Flammable atmosphere, during subsequent operations. Leak of hydrogen/bio-oil or sulfiding agent /steam into enclosure. High pressure spray of (jet flame) of combustible liquid and potential creation of flammable atmosphere mitigated by steam.	Hydrogen monitors on skid and in enclosure. Enclosure Design – Class 1 Division 2. Enclosure Ventilation System. Flammable vapor monitor on skid. Low pressure alarm - R-130.	C C C C
H.1-15	7	What if too high pressure for low pressure system?	Over pressurization of low pressure system components due to excessive nitrogen pressure	Unlikely	Energetic event - over-pressurization of low pressure system (>100 psi)	Pressure regulation of the low pressure nitrogen supply to 100 psi. Pressure regulation of the low pressure nitrogen system pressure to 10 psi. Low pressure component PRVs set at ≤ 100 psi. Pressure Test Procedure.	C
H.1-16	7	What if too high pressure for high pressure system?	Over pressurization of high pressure system components due to excessive nitrogen pressure.	Unlikely	Energetic event - over-pressurization of high pressure system (>3000 psi)	Pressure regulation of the high pressure nitrogen supply to 3000 psi. Pressure regulation of high pressure nitrogen system pressure set at 2500 psi. High pressure component PRVs set at 3000 psi. High pressure vessel and component design pressure ≥ 3000 psi. High pressure alarms. High pressure interlocks.	C C

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations							
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
H.1-17	7	What if you inadvertently use Hydrogen instead of nitrogen for leak check?	Failure to use correct gas for pressure check (combined with pre-existing leak or failure to re-assemble properly) results in potential flammable atmosphere in the enclosure with a piece of equipment not qualified for the hydrogen atmosphere.	Unlikely	Flammable atmosphere. Hydrogen buildup and deflagration in Enclosure	Pressure Test Procedure. Valve and line labeling. Hydrogen monitor on skid and in enclosure. Enclosure Ventilation System operable prior to pressurizing the system	C C C
H.1-18	7	What if you inadvertently use Hydrogen instead of nitrogen for leak check?	Failure to use correct gas for pressure check results in Hydrogen/Air atmosphere in the reactor system, potential ignition of flammable atmosphere in the system at a transition point .	Likely	Energetic event - Deflagration in reactor column.	Pressure Test Procedure. Valves and Line labeling.	C Lack of ignition source unless we are reusing the catalyst. If we are reusing column, it is kept at pressure. There is no oxygen.
H.1-19	8	What if there is failure to line up properly for operations?	Failure to correctly align system for operations after pressure test results in blocked flow within the system up to liquid separator.	Likely	Energetic event during subsequent operations. Deadhead within system with potential failure of pressure boundary due to high pressure in V-140 and reactor.	Design of R-130/V-140 and component pressure \geq 3000 psi MAWP. R-130/V-140 PRVs set at 3000 psi. Pressure regulation of the hydrogen supply to 3000 psi. Pressure regulation of hydrogen system pressure set at 2500 psi. High pressure alarm in R-130. High-high pressure interlock in R-130	C C
H.1-20	8	What if an already closed valve is inadvertently opened?	Inadvertent opening of (drain/manual transfer) valve results in venting to enclosure or header	Unlikely	Exposure to personnel. Potential for nitrogen release into enclosure or vent.	Procedural Step. Drains are double valved, valved and capped, or valve and quick disconnect.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations							
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments	
H.1-21	8	What if failure to reopen a valve on the low pressure tanks?	Failure to open vent isolation valve in low pressure system results in blocked flow within the system during sulfiding or operations.	Likely	Energetic event. Deadhead within system, during subsequent operations. High pressure in vessels.	Procedural Step. PRVs on low pressure vessels. C	
H.1-22	9	What if we transfer bio-oil too fast or at too high of pressure?	Transfer of bio-oil to V-120 at greater than expected pressure or flow results in 1 system breach	Likely	Spray or spill. Release of bio-oil into enclosure (also see H.1.24). Filter breakthrough. (See H.1.27).	Pump can only achieve maximum supplied air pressure. Air system pressure set at nominally 100 psi (normal operating pressure is 80 psi). Filters are rated at 250psi. V-120 rated at 135psi. PRV set at 70. 3/4 inch stainless steel transfer line is rated at >3000psi.	System designed for maximum flow from pump at maximum air supply pressure.
H.1-23	9	What if there is transfer too much bio-oil (over fill)?	Failure to stop transfer results in over fill of V-120.	Likely	Spray or spill. Overfill V-120 resulting in release of bio-oil into the vent system.	V-120 level indicator. V-120 high-high level interlocks. - Interlock to pump (automatic mode). - Procedure, manual transfer mode.	
H.1-24	9	What if there is a leak in the bio-oil line?	Leak in transfer line results in spill /spray to enclosure.	Likely	Spray or spill. Release of bio-oil into enclosure.	Filtered oil (feed line) ¾ SS tubing. Secondary containment provided by enclosure.	This portion is not pressure checked every time.
H.1-25	9	What if the filters Plug?	Potential plug leading to high pressure in transfer line from drum to V-120.	Likely	Spray or spill. Release of bio-oil into enclosure (also see H.1.24). Filter breakthrough (See H.1.27).	Round sanitary clamp. Filter is open at both ends. Use second filter. The bypass allows you to go to second filter. These will be changed every week.	
H.1-26	9	What if air gets in the system? Is bio-oil foam a hazard?	Air in reactor	Likely	Process Upset. Unable to pump.	Low level control in V-120 and interlocks associated with it. ISCO pump shutoff due to insufficient liquid refill.	Filters would most likely break up foam.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 1. Prestart Operations							
1) Install reactor. 2) Chain out inter-skid area prior to working on upper head. 3) Load catalyst. 4) Seal reactor. 5) Pre-op valve position check for entire system. 6) Connect bio-oil tank. 7) Pressure check system. 8) Put valves to flow positions. 9) Transfer bio-oil to feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
H.1-27	9	What if you don't filter?	Filter by-passed or breached results in unfiltered bio-oil to V-120, results in the potential plugging of the plugging the ISCO injector or slow plugging of catalyst bed during subsequent operations.	Likely	Process Upset. R-130 is designed to handle solids so no direct hazard to process. ISCO ejector plugging would lead to loss feed (Process upset) a pump is design for full pressure. For potential plug in R-130 See H.4-6	Procedural control on use of bypass. ISCO Pump high pressure set point (process controlled). ISCO Pump firmware maximum pressure of 3750psi. ISCO Pump shear pin at 4500 psi.	
H.1-28	9	What if there is a failure in the pressure boundary (V-120)?	Failure of V-120 results in leak of bio-oil to the enclosure.	Very Unlikely	Spray or spill/Exposure of personnel. Bio-Oil on Floor also release of nitrogen to enclosure nitrogen.	Design V-120 135 psi MAWP.	

Hydrotreater Process Step 2. Startup/Sulfiding							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Put sulfiding tank in place. 4) Direct product valves to slop tank. 5) Fill pumps with sulfiding solution. 6) Pressurize reactor to operating pressure. 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow. 8) Bring reactor to sulfiding temperature. 9) Begin sulfiding flow. 10) Ramp temperature through sulfiding procedure. 11) Block out and remove sulfiding tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
H.2-1	1	What if you leave non-Class 1 Div 2 equipment in environment	Presence of non-Class 1 Division 2 equipment presents a potential for a subsequent ignition source, given a like in the process boundary	Likely	Flammable atmosphere. Potential ignition of a flammable vapor given leak sufficient to result in a flammable atmosphere.	Pressure Test Procedure. Enclosure Ventilation System. Hydrogen monitors on skid and in enclosure. Flammable vapor monitor on skid.	C C C

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 2. Startup/Sulfiding							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Put sulfiding tank in place. 4) Direct product valves to slop tank. 5) Fill pumps with sulfiding solution. 6) Pressurize reactor to operating pressure. 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow. 8) Bring reactor to sulfiding temperature. 9) Begin sulfiding flow. 10) Ramp temperature through sulfiding procedure. 11) Block out and remove sulfiding tank.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
H.2-2	1	What if non Class 1 Div 2 equipment is brought into the enclosure during operations.	Introduction of non-Class 1 Division 2 equipment presents a potential for a subsequent ignition source, given a leak in the process boundary	Likely	Flammable atmosphere. Potential ignition of a flammable vapor given leak sufficient to result in a flammable atmosphere.	Pressure Test Procedure. Enclosure Ventilation System Hydrogen monitors on skid and in enclosure. Limit access to trained operators. Procedural steps in place during operations. Limit what you can take into the enclosure during the operation [use of anti-sparking tools].	C C
H.2-3	2	What if there is failure to initiate purge of electrical cabinets and furnace?	Failure to initiate purge results in the potential for a flammable atmosphere, given a leak in the process boundary, to reach ignition sources within the cabinets.	Likely	Flammable atmosphere. Potential ignition of a flammable vapor given leak sufficient to result in a flammable atmosphere.	Procedural step – initiate purge Pressure monitoring and alarms on cabinets and furnace enclosure. Enclosure Ventilation System Hydrogen monitors on skid and in enclosure. Flammable vapor monitors on skids. Pressure Test Procedure.	C C C
H.2-4	3	What if the sulfiding tank is not put in place?	Failure to connect V-125 to process results in not adding sulfiding agent to the catalyst.	Likely	Process upset. Failure to activate catalyst.	Procedural step	
H.2-5	3	What if it is other than sulfiding agent?	Failure to correctly put sulfiding agent in V-125 results in the failure to activate the catalyst.	Likely	Process upset. Failure to activate catalyst.	Procedural step	
H.2-6	4	What if the product valves are not aligned to slop tank?	Failure to align valves properly results in misdirection of sulfiding solutions.	Likely	Process upset. Sulfiding solution directed into the product tank instead of slop tank.	Procedural step	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 2. Startup/Sulfiding							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Put sulfiding tank in place. 4) Direct product valves to slop tank. 5) Fill pumps with sulfiding solution. 6) Pressurize reactor to operating pressure. 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow. 8) Bring reactor to sulfiding temperature. 9) Begin sulfiding flow. 10) Ramp temperature through sulfiding procedure. 11) Block out and remove sulfiding tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
H.2-7	5	What if there is too much pressure to V-125 from nitrogen pad?	Failure to set low pressure nitrogen pad pressure correctly results in overpressurizing V-125 with up to 100 psi of nitrogen.	Likely	Energetic event - failure of V-125 vessel pressure boundary. Flammable atmosphere. Spill of combustible liquid and potential creation of flammable atmosphere.	Pressure regulation of the low pressure nitrogen supply to 100 psi. Pressure regulation of the low pressure nitrogen system pressure to 10 psi. Design V-125 155 psi MAWP V-125 PRV set at ≤ 100 psi. Pressure Test Procedure.	C C
H.2-8	5	What if there is failure to connect vent line V-125 to rupture disk?	Failure to connect vent line to header results in venting of V-125 contents to enclosure on system overpressure/failure of rupture disk and release of sulfiding solution /nitrogen to enclosure atmosphere.	Likely	Spill of sulfiding solution to the enclosure.	Procedural step. Connect the vent line prior to the nitrogen and outlet.	
H.2-9	6	What if there is failure to verify pressure and there is low pressure?	Failure to pressurize the reactor with nitrogen prior to starting flow of hydrogen results in undetected leak or unintended flow path.	Unlikely	See other pressure boundary scenarios. In no leak, the hydrogen would pressurize the reactor on system startup.	Low pressure alarms, procedural steps.	
H.2-10	6	What if there is over pressurize the system?	Failure to set hydrogen pressure correctly results in filling reactor with 3000 psi hydrogen.	Unlikely	Energetic event - over-pressurization of R-130/V-140 piping pressure boundary	Design of R-130/V-140 and component pressure ≥ 3000 psi MAWP. R-130/V-140 PRVs set at 3000 psi. Pressure regulation of the hydrogen supply to 3000 psi. Pressure regulation of hydrogen system pressure set at 2500 psi. High pressure alarm in R-130. High-high pressure interlock in R-130	C C

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 2. Startup/Sulfiding							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Put sulfiding tank in place. 4) Direct product valves to slop tank. 5) Fill pumps with sulfiding solution. 6) Pressurize reactor to operating pressure. 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow. 8) Bring reactor to sulfiding temperature. 9) Begin sulfiding flow. 10) Ramp temperature through sulfiding procedure. 11) Block out and remove sulfiding tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
					Procedural step for pressure set point. Procedural step to verify the off gas flow		
H.2-11	8	What if the furnace controller fails high resulting in too fast heatup?	Furnace controller fails high resulting in too fast heatup with potential impact to catalyst.	Likely	None identified.	Limited by design of heater such that the worst case is that you heat up in allowable range.	The heatup rate is less than 5 degrees C per minute.
H.2-12	8	What if the catalyst is heated above desired sulfiding temperature?	Failure to stop heating the reactor at desired temperature results in start of sulfiding with catalyst at higher than desired temperature.	Likely	Process upset to the catalyst.	Procedural step to monitor temperature.	
H.2-13	8	What if there is failure to heat system up to desired sulfiding temperature?	Failure to heat the reactor to desired sulfiding temperature results in start of sulfiding too early with reactor at lower than desired temperature.	Likely	Process upset to the catalyst.	Procedural step to monitor temperature.	
H.2-14	9	What if flow rate of sulfide is wrong?	Failure to properly transfer (flowrate) of the sulfiding solutions results in incomplete activation of catalyst.	Likely	Process upset to the catalyst.	Process monitoring.	Flow rate is limited by the pump to 400 ml / min. which would only last 2.5 minutes
H.2-15	9	What if valve HV - 2006 is closed?	Failure to open HV-2006 results in deadheading the flow with over-pressurization of the transfer line (pump pressure 4500 psi) resulting in leak.	Likely	Spray or Spill. High pressure spray of sulfiding solution.	Transfer Line (tubing) is rated at 4800 psi. Pressure Indicator PI-2011 ISCO Pump high pressure set point (process controlled). ISCO Pump firmware maximum pressure of 3750psi. ISCO Pump shear pin at 4500 psi	
H.2-16	9	What if there is a failure in the pressure boundary?	Failure in the pressure boundary results in spray or leak of sulfiding solution to the enclosure.	Very Unlikely	Spray or leak of sulfiding solution to the enclosure	Pressure Test Procedure. Design of V-125 and transfer line components.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 2. Startup/Sulfiding							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Put sulfiding tank in place. 4) Direct product valves to slop tank. 5) Fill pumps with sulfiding solution. 6) Pressurize reactor to operating pressure. 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow. 8) Bring reactor to sulfiding temperature. 9) Begin sulfiding flow. 10) Ramp temperature through sulfiding procedure. 11) Block out and remove sulfiding tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
H.2-17	9	What if the drain valve HV-2009 is open?	Failure to Close HV-2009 results in spray or leak of sulfiding solution to the enclosure	Unlikely	Spray or leak of sulfiding solution to the enclosure	HV-2018 Action: Replace T upstream HV-2009 with 3-way Valve. Procedural check that drain valve is closed and plugged.	
H.2-18	10	What if the furnace controller fails high resulting in too fast heatup.	Failure of the furnace controller (high) resulting in too fast heatup to reactor during sulfiding.	Likely	Process upset. H ₂ S evolution at higher than expected rate.	Limited by design of heater such that the worst case is that you heat up in allowable range. H ₂ S monitor on vent stack.	
H.2-19	10	What if the catalyst is heated above 400°C	Failure of the furnace controller (high) resulting in sulfiding with reactor at higher than desired temperature (400°C).	Likely	Process upset to the catalyst.	Procedural step to monitor temperature.	
H.2-20	10	What if the reactor is heated over 450°C?	Failure of the furnace controller (high) resulting in failure of reactor pressure boundary (>450°C).	Likely	Energetic event- failure of reactor pressure boundary	Software prevents operator from changing settings above maximum set point of 425C. There is an internal thermocouple interlocked to furnace control. Cascade furnace control R-130 High High temperature. Design of R-130, 3000 psi MAWP at 537°C (shell).	C C
H.2-21	10	What if operator fails to heat system up to 400°C?	Start sulfiding too early with reactor not at desired temperature.	Likely	Process upset to the catalyst.	Procedural step to monitor temperature.	
H.2-22	11	What if there is failure to isolate the sulfiding tank before you disconnect it?	Failure to isolate the sulfide tank (V-125) results in opening disconnects on tank while pressurized results in release of sulfiding solution via venting back into enclosure.	Likely	Spray or Spill. Pressurized spray of sulfiding solution. Potential for oxygen deficient atmosphere.	Procedural step. Disconnect vent last. Quick disconnects are closed on both sides except for vessel vent. Pressure boundary controls between V-125 and reactor.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 2. Startup/Sulfiding 1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Put sulfiding tank in place. 4) Direct product valves to slop tank. 5) Fill pumps with sulfiding solution. 6) Pressurize reactor to operating pressure. 7) Flow hydrogen at sulfiding flowrate and verify offgas handling system flow. 8) Bring reactor to sulfiding temperature. 9) Begin sulfiding flow. 10) Ramp temperature through sulfiding procedure. 11) Block out and remove sulfiding tank.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
H.2-23	What if there is a failure in the pressure boundary (V-125)?	Failure in pressure boundary (V-125) results in release of sulfiding solution (or acetone-cleanout) and nitrogen to the enclosure		Spray or Spill. Spray or leak of sulfiding solution to the enclosure Potential for oxygen deficient atmosphere.	Design of V-125.	
H.2-24	What if there is a failure in the pressure boundary (nitrogen)?	Failure in the Low Pressure Nitrogen Pressure boundary.		Exposure of Personnel. ~10-15 psi release of nitrogen to enclosure, potential for oxygen deficient atmosphere. Loss of ability to transfer.	Design of Low Pressure Nitrogen Piping.	
H.2-25	What if there is too much pressure (nitrogen)?	Failure to set Low Pressure Nitrogen Supply regulator results in over pressurization of system and release of nitrogen to the enclosure.		Exposure of Personnel Potential for oxygen deficient atmosphere	Piping System design pressure is 2500 psi. PCV-2001 sets pressure to ~10 psi. Overpressure relief on Supply system provided by PCV-2030 (15 psi) vented to offgas vent header. Overpressure vented (V-120, V-125) through LP relief header.	
H.2-26	What if there is too much pressure (nitrogen)?	Failure to correctly set low pressure nitrogen (PCV-2001) results in over-pressurization of V-120 /125	Very Unlikely	Spray or Spill. Spray or leak of sulfiding solution to the enclosure Potential for oxygen deficient atmosphere.	Vessel Design V-120, 135 psi. Vessel Design V-125, 155 psi. Pressure regulation of the low pressure nitrogen supply to 100 psi. Pressure regulation of the low pressure nitrogen system pressure to 10 psi. Overpressure relief on Supply system provided by PCV-2030 (15 psi) vented to offgas vent header. Overpressure vented (V-120, V-125) through LP relief header. Overpressure vented through LP relief header.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 3. Bio-oil feeding							
1) Adjust hydrogen flow and temperature to operating conditions. 2) Fill pumps with bio-oil from feed tank. 3) Start bio-oil supply drum recirculation/take-up loop. 4) Direct product valves to L/L separator and A or B product tanks. 5) Start bio-oil feed at ~30% of target flowrate. 6) Allow system to equilibrate. 7) Gradually bring reactor to target flowrate.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls C = Critical Control	Comments
H.3-1	3	What if there is failure to initiate bio-oil supply from feed drum?	Failure to initiate flow of bio-oil from feed drum results in V-120 will empty during the process. Nitrogen to the ISCO pump.	Likely	Process impact on loss of feed.	Low level Interlock V-120. ISCO pump will shutoff due to insufficient liquid refill.	
H.3-2	4	What if there is failure to realign valves to L/L separator and product tanks?	Failure to realign valves results in bypass of LG-147 (liquid-liquid separator) with direct transfer to the V-162 (slop tank).	Likely	Spray or Spill. Possibility to overflow the V-162 tank and overflow V-162 into vent header, which could plug the vent and/or low pressure nitrogen feed.	Tank is designed for full flow from V-140 (LV-4003). Procedural check in place. PSV 4016 set pressure at 70psi.	Volume of V-162 could contain overflow for up to 19 hours.
H.3-3	4	What if there is failure to align 3 way valve to product tanks? Deadhead	Failure to align 3 way valve to product tanks results in deadhead on line and overflow of LG-147.	Likely	Spray or Spill. Potential to overflow to product gas header and plug (V-153 or WTM-152).	LG-147 visual indication during operator rounds. Product scales on V-160 and V-161. Local indication on wet WTM-152 test meter. Relief valves on product gas header at 10 psi. Relief Valve on LG-147 feed line at 70 psi.	
H.3-4	4	What if you align to a product tank that is already full?	Operator aligns to a "full" product tank resulting in overflow the product tank.	Likely	Spray or Spill. Overflow tank with potential overflow to product gas header line and plug (V-153 or WTM-152).	LG-147 visual indication during operator rounds. Product scales on V-160 and V-161. Local indication on wet WTM-152 test meter. Relief valves on product gas header at 10 psi. Relief Valves on V-160A/B and V-161A/B set at 70 psi. Relief Valve on LG-147 feed line at 70 psi.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 3. Bio-oil feeding 1) Adjust hydrogen flow and temperature to operating conditions. 2) Fill pumps with bio-oil from feed tank. 3) Start bio-oil supply drum recirculation/take-up loop. 4) Direct product valves to L/L separator and A or B product tanks. 5) Start bio-oil feed at ~30% of target flowrate. 6) Allow system to equilibrate. 7) Gradually bring reactor to target flowrate.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
H.3-5	4	What if there is failure to open vent line on correct product tank?	Pressurize the product tank.	Likely	Spray or Spill. Pressurize tank with potential overflow to Low Pressure relief header	LG-147 visual indication during operator rounds. Product scales on V-160 and V-161. Local indication on wet WTM-152 test meter. Relief valves on product gas header at 10 psi. Relief Valves on V-160A/B and V-161A/B set at 70 psi. Relief Valve on LG-147 feed line at 70 psi.	You always go to A tank for primary and switch to B tank temporarily.
H.3-6	5	What if the Bio-oil feed rate is started at more than desired?	Excessive feed rate of bio-oil results in potential excessive exothermic reaction in catalyst bed with failure of reactor pressure boundary due to excessive temperature.	Likely	Energetic event- failure of R-130 pressure boundary.	Procedural step. There is temperature and feedback to the operator. R-130 High High temperature. Audible alarms on internal thermocouples.	C Operator Response to audible alarm should be to turn off the bio-oil and/or the hydrogen.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
H.4-1	1	What if the ISCO pump freezes (open valves).	Failure in ISCO pumping results in liquid backflow from reactor. (Check valves are assumed to leak and upstream vessels subject to hydrogen backflow).	Unlikely	Energetic event- Pressurization of V-120	PSE2005 @ 100 psi sized for backflow. Check Valve (CK-2007)	C
H.4-2	1	What if the pumps run in phase? Will they cause problems?	Failure in pumping control (synchronized) results in exothermic reaction. [If combined with a plug - refer to H.4-7]	Likely	Process Upset. Local temperature increase slight pressure increase. Refer to H.4-7	Limited to 1 liter due to design of pumps. System would slow down and not get as much. It would not refill and shut off. See hazard controls for the exothermic event H.4-7	Flow rate is limited by the pump to 400 ml / min. which would only last 2.5 minutes
H.4-3	1	What if the pumps run in phase? Will they cause problems?	Failure in pumping control (synchronized) results in excessive flow of bio-oil to Flood the catalyst bed with bio-oil.	Likely	Process Upset. Pressurization of system due to plugging by high viscosity product.	Limited to 1 liter due to design of pumps. Design of the system for full pressure to receive on this scenario.	
H.4-4	1	What if there is a leak in the ISCO pump?	Seal on piston and/or pump leak results in release of Bio-oil to the enclosure..	Likely	Spray or Spill. Release of Bio-oil to the enclosure.	There is a catch under the seal and it would run down a tube into a small bottle or built in secondary container. For large leak pumps would run out of phase and shut down.	Flow rate is limited by the pump to 400 ml / min. which would only last 2.5 minutes
H.4-5	1	What if there is a leak in the ISCO pump?	Seal on piston and pump leak with backflow of hydrogen through check valves.	Unlikely	Spray or Spill. Release of Bio-oil and hydrogen to the enclosure.	There is a catch under the seal and it would run down a tube into a small bottle or built in secondary container. For large leak pumps would run out of phase and shut down. Ventilation of enclosure, hydrogen monitors on skid and enclosure..	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
H.4-6	1	What if there is excessive pressure in the reactor?	There is a plug in the system and we continue to pump (normal operation), challenging the pressure boundary of the system.	Likely	Energetic event failure of Reactor	R-130 Design pressure 3000 psi Pressure relief valve set at 3000 psi. ISCO Pump high pressure set point (process controlled). ISCO Pump firmware maximum pressure of 3750psi. ISCO Pump shear pin at 4500 psi. Pressure set point on hydrogen system (3000 psi). High-High pressure interlock at 2700 psi. Process control alarms for high pressure.	C C
H.4-7	1	What if there is an excessive exothermic reaction resulting in the pressure increase?	Exothermic reaction in reactor column combined with a plug, results in challenging the pressure boundary of the system.	Unlikely	Energetic event failure of Reactor	R-130 Design pressure 3000 psi Pressure relief valve set at 3000 psi. Pressure set point on hydrogen system (3000 psi). High-High pressure interlock at 2700 psi. ISCO Pump high pressure set point (process controlled). ISCO Pump firmware maximum pressure of 3750psi. ISCO Pump shear pin at 4500 psi. Process control alarms for high pressure Procedural step. There is temperature and feedback to the operator. Audible alarms on internal thermocouples.	C C Operator Response to audible alarm should be to turn off the bio-oil feed and/or the hydrogen.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-8	What if there is a failure in the reactor vessel?	Material failure (e.g. design flaw, undetected flaw) or leak at the flange connection at head connections or a failure at the weld results in a spray leak	Unlikely	Flammable atmosphere. High pressure release to enclosure (steam, hydrogen, or hydrocarbons)	R-130 Design Routine internal inspection vessel. Pressure Test Procedure. Operating within design parameters-overpressure over-temperature alarms and controls. Enclosure Design – Class 1 Div 2. Enclosure Ventilation System. Hydrogen monitors on skid and in enclosure. Flammable vapor monitor on skid. Expanded metal screen and acrylic shield on walkway on north side of flange. Graylock around flange would generally stop direct steam impingement.	C C C C C	
H.4-9	What if there is a failure in the reactor vessel.	Material failure (e.g. design flaw, undetected flaw) results in catastrophic failure of the vessel	Very Unlikely	Energetic event - failure of Reactor	R-130 Design Routine internal inspection vessel. Pressure Test Procedure. Operating within design parameters - overpressure over temperature alarms and controls.	C C	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-10	What if there is flame impingement due to hydrogen leak.	Catastrophic failure of the reactor vessel due to flame impingement from a hydrogen fire (hydrogen line break) results in loss of pressure integrity.	Extremely Unlikely	Energetic event - failure of Reactor	Design of hydrogen pipe system. Excess flow valve on hydrogen supply. Flame detection inside enclosure. Hydrogen monitor on skid and enclosure. Fire suppression system in enclosure. Reactor column shielded by furnace enclosure which would limit exposure and rapid temperature rise to heat up the vessel. Operator response and emergency stop.	C C	
H.4-11	What if there is a flame impingement due to a flammable liquid fire?	Catastrophic failure of the reactor due to Flame impingement from a flammable liquid fire results in loss of pressure integrity.	Extremely Unlikely	Energetic event - failure of Reactor	Design of Product Tank (V-160 A/B). Pressure Test Procedure. Distillation skid has separate containment from the hydrotreater skid. Enclosure Design – Class 1 Div 2 Flammable vapor monitor on skid Flame detection inside enclosure. Fire suppression system in enclosure Reactor column is shielded by furnace enclosure which would limit exposure and rapid temperature rise to heat up the vessel. Operator response and emergency stop.	C C	Event may be incredible based on lack of quantity or heat energy from a pool fire. Size of product tank. V-160A/B is 19 liters. This is a day's worth of running production at 1-2 liter/hr (38 liters total volume of both product tanks).

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-12	What if we lose hydrogen flow to the reactor?	Loss of hydrogen pressure results in process upset (no reaction) and pressure decrease over time. If continued filling of the reactor with bio-oil occurred, the potential for subsequent plugging- once you plug the reactor you could over pressurize – this would require a long time.	Likely	Process upset. Loss of product quality. Overpressurization. See energetic Reactor overpressure events.	L/L mass flow alarm and an interlock to shut off hydrogen and the ISCO pump. There is also a low mass flow alarm. Procedural monitoring of system.		System not set to shut down or trip. It would keep running for a while due to low usage
H.4-13	What if you lose heaters?	Loss of heat input resulting in incomplete reaction. If continued filling of the reactor with bio-oil occurred there is the potential for subsequent plugging- once you plug the reactor you could over pressurize – this would require a long time.	Likely	Process upset. Loss of product quality. Overpressurization. See energetic Reactor overpressure events.	Sufficient time for Operator response. Process indicators.		
H.4-14	What if you misalign thermo couples to zone?	Operator moves the thermocouple tree out of alignment with the reactor heating zone resulting in unstable furnace control.	Likely	Process upset. Loss of product quality	Administrative controls. Indicator on shell would indicate over temperature condition on one zone. On large temperature differential between the center and the shell controller would ramp heater output down.		

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-15	What if the thermowell fails?	Failure of thermowell pressure boundary results in spray leak	Unlikely	Flammable atmosphere. Steam, flammable vapor, hydrogen, potential liquid leak to the enclosure.	Preventative maintenance and inspection. Routine internal inspection vessel. Design of R-130 (including thermowell). Pressure Test Procedure. Operating within design parameters - overpressure over-temperature alarms and controls. Enclosure Design –Class 1 Div 2. Enclosure Ventilation System. Hydrogen monitors on skid and in enclosure. Flammable vapor monitor on skid. Thermo-well is replaceable.		.Release is directed away from personnel. C Thermowell pressure boundary is a robust system but was qualitatively judged to be more susceptible to leaks than the Reactor Vessel. C
H.4-16	What if we have high pressure associated with this portion of the separator?	Blockage of flow path (F-143 or F-4019) results in high pressure in separator.	Likely	Process Upset. Partial blockage of flow and pressurization of reactor. Overfill of V-140 could divert the liquid to the gas system causing it to plug also.	Design of High pressure components. Pressure Relief Valve PSV-4002 set at 3000 psi. Level control on V-140. Pressure indicators and alarms. Pressurization controls from reactor.		
H.4-17	What if we have high pressure associated with this portion of the separator?	Blockage of flow path (F-143 or F-4019) results in high pressure in separator.	Unlikely	Total blockage of flow, pressurization of system (back to reactor).	Design V-140 –3000 psi MAWP Pressure Relief Valve PSV-4002 set at 3000 psi. Level control on V-140. Pressure indicators and alarms. Overpressurization controls from reactor.	C C	
H.4-18	What if we have failure of system boundary V-140/LG-142?	Material failure (e.g. design flaw, undetected flaw) results in failure of V-140 pressure integrity.	Very Unlikely	Energetic event – failure in V-140/LG-142 pressure boundary.	Design of V-140/LG-142 Level control on V-140. Pressure indicators and alarms. Pressure Test Procedure.	C C	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-19	What if we have failure of LG-142?	Material failure (e.g. design flaw, undetected flaw) results in failure of LG-142 pressure integrity	Unlikely	Flammable atmosphere. Release steam, and flammable vapors, treated bio-oil to enclosure. Bound by line shear.	Robust design for glass components. Pressure indicators and alarms. Pressure Test Procedure.	C	C
H.4-20	What if we have failure of high pressure piping (leak/ spray)?	Material failure (e.g. design flaw, undetected flaw) or leak at a flange Gasket failure, swagelock leak results in a spray leak.	Unlikely	Flammable atmosphere. Release steam, hydrogen and flammable vapors, treated bio-oil to enclosure.	Design high pressure components. Pressure Test Procedure. Operating within design parameters Enclosure Design –Class 1 Div 2. Enclosure Ventilation System. Hydrogen monitors on skid and in enclosure. Flammable vapor monitor skid.	C	C
H.4-21	What if there is a low failure in LIT-4003?	LIT-4003 fails low resulting in closing LV-4003 which stops the aqueous flow and increases the liquid level in V-140.	Likely	Process upset. Partial blockage of flow and pressurization of reactor. Overfill of V-140 could divert the liquid to the gas system causing it to plug also.	Operator response to the low low alarm on the level indicator LIT-4003. Visual inspection of LG-142. Pressure indicators and alarms. Pressurization controls from reactor.		
H.4-22	What if higher than expected pressure downstream of LV4003?	Failure of LV-4003(full open) or failure/opening of the bypass line results in over pressurization of LG-147 or low pressure components downstream	Likely	Energetic event - failure of pressure boundary (LG-147) and release of bio-oil to enclosure.	PSV-4016 set at 70psi. LG-147 designed at 100 psig MAWP. LG-147 vented to product gas header. PSV-5001 in product gas vent header downstream of LG-147 is set at 10psi.	C	C

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-23	What if higher than expected pressure downstream PCV4007?	Failure of PCV-4007 (full open) or failure/opening of the bypass line results in over pressurization of product off gas header and failure of downstream components ² due to high velocity flow (Impact to Wet Test Meter).	Likely	Flammable atmosphere. Release of hydrogen or flammable vapors to enclosure but although most likely would vent through stack or back pressure through vented vessels and pressure relief to LP Relief Header. Ultimately drop reactor pressure.	The badger valve (PV-4005) would try to control the pressure. PSV-5001 set at 10psi. Vent system flow path design (1/2 or greater SS Tubing. Low alarm at PIT-4005 and PIT-3001. Design of vent system. Enclosure Design – Class 1 Div 2 Enclosure Ventilation System.	C C	
H.4-24	What if high pressure downstream PV-4005?	Fail open PV4005 or open bypass results in 100 psig pressure (PCV-4007) downstream.	Likely	High pressure at WTM-152.	PSV-5001 set at 10psi. Vent system flow path design (1/2 or greater SS Tubing).		
H.4-25	What if V-153 is blocked?	Failure to drain V-153 results in high liquid level.	Likely	Process upset. Liquid to the WTM152.	Sight Glass SG-153 normally empty. Drain valve HV-5001 manually opened to remove the liquid in V-153.		
H.4-26	What if there is a leak in the low pressure vent system?	Failure at a connection or the WTM seal results in release of hydrogen or flammable vapor to enclosure.	Likely	Flammable atmosphere. Potential creation of flammable atmosphere.	Design of vent system. Procedural step calibration of WTM. Enclosure Design – Class 1 Div 2 Enclosure Ventilation System. Hydrogen monitors on skid and in enclosure. Flammable vapor monitor on skid. Fire suppression system in enclosure. Containment pan on skid and by the enclosure.	C C	

² In particular, PI-4008 had a minimum burst pressure of ~ 2200 psig; it has been replaced with a gage that has a minimum burst pressures in excess of 3000 psig.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	C	Comments
H.4- 27	What if you don't switch tanks when they are full?	Failure to switch from full tank results in overfilling tank with the potential to backup to LG-147 or into the product gas header line and plug (V-153 or WTM-152).	Likely	Spray or Spill. Overfill of LG-147 Could divert the liquid to the gas system causing it to plug also. Partial blockage of flow and pressurization of reactor.	Level indication V-160A. H/H alarm. Weight indication set at H (12 kg) and H/H interlock (14kg) to ISCO pump. Trips LV-4003 to close.		
H.4- 28	What if there is a leak in product bio-oil system downstream of LG-147.	Failure of connection or open drain valve on V-160 A/B results in release of hydro-treated bio-oil to containment and/or to enclosure. 19 liters maximum material spill from completely full vessel V-160A/B.	Unlikely	Flammable atmosphere. Spill of combustible liquid (treated Bio-oil) and potential creation of flammable atmosphere.	Pressure Test Procedure. Design V-160A/B and piping. Drains are double valved, valved and capped, or valve and quick disconnect. Enclosure Design – Class 1 Division 2 Enclosure Ventilation System. Flammable vapor monitor on skid. Fire suppression system in enclosure. Containment pan on skid and by the enclosure.	C	C C

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-29	What if high pressure V-160A/B?	Failure in low pressure nitrogen system results in high pressure in V-160A/B and failure of pressure boundary release treated bio-oil and nitrogen to enclosure.	Likely	Energetic event – failure of V-160A/B pressure boundary. Spill/Spray of combustible liquid (treated bio-oil) and potential creation of flammable atmosphere. Creation of oxygen deficient atmosphere.	Design of V-160A/B 155 psi. V-160A/B PRV set at 70 psi. Pressure regulation of the low pressure nitrogen supply to 100 psi. Pressure regulation of the low pressure nitrogen system pressure to 10 psi. Enclosure Design – Class 1 Division 2 Enclosure Ventilation System. Flammable vapor monitor on skid. Fire suppression system in enclosure. Containment pan on skid and by the enclosure.	C C	
H.4-30	What if there is a bypass of LG-147?	Failure to close or inadvertent opening of HV-4022 results in directing aqueous and treated bio-oil into the tank V-162.	Likely	Process Upset loss of product.	Valve lineup procedure. Tank V-162 is 38 liters. System designed to 180 psi but open to atmosphere. Weight of product vessels would indicate lack of filling. Visual inspection (low level) of LG-147.		
H.4-31	What if there is a leak in product water system downstream of LG-147?	Failure of connection or open drain valve on V-161A/B results in release of product water to containment and/or to enclosure. 19 liters maximum material spill from completely full vessel V-161A/B.	Unlikely	Spray or Spill. Spill of water to containment and/or to enclosure.	Pressure Test Procedure. Design V-161A/B and piping. Drains are double valved, valved and capped, or valve and quick disconnect. Containment pan on skid and by the enclosure.		Spill of product is mostly water.

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 4. Operation							
1) Monitor feed and product levels. 2) When product drums are at 85 to 90% full, switch to other product tanks. 3) Download water vessel to product container. 4) Download oil vessel to product container or transfer to still skid feed tank.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control		Comments
H.4-31	What if high pressure in V-161A/B?	Failure in low pressure nitrogen system results in high pressure in V-161A/B and failure of pressure boundary releases water and nitrogen to enclosure.	Likely	Energetic event – failure of V-161A/B pressure boundary. Creation of oxygen deficient atmosphere.	Design of V-161A/B 155 psi. V-161A/B PRV set at 70 psi. Pressure regulation of the low pressure nitrogen supply to 100 psi. Pressure regulation of the low pressure nitrogen system pressure to 10 psi.	C C	
H.4-32	What if there is a failure to connect properly connect transfer line to transport vessel?	Failure to connect properly connect transfer line from V-161A/B to transport vessel results in spill of water	Likely	Spray or Spill. Spill of water to enclosure.	Design of quick disconnects closed unless properly engaged.		
H.4-33	What if there is a failure to connect properly connect transport vessel ventline?	Failure to properly connect transport vessel ventline to low pressure relief header results in venting of nitrogen to enclosure	Likely	Personnel Exposure. Creation of oxygen deficient atmosphere.	Design of quick disconnects closed unless properly engaged.		

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 5. Transfer to still feed tank							
1) Pad oil product container. 2) Depad still feed tank. 3) Connect transfer line. 4) Open transfer valves. 5) When empty, close transfer valves. 6) Pad still tank. 7) Depad product container. 8) Remove transfer line.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments	
H.5-1	What if there is failure to depad V-180?	Operator fails to depad V-180 prior to starting transfer from V-160A/B results in inability to transfer due to high pressure in V-180 (nominal pressure is the same in both systems).	Likely	Process upset. No transfer. Nominal pressure is the same in both systems.	Weight indication on V-160A. Level indicator on V-180. High-High level alarm on V-160A. Procedural step.		
H.5-2	What if there is failure to properly connect the transfer lines from 160A to V-180?	Failure to properly connect transfer line to V-180 results in spill or spray of hydro-treated bio-oil to the enclosure.	Likely	Flammable atmosphere. Spill/Spray of combustible liquid (treated bio-oil) and potential creation of flammable atmosphere.	Design of quick disconnects (closed unless properly engaged). Enclosure Design –Class 1 Div 2. Enclosure Ventilation. Containment for both skids and enclosure. Flammable vapor monitoring on hydrotreater skid. Fire suppression system in enclosure.	C	Bounds line failures.
H.5-3	What if there is failure to close the transfer valves and restore the pad to V-180?	Operator applies pad to V-180 without closing the three valves (HV-8017 & HV- 6028 & HV 6016) results in nitrogen flows backflow until pressure equalizes or release of nitrogen enclosure via disconnect on transfer line.	Likely	Creation of oxygen deficient atmosphere.	Design of quick disconnects (closed unless properly engaged). Enclosure Design – Class 1 Division 2. Enclosure Ventilation. Procedure.		

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 6. Shutdown							
1) Stop oil feed and turn off reactor heaters. 2) Continue product vessel monitoring per “operation” section. 3) Empty pumps back to bio-oil feed tank. 4) Reduce gas flow once product collection has diminished. 5) Allow reactor to cool.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
H.6-1	3	What if there is failure to isolate the reactor from the feed pumps?	Operator opens HV2009 without closing HV2006 resulting in backflow of steam/hydrogen, flammable vapors, bio-oil into enclosure.	Likely	Flammable atmosphere. Release of steam, hydrogen, flammable gas, bio-oil into enclosure with personnel in the area.	HV-2018 Action: Replace T upstream HV-2009 with 3-way Valve. Check Valve (CK-2007) Procedural step.	C

Hydrotreater Process Step 7. Flush							
1) Reactor should be around 150C or lower for this procedure. 2) Load acetone into pumps via transfer tank. 3) Direct product valves to slop tank. 4) Inject acetone into reactor. 5) Shut down feed system and allow reactor to cool below 100C. 6) Halt gas flow and depressurize reactor. 7) Flush with Nitrogen. 8) Verify that all systems are off.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
H.7-1		What if the reactor is greater than desired temperature?	Operator initiates flush prior to cooling below desired temperature results in failure to adequately clean catalyst/reactor.	Likely	Process upset, inefficient cleaning Energetic Event. Potential plug of reactor and energetic failure due to overpressure (continued pumping of acetone).	Procedural step Design of R-130 pressure is 3000 psi MAWP. R-130 PRV set at 3000 psi. High-High pressure interlock at 2700 psi. ISCO Pump high pressure set point (process controlled). ISCO Pump firmware maximum pressure of 3750psi. ISCO Pump shear pin at 4500 psi Process control alarms for high pressure.	C C
H.7-2		What if we don't align product valves to slop tank?	Failure to properly align valves results in misdirection of acetone solutions to the product tank instead of slop tank.	Likely	Process upset. Loss of product due to mixing of acetone solution with product.	Procedural step	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 7. Flush						
1) Reactor should be around 150C or lower for this procedure. 2) Load acetone into pumps via transfer tank. 3) Direct product valves to slop tank. 4) Inject acetone into reactor. 5) Shut down feed system and allow reactor to cool below 100C. 6) Halt gas flow and depressurize reactor. 7) Flush with Nitrogen. 8) Verify that all systems are off.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls C = Critical Control	Comments
H.7-3	What if other than acetone in V-125?	Operator error results in filling V-125 with sulfiding solution instead of acetone.	Likely	Process upset. Coke the catalyst and potentially evolve higher than expected H2S.	H2S monitor on vent stack. Procedural step.	
H.7-4	What if too much pressure to V-125 from nitrogen pad?	Failure to correctly set (or failure of pressure control valve) low pressure nitrogen pressure results in overpressurize V-125 with > 10 psi up to 100 psi of nitrogen resulting in failure of pressure boundary and release of acetone /nitrogen to enclosure.	Likely	Energetic event - failure of V-125 pressure boundary. Flammable atmosphere. Spill of flammable liquid and potential creation of flammable atmosphere with personnel present. Creation of an oxygen deficient environment.	Pressure limit on the low pressure system. Pressure set point, pressure control for system, Design of V-125 155 psi MAWP V-125 PRV set at 100 Enclosure Design –Class 1 Div 2. Enclosure Ventilation System. Flammable vapor monitoring on skid. Fire suppression system in enclosure.	C C
H.7-5	What if there is failure to connect vent line V-125 to rupture disk?	Failure to connect vent line to header results in venting of V-125 contents to enclosure on system overpressure/failure of rupture disk and release of acetone /nitrogen to enclosure.	Likely	Flammable atmosphere. Spill of flammable liquid and potential creation of flammable atmosphere with personnel present. Creation of an oxygen deficient environment.	Procedural step. Connect the vent line prior to the nitrogen and outlet. Flammable vapor monitoring on skid. Fire suppression system in enclosure. Enclosure Design –Class 1 Div 2. Enclosure Ventilation System	C C
H.7-6	What if flow rate of acetone is too high?	Set pump flow rate too high.	Likely	Process upset. Potential to overwhelm liquid to gas separator V-140 resulting in over flow to the product gas system and out to the vent system.	Process monitoring. Same controls as Plugging and overflowing V-140.	Flow rate is limited by the pump to 400 ml / min. which would only last 2.5 minutes

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Hydrotreater Process Step 7. Flush							
1) Reactor should be around 150C or lower for this procedure. 2) Load acetone into pumps via transfer tank. 3) Direct product valves to slop tank. 4) Inject acetone into reactor. 5) Shut down feed system and allow reactor to cool below 100C. 6) Halt gas flow and depressurize reactor. 7) Flush with Nitrogen. 8) Verify that all systems are off.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments	
H.7-7	What if valve HV - 2006 is closed?	Deadhead the flow.	Likely	Flammable atmosphere. Line pressure goes to 4500psi resulting in a spray/leak of acetone creating a flame or flammable atmosphere in enclosure.	Transfer Line (tubing) is rated at 4800 psi. Pressure Indicator PI-2011 ISCO Pump high pressure set point (process controlled). ISCO Pump firmware maximum pressure of 3750psi. ISCO Pump shear pin at 4500 psi	C	
H.7-8	What if there is a failure in the pressure boundary?	Failure in V-125 or piping system pressure boundary results in spray/spill of acetone.	Very Unlikely	Flammable atmosphere. Spill/Spray of flammable liquid and potential creation of flammable atmosphere	Pressure Test Procedure (prior to operations). Design of V-125. Enclosure Design –Class 1 Div 2. Enclosure Ventilation	C C	
H.7-9	What if the drain valve HV-2009 is open?	Failure to close drain valve after pumping feed back to V-120 results in loss of acetone solution.	Unlikely	Flammable atmosphere. Spill/Spray of flammable liquid and potential creation of flammable atmosphere.	Procedural check that drain valve is closed. Enclosure Design –Class 1 Div 2. Enclosure Ventilation. Containment for skid.	C C	
H.7-10	What if temperature increases during Cleaning > 350C?	Heaters turn on raising the temperature or exothermic reaction between catalyst acetone and hydrogen results in temperature increase during cleaning.	Unlikely	Process upset. Potential loss of catalyst.	Procedural controls. Design of R-130 (temperature). Temperature alarms.		Bench Scale testing.
H.7-11	What if gas flow stopped to early (Reactor above 100C)?	Hydrogen flow stopped too early (reactor above 100C) results in loss of cooling to catalyst.	Likely	Process upset. Potential loss of catalyst.	Procedural Control.		

Hydrotreater Process Step 8. Refit

1) Depressurize and verify zero energy state on all hydrotreater subsystems. 2) Chain out inter-skid area prior to working on upper head. 3) Open upper reactor head
4) Remove catalyst.

Hydrotreater/Distillation Column Hazard Analysis Report
Table 3-4. What-If Hazards Analysis Results

Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
H.8-1	What if fail to depressurize before breaking into the system?	Operator fails to depressurize reactor vessel prior to breaching pressure boundary resulting in release of nitrogen.	Likely	Personnel exposure. Release of Nitrogen to the enclosure. Potential personnel exposure to high pressure nitrogen.	Procedural. Pressure indicator on reactor. Enclosure Ventilation System. Flammable vapor monitor and hydrogen monitor on skid would detect significant flammable vapor /hydrogen release.	
H.8-2	What if fail to purge with nitrogen before breaking into the system?	Operator fails to perform nitrogen purge after acetone flush resulting in release of hydrogen/acetone vapors to the enclosure	Likely	Flammable atmosphere. Release of hydrogen gas - Creation of flammable environment with personnel present.	Procedural. Enclosure Ventilation System. Flammable vapor monitor on skid. Hydrogen monitor on skid and in enclosure	Nitrogen flush performed prior to disassembly. (possibly between step 6 and 7 of flush)
H.8-3	What if fail to purge and depressurize before breaking into the system?	Operator fails to purge and depressurize reactor vessel prior to breaching pressure boundary resulting in release of high pressure hydrogen/acetone vapors to the enclosure	Unlikely	Flammable atmosphere. Spray of hydrogen gas - Creation of flammable environment with personnel present. Potential personnel exposure to high pressure hydrogen and acetone vapors.	Pressure indicator on reactor. Procedural. Verify zero energy-procedural step and hold point. This defines transition to non Class I/Div 2. Enclosure Ventilation System. Flammable vapor monitor on skid. Hydrogen monitor on skid and in enclosure.	C Nitrogen flush performed prior to disassembly. (possibly between step 6 and 7 of flush)

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 1. Prestart Operations						
1) Seal process tanks. 2) Pre-op valve position check for entire system. 3) Pressure check system (purge and pad all subsystems). 4) Transfer feed to tank via hydrotreater skid or transfer tank using tank pads. 5) Alternately, feed can be loaded into one of the bottoms product tanks and padded over. 6) Put valves to flow positions, including bottoms and distillate product tanks. 7) Prime feed pump and turn to auto control.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls C = Critical Control	Comments
D.1-1	What if you fail to properly reassemble seals / flanges / piping connections?	Failure to re-assemble or failure in seals/flanges/piping connections results in loss of pressure boundary integrity and release of low pressure nitrogen into enclosure.	Likely	Creation of oxygen deficient atmosphere with personnel present.	Pressure Test Procedure. Enclosure Ventilation System operable when system is pressurized. Design of pressure vessels and components. Pressure indication on the distillation column.	
D.1-2	What if valve is left open?	Failure to close vent valve prior to starting pressure check.	Likely	Process Upset. Vent to vent header	Valve lineup procedure. Pressure Test Procedure. Pressure indication through- out system.	
D.1-3	What if valve is left open? (see HV-8007/8, etc.)	Failure to close valve (drain valve) resulting in nitrogen released into enclosure.	Very Unlikely	Personnel exposure. Creation of oxygen deficient atmosphere with personnel present. Potential for small (residual amounts) flammable liquid accumulation.	Valve lineup procedure. Pressure Test Procedure. Ventilation system operable when system is pressurized. Drains are double valved, valved and capped, or valve and quick disconnect.	
D.1-4	What if failed to pressure check part of system due to valve misalignment?	Inadequate pressure check, combined with pre-existing leak results in leak at operating temperature and pressure, releases of treated bio-oil/ intermediate product vapors/ nitrogen into enclosure.	Unlikely	Spray or Spill. Release of treated bio-oil/ intermediate product vapors/ nitrogen into enclosure. (subsequent operation)	Valve lineup procedures. Pressure Test Procedure -pressure indicators on individual tanks and sub-systems. Flammable vapor monitor on skid. Enclosure Design – Class 1 Division 2. Enclosure Ventilation System.	
D.1-5	What if fail to do the pressure test?	Failure to perform pressure check, combined with pre-existing leak results in leak at operating temperature and pressure, releases of treated bio-oil/ intermediate product vapors/ nitrogen into enclosure.	Unlikely	Spray or Spill. Release of processed bio-oil intermediate product vapors/ nitrogen into enclosure. (subsequent operation)	Pressure Test Procedure.(detection of no pressure) Flammable vapor monitor on skid. Enclosure Design – Class 1 Division 2. Enclosure Ventilation System.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 1. Prestart Operations						
1) Seal process tanks. 2) Pre-op valve position check for entire system. 3) Pressure check system (purge and pad all subsystems). 4) Transfer feed to tank via hydrotreater skid or transfer tank using tank pads. 5) Alternately, feed can be loaded into one of the bottoms product tanks and padded over. 6) Put valves to flow positions, including bottoms and distillate product tanks. 7) Prime feed pump and turn to auto control.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
D.1-6	What if too high pressure for low pressure system?	Failure in supply (Nitrogen Tank) regulator results in over pressurization of low pressure system components due to excessive nitrogen pressure.	Unlikely	Energetic event - failure of low pressure system (>100 psi)	Pressure regulation of the low pressure nitrogen supply to 100 psi. Pressure regulation of the low pressure nitrogen system pressure to 10 psi. Pressure regulator to offgas vent header (PCV-9008) set at 15 psig. Design of low pressure components Low pressure component PRVs set at ≤ 100 psig. Pressure Test Procedure (verify pressure).	C C
D.1-7	What if too high pressure for low pressure system?	Failure in PCV-9006 results in pressurization of low pressure system components due to excessive nitrogen pressure.	Unlikely	Energetic event - failure of low pressure system (~100 psi)	Pressure regulation of the supply to 100 psig. Design of Pressure vessel and System components ≥MAWP 135 except for the still (V-184, MAWP 70 psig). Distillation skid pressure components PRVs set at 70 psig. Pressure Test Procedure.	C C
D.1-8	What if you inadvertently use Hydrogen instead of nitrogen for leak check? (Requires connection of Low Pressure Nitrogen Supply to Hydrogen bottle?)	Failure to use correct gas for pressure check (combined with pre-existing leak or failure to re-assemble properly) results in Potential flammable atmosphere in the enclosure with a piece of equipment not qualified for the hydrogen atmosphere.	Very Unlikely	Flammable atmosphere. Deflagration in Enclosure	Hydrogen monitors on skids and enclosure. Enclosure Ventilation System. Procedures Test Procedure. Valve and line labeling. Different gases have different bottle fitting.	C C C
D.1-9	What if hydrogen is introduced to distillation system	Failure to isolate V-160 from skid before transfer, combined with upset condition that	Very Unlikely	Process Upset. Hydrogen released to vent system (normal operations).	Valve line on transfer. See process hydrotreater process controls.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 1. Prestart Operations						
1) Seal process tanks. 2) Pre-op valve position check for entire system. 3) Pressure check system (purge and pad all subsystems). 4) Transfer feed to tank via hydrotreater skid or transfer tank using tank pads. 5) Alternately, feed can be loaded into one of the bottoms product tanks and padded over. 6) Put valves to flow positions, including bottoms and distillate product tanks. 7) Prime feed pump and turn to auto control.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
	from hydrotreater?	introduces process gas (requires multiple conditions).				
D.1-10	What if we transfer product too fast or at too high of pressure?	Transfer of product at greater than expected pressure or flow results in system breach and release of treated bio-oil/intermediate products (recycle from V-191-194) into enclosure	Unlikely	Flammable atmosphere. Spray or spill of flammable liquid and vapors	Pressure Limited to Low pressure Nitrogen pressure. V-180 rated at 135psi MAWP. Design 1/2 inch stainless steel transfer line V-180 PRV set at 70.	C C C System designed for maximum flow from pump at maximum air supply pressure.
D.1-11	What if we transfer too much bio-oil (over fill)?	Failure to stop transfer results in over fill of V-180. Requires multiple transfers from V-160A/B	Unlikely	Spray or Spill. Overfill V-180 resulting in release of bio-oil into the vent system.	Level indicator on V-180 and H/H alarm. V-180 sized at 140 liters	Would require 6 or 7 transfers.
D.1-12	What if there is a leak in the bio-oil line?	Leak in transfer line from Hydrotreater results in spill /spray to enclosure.	Likely	Spray or Spill. Release of treated bio-oil into enclosure.	Pressure boundary design. Secondary containment provided by enclosure.	
D.1-13	What if air gets in the system?	Air in V-180 during manual cleaning of vessel.	Likely	Energetic event - Air in system results in potential deflagration in V-180, if not purged.)	Pressure Test Procedure – with nitrogen purge. P-181 will not pump gas.	C
D.1-14	What if we failed to line up properly for operations? (can HV-9025/HV-9021 block flow?)	Failure to correctly align system for operations after pressure test results in blocked flow within the system distillation column.	Likely	Deadhead within system. High pressure in distillation column or piping.	Valve Lineup Procedure. Multiple PRVs (PRV on vessels, PRV on pump), Multiple process control alarms on high level, high pressure.	C
D.1-15	What if we inadvertently open an already closed valve?	Inadvertent opening of (drain/manual transfer) valve results in venting to enclosure or header	Unlikely	Potential for nitrogen release into enclosure or vent.	Procedures in place. Majority is double- valved or pathways to enclosure are valved and capped.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process 2. Startup							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Turn on coolant to HX and pump bottoms. 4) Turn on nitrogen purge to heatup setpoint and set system backpressure. 5) Engage feed pump and set backpressure loop. 6) Fill still bottom to submerge heater elements via feed control badger and/or bypass. 7) Turn on still heater and external jacket heater 8) As liquid level drops in still, set feed badger to maintain liquid height in still							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
D.2-1	1	What if you leave non-Class 1 Div 2 equipment in environment?	Potential for flammable atmosphere to reach ignition sources.	Unlikely	Flammable atmosphere. Potential ignition of a flammable vapor given leak sufficient to result in a flammable atmosphere.	Procedure steps. Pressure Test Procedure. Enclosure Ventilation System. Alarms for flammable vapors on skid.	C C
D.2-2	1	What if you bring in non-Class 1 Div 2 equipment into the enclosure during operations?	Potential for flammable atmosphere to reach ignition sources.	Unlikely	Flammable atmosphere. Potential ignition of a flammable vapor given leak sufficient to result in a flammable atmosphere.	Procedure steps. Pressure Test Procedure. Enclosure Ventilation System. Alarms for flammable vapors on skid. Limit access to trained operators. Procedural steps in place during operations.	C C
D.2-3	2	What if you fail to initiate purge of electrical?	Potential for flammable atmosphere to reach ignition sources.	Unlikely	Flammable atmosphere. Potential ignition of a flammable vapor given leak sufficient to result in a flammable atmosphere.	Enclosure Design – Class 1 Div 2, Pressure monitoring and alarm on cabinets (Z-purge). System design Pressure Test Procedure. Enclosure Ventilation System. Flammable vapor monitor on skid.	C C C C
D.2-4	3	What if you fail to start coolant flow?	Loss of cooling to HE-185.	Likely	Spray or Spill. Vent lighter components to vent header from V-186. Potential to fill vent header with liquid (which would go to stack) and plug system, leading to back pressure on the distillation column. Steam in the water jacket.	Flow monitor, temperature alarm on Chilled Water system. Manual flow indicator FIC-8001 (would not see at computer). PRVs, pressure indication, pressure alarms on distillation column.	
D.2-5		What if you fail to start coolant flow?	Loss of tempered water to P-182.	Likely	Spray or Spill Failure of pump seals and leak of heavy components to secondary containment.	Temperature, local flow indication on tempered water. Secondary containment.	
D.2-6		What if P-182 is over-cooled?	Set temperature control on tempered water too low.	Likely	Process upset. Inability to pump from bottom of column. Increase level in distillation. Potential failure of pump.	Temperature and flow indication. Pressure on the line from the pump. Level indication on columns and product tanks.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process 2. Startup							
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Turn on coolant to HX and pump bottoms. 4) Turn on nitrogen purge to heatup setpoint and set system backpressure. 5) Engage feed pump and set backpressure loop. 6) Fill still bottom to submerge heater elements via feed control badger and/or bypass. 7) Turn on still heater and external jacket heater 8) As liquid level drops in still, set feed badger to maintain liquid height in still							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
					Temperature indication on product tanks. Temperature indication, alarm, interlock to Chiller system on L/L.		
D.2-7	4	What if too much pressure to from nitrogen purge?	Overpressurize V-184/V-186 with greater than 100 psi of nitrogen and blocked vent header.	Unlikely	Energetic event - failure of V-184/V-186 pressure boundary.	Pressure limit on the low pressure system. Pressure set point, pressure control for system. Design of V-184/V-186. PRV on V-184 set at 70 psi. Pressure indication on vent header.	C C
D.2-8	4	What if too little pressure to from nitrogen purge?	Failure op open/close HV-8008. Run out of nitrogen.	Likely	Process upset. Incomplete purge.	Procedural steps. Local flow indication.	May be a desired normal operational scenario
D.2-9	4	What if there is a failure in the pressure boundary (nitrogen)?	Failure in nitrogen line.	Unlikely	Personnel Exposure. Nitrogen release to enclosure. Potential backflow of flammable vapors from system. Loss of ability to transfer. Possible process upset. Incomplete purge.	LP Nitrogen piping inside Enclosure is Stainless Steel, ASME B-31.3. Flammable vapor detection on skid. Enclosure ventilation.	
D.2-10	5	What if back pressure too high?	Set back pressure within distillation column too high (e.g., max of V-182).	Likely	Process upset. Eventual increase of temperatures in top of distillation column.	Pressure and temperature indication in distillation column. H/H pressure alarm on column. Temperature alarm.	
D.2-11	5	What if back pressure too low?	See "no nitrogen flow".				
D.2-12	6	What if fill distill too high?	Failure to stop pumping.	Likely	Process upset. Overfill to distillate product tanks. Overflow to vent header.	Level indication and alarm on V-184, V-186. Visual indication in V-186. Pressure indicator PI-8023.	
D.2-13	6	What if fill distill too low?	Failure to submerge heaters.	Likely	Process upset. Damage heater elements with excessive heat.	Temperature indication on heater JE-N-8028. H/H trips to zero % output on heater element. Safety H/H trips power to heater. Level indication in column.	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process 2. Startup						
1) Clear area of all maintenance work and equipment not compatible with Class 1 Div 2 environment. 2) Initiate purge of electrical cabinets and furnace. 3) Turn on coolant to HX and pump bottoms. 4) Turn on nitrogen purge to heatup setpoint and set system backpressure. 5) Engage feed pump and set backpressure loop. 6) Fill still bottom to submerge heater elements via feed control badger and/or bypass. 7) Turn on still heater and external jacket heater 8) As liquid level drops in still, set feed badger to maintain liquid height in still						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
D.2-14	What if no still heater?	Failure to turn on still heater.	Likely	Process upset. No heat-up.	Temperature indication on column and still.	
D.2-15	What if no jacket heater?	Failure to turn on jacket heater.	Likely	Process upset. Longer than expected heat-up rate.	Temperature indication on column and still.	
D.2-16	What if still heater too high?	Loss of still heater control.	Likely	Process upset. Faster than expected boil-off of product. Potential uncovering of heater and damage to heater (see above). Process upset.	Thermocouple on still heater. Level indication in column. Output flow indication.	
D.2-17	What if jacket heater too high?	Loss of jacket heater control results in over-heating.	Likely	Energetic Event. Potential failure of pressure boundary due to excessive temperature. Faster than expected boil-off of product (see above).	Temperature indication on heater JE-N-8023. High-High Temperature on V-184.	C
D.2-18	8 What if feed rate is too high?	Feed rate set too high.	Likely	Process upset. Potential eventual overflow into vent system.	Procedural step on start-up of reflux. Level indication and alarm on V-184, V-186. Visual indication in V-186. Pressure indicator PI-8023 High-High provides alarm and shuts off pump.	
D.2-19	8 What if feed rate is too low?	Feed rate set too	Likely	See loss of still heater control.		

Distillation Process Step 3. Reflux						
1) Observe reflux in sight glass via level sensor. 2) Once distillate reaches 8 inches, engage reflux pump (P-183) and set backpressure loop. 3) Prime reflux pump. 4) Set reflux badger to target kg/hr. 5) Set product badger to target liquid level in sight glass. 6) Reduce nitrogen flow to target setpoint and adjust system backpressure.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
D.3-1	1 What if reflux level too high?	Failure to start reflux pump.	Likely	Process upset. Overflow to distillate product tanks.	Procedural step. Level indication and alarm on V-186. Visual indication in	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 3. Reflux							
1) Observe reflux in sight glass via level sensor. 2) Once distillate reaches 8 inches, engage reflux pump (P-183) and set backpressure loop. 3) Prime reflux pump. 4) Set reflux badger to target kg/hr. 5) Set product badger to target liquid level in sight glass. 6) Reduce nitrogen flow to target setpoint and adjust system backpressure.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls C = Critical Control	Comments	
				Overflow to vent header.	V-186. Pressure indicator PI-8023.		
D.3-2	1	What if reflux level too low?	Likely	Process upset.	Low level alarm. L/L interlock to stop P-183.		
D.3-3	2	What if we fail to set reflux back pressure (PCV-8024) correctly?	Likely	Process upset. Build up in V-186 and overflow.	High-High level for LIT-8028 (95%) to manual 100% output.		
D.3-4	2	What if we fail to set reflux back pressure (PCV-8024) correctly?	Likely	Process upset. More or less than expected product to distillation.	Procedural step. Level indication and alarm on V-186. Visual indication in V-186. Pressure indicator PI-8023.		
D.3-5	4	What if fail to set reflux badger to target rate?		See D.3-1 and D.3-2.			
D.3-6	5	What if fail to set product (bottoms) badger to target rate?		See D.3-1 and D.3-2.			
D.3-7	6	What if we fail to set feed pressure correctly?		See D.3-3 and D.3-4.			

Distillation Process Step 4. Operation							
1) Set feed rate badger to target feed rate. 2) Turn on and prime bottoms level control pump to target setpoint. 3) Monitor liquid level on bottoms and distillate tanks, and switch to alternate tank when full. 4) Monitor feed tank level.							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls C = Critical Control	Comments	
D.4-1	1	What if we fail to set feed rate (FV-8014) correctly?	Likely	Process upset Recycle back to V-180. Drive still to low level.	L/L alarms on V-184. Temperature interlocks that shut down still heaters. Temperature interlock for jacket heater. User set flow alarm on FIC-8014.		
D.4-2	1	What if pump (P-181) fails to pump?	Unlikely	Process upset Drive still to low level.	L/L alarms on V-184. Temperature interlocks that shut down still heaters. Temperature interlock for jacket heater. User set flow alarm		

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 4. Operation						
1) Set feed rate badger to target feed rate. 2) Turn on and prime bottoms level control pump to target setpoint. 3) Monitor liquid level on bottoms and distillate tanks, and switch to alternate tank when full. 4) Monitor feed tank level.						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
					on FIC-8014 pump indication if loss of electrical power to the pump.	
D.4-3	1	What if we have excessive pressure in the Distillation Column?	Likely	Energetic event - failure of V-184	V-184 Design pressure V-184 PRV set at 70 psi. Pressure relief and control on pump. Pump high pressure set point.	C C Bottoms pump P-182 would try to maintain level in V-184
D.4-4	3	What if there is a failure in the Distillation Column?	Very Unlikely	Energetic event - failure of V-184	V-184 Design pressure Pressure Test Procedure. Operating within design parameters - overpressure over temperature alarms and controls.	C C
D.4-5	3	What if there is a flame impingement due to a flammable liquid fire?	Extremely Unlikely	Energetic event - failure of V-184	Design of distillation skid components pressure components. Enclosure Design – Class 1 Div 2. Flame detection inside enclosure. Flammable vapor monitor on skid. Fire suppression system in enclosure. Operator response and emergency stop.	C C
D.4-6	3	What if you lose heaters?	Likely	Process upset (see previous loss of heater hazards)		
D.4-7	3	What if there is a leak in the low pressure vent system?	Very Unlikely	Flammable atmosphere. Flammable atmosphere. Flammable vapors in enclosure.	Design of vent system. Enclosure Ventilation System. Enclosure Design – Class 1 Div 2. Flammable vapor monitor skid.	C
D.4-8	3	What if you don't switch tanks when they are full?	Likely	Process upset. Backup to vent header.	Level indication, H/H and L/H level alarm. Product tanks are sized for a run.	
D.4-9	3	What if there is a leak downstream of Distillation?	Likely	Flammable atmosphere. Flammable vapors or liquid in enclosure.	Pressure test Procedure. Design of distillation skid components. Enclosure Ventilation System. Enclosure Design – Class 1 Div 2.	C C C

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 4. Operation							
1) Set feed rate badger to target feed rate. 2) Turn on and prime bottoms level control pump to target setpoint. 3) Monitor liquid level on bottoms and distillate tanks, and switch to alternate tank when full. 4) Monitor feed tank level.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
			enclosure.			Flammable vapor monitor skid. Containment pan on skid that could capture the spill.	
D.4-10	3	What if bypass valve is open?	Bypass valve is opened or fails.	Likely	Process upset. Higher than expected flow rate in distillation column	Flow indication. Other controls for higher than expected flow (see startup controls)	
D.4-11	3	What if there is a failure in the pressure boundary?	Failure in pressure boundary results in release of flammable liquid/vapors	Very Unlikely	Flammable atmosphere. Fire or flammable atmosphere in enclosure.	Pressure Test Procedure. Design of distillation skid components. Enclosure Design – Class 1 Div 2. Enclosure Ventilation System. Flammable vapor monitor on skid.	C C
D.4-12	3	What if there is a failure in the pressure boundary?	Failure of water jacket pressure boundary, leak into distillation system.	Very Unlikely	Process upset. Steam, water vapor into system. Eventual leak of product back into the chilled water reservoir outside enclosure.	Pressure Test Procedure. Design of distillation skid components. Low level indication on Chiller system. Flow monitor, temperature alarm on Chilled Water system. Manual flow indicator FIC-8001 (would not see at computer).	
D.4-13	3	Over pressure of V-191 thru V-194 due to low pressure nitrogen?	Failure in supply (Nitrogen Tank) regulator results in over pressurization of V-191 – V-194 due to excessive nitrogen pressure.	Unlikely	Energetic event - failure of low pressure system (>100 psi)	Pressure regulation of the supply to 100 psig. Pressure regulation (PCV-9006) set at 10 psig regulates downstream system pressure) Pressure regulator to offgas vent header (PCV-9008) set at 15 psig. Low pressure component PRVs set at ≤ 100 psig. Design of Low pressure components. Pressure Test Procedure.	C C C

Hydrotreater/Distillation Column Hazard Analysis Report
Table 3-4. What-If Hazards Analysis Results

Distillation Process Step 5. Shutdown							
1) Turn off still heater and jacket. 2) Halt feed pump and set feed badger to zero. 3) Close reflux badger. 4) Set reflux level control to zero to drain reflux glass into distillate product. 5) Turn off reflux pump after low level indicator. 6) Set bottoms level control to zero. 7) Turn off bottoms level pump after low level indicator. 8) Turn on nitrogen sweep to low level.							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
D.5-1	1	What if you fail to off heater and jacket before stopping flow?	Shut down pumps before the heaters are shutdown.	Likely	(see boil off of columns)		
D.5-2		What if you run out of product?			(see boil off of column)		
D.5-3	2	What if you fail to stop flow?			(see overflow of column or loss of heaters)		
D.5-4	3	What if you fail to close reflux badger?	Failure to close FV-8027.	Likely	Process upset. Loss of some product.		
D.5-5	3	What if you close reflux badger too early?	Close FV-8027 too early.	Likely	Process upset. Minor impact on product quality.		
D.5-6	4	What if you close depressurize reflux?	Failure to set reflux level control to zero.	Likely	Process upset. Loss of some product		
D.5-7	4	What if you open bypass to drain reflux (while pressurized)?	Drain too early.	Likely	Flammable atmosphere. Potential spill of flammable liquids to enclosure	Enclosure Ventilation System. Enclosure Design – Class 1 Div 2. Flammable vapor monitor skid. Containment pan on skid that could capture the spill.	C C
D.5-8		What if you fail to correctly align during unloading?	Failure to properly connect to Apache tank.	Likely	Flammable atmosphere. Spills of flammable liquid into enclosure	Enclosure Ventilation System. Enclosure Design – Class 1 Div 2.	
D.5-9		What if you over fill Apache tank?	Overflow product to vent header.	Likely			

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,							
Hazard ID/ Process Step		What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
U-1		What if loss (blockage) of process vent header?	Overflow of flammable liquids into vent header. Would require continued operations for extended	Very Unlikely	Spray or spill. Flammable liquid accumulation in stack in unoccupied area vapors would dissipate out the stack.	(see overflow scenarios)	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
		period of time.					
U-2	What if loss (blockage) of process vent header?	Loss of vent header.		Process upset. Pressurize low pressure side WTM-152, V-153, LG-147, LG-142, V-140 and reactor and all associated piping.	(See earlier (system specific) block flow events).		
U-3	What if ventilation flowpath is lost?	Failure of stack due to high wind.	Very Unlikely	Blockage of vent flow due to collapsed or bent stack. Loss of ventilation. Potential loss of flow or back flow into vent header. Blockage of exhaust gas flow and potential creation of flammable environment in enclosure and vent stack.	Exhaust flow switch initiates Scenario A on loss of flow.		
U-4	What if ventilation flowpath is lost?	Failure of stack due to high wind.	Very Unlikely	Process upset. No immediate release. Break of stack at ground level. Vent of effluent at ground level. Potential loss of ventilation fan.	Design of Stack.		
U-5	What if ventilation is lost?	Failure of ventilation fan.	Likely	Potential flammable concentrations of hydrogen or vapors in stack. Vapors would dissipate out the stack.	Loss of ventilation fan trips process controls.		
U-6	What if loss of Enclosure Ventilation?	Enclosure ventilation is lost.	Likely	Loss of environmental control in enclosure.	Loss of ventilation shuts off the hydrogen flow, the heaters and the pumps via shutdown scenario A.		
U-7	What if relief header flow is lost? Mud daubers commonly plug drain at 382 (100 psi)	Relief header is blocked by bird/bees nests.	Unlikely	Inadequate pressure relief.	Administrative controls to check relief header. Design of system includes bird screens, double release path at top. Design pressure of knockout pot is 12 psi.		
U-8	What if relief header flow is activated?	Activation of pressure relief	Likely	Flammable atmosphere. Potential flammable atmosphere in relief header and knockout pot.	Design of knockout pot and lines.	C	Auto-ignition would require high temperature.
U-9	What if there is a pool Fire in Enclosure	Leak of flammable liquid accumulation in enclosure, secondary containment and subsequent pool fire.	Unlikely	Energetic Event. Potential impingement on vessels, lines, or structure. Structural failures and impingement could lead to line or	Design of Product Tank (V-160 A/B). Pressure Test Procedure. Distillation skid has separate containment from the hydrotreater	C	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
				vessel ruptures.	skid. Enclosure Design – Class 1 Div 2 Flammable vapor monitor on skid Flame detection inside enclosure. Fire suppression system in enclosure Reactor column is shielded by furnace enclosure which would limit exposure and rapid temperature rise to heat up the vessel. Operator response and emergency stop.		
U-10	What if there is an impingement (jet) fire (hydrogen or pressurized flammable liquid line) in Enclosure?	Line leak of hydrogen supply or pressurized flammable liquid line.	Unlikely	Energetic Event. Potential impingement on vessels, lines, or structure. Structural failures and impingement could lead to line or vessel ruptures.	Design of hydrogen pipe system. Excess flow valve on hydrogen supply. Flame detection inside enclosure. Hydrogen monitor on skid and enclosure. Fire suppression system in enclosure. Reactor column shielded by furnace enclosure which would limit exposure and rapid temperature rise to heat up the vessel. Operator response and emergency stop.	C C	
U-11	What if there is a fire in electrical power cabinets inside enclosure?	Loss of function of various components (pumps, valves, control systems). Potential multiple spurious actions.	Very Unlikely	(The scenarios identified for other hazards, including the bounding scenario of vessel over pressurization.)	Vessel protection, pressure relief. Enclosure Design. Design of electrical cabinets. All cables in conduit.	Two power cabinets. Two separate instrument cabinets.	
U-12	What if the water mist system actuates?	Inadvertent actuation results in water mist during operation.	Unlikely	Process upset. No immediate release. Spraying water on hot systems, leading to loss of pressure boundary due to thermal stress (e.g., reactor and distillation columns).	Column design. The mist system is a low volume system. Top of vessels are not insulated and could be at 160 C. Columns are not constrained.		
U-13	What if the water mist system actuates?	Inadvertent actuation results in water mist during	Unlikely	Process upset. No immediate release. Shorting in electrical	Cabinets are sealed and purged.		

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments	
		operation.		cabinets.			
U-14	What if Fire in enclosure?	Fire department quenches vessel.		Process upset. No immediate release. Spraying water on hot systems, leading to loss of pressure boundary due to thermal stress (e.g., reactor and distillation columns). Note: Standard response to vessels in fire including liquid gases is to spray water and move to safe distance.	Notification of fire department would only occur with initiation of Scenario C.		
U-15	What if Fire in PDL-West?	Fire outside enclosure initiates evacuation.	Likely	Process upset. No immediate release. Evacuation of PDL-West resulting in unattended operation of the system.	Fire alarm system activation initiates Scenario A.		
U-16	What if process control is lost?	Loss of process control due to PLC failure.	Unlikely.	Process upset. No immediate release. PLC fails to indeterminate state.	PLC design such that all control goes to their failed states (fail safe) as controlled by skid. PLC is protected by UPS.		
U-17	What If you lose power and you are in the middle of the run?	Short term loss of power. (Seconds- expected monthly).	Likely	Process upset. No immediate release. VFD on exhaust fan goes offline on a fault but hydrotreater system does not recognize it.	Process monitoring and control on UPS and still available. Loss of ventilation shuts off the hydrogen flow, the heaters and the pumps via shutdown scenario A. Process can start on resumption of ventilation flow.		Back pressure regulator allows reactor to lose pressure slowly.
U-18	What if longer term loss of power and you are in the middle of the run?	Longer term loss of power (minutes – expected a few times a year).	Likely	Process upset. No immediate release. Loss of exhaust fan and compressed air. Loss of MAU. Loss of normal power lighting.	Process monitoring on UPS and still available. E-Stop maintained. Loss of ventilation shuts off the hydrogen flow, the heaters and the pumps via shutdown scenario A. Alarm on Z purge. Reactor pressure maintained in stable condition with slow decay.		
U-19	What if longer term loss of power and you are in the middle of the	Extended power outage (> than UPS capacity).	Likely	Process upset. No immediate release. Forced Shutdown. Loss of process monitoring and control.	Procedures to initiate shut-down. Loss of fire system UPS battery would result in opening XV-4020.		

Hydrotreater/Distillation Column Hazard Analysis Report
Table 3-4. What-If Hazards Analysis Results

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,							
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments	
	run?			Loss of exhaust fan and compressed air. Loss of MAU. Loss of normal power lighting.			
U-20	If there is loss instrument air, what happens from system overall?	Loss of air compressor. Failure in the compressed air delivery system.	Likely	Process upset. No immediate release. Pneumatic hydrogen and nitrogen valves close, badger valves close. The ISCO pump valves would close. Loss of Z purge.	Enclosure ventilation is maintained. E-Stop functionality is maintained. Alarm on z-purge. Alarm notification on loss of hydrogen. Reactor pressure boundary is stable. Distillation pressure boundary is stable.		
U-21	What if there is loss of the chilled water?	Loss of cooling to V-140 results in excessive vapors and steam carryover to off gas system.	Likely	Process upset. Condensation leads to potential plug of off gas system.	Switch over to tempered water. See controls for loss of off-gas scenarios.		
U-22	What if there is loss of the chilled water?	Loss of cooling to V-140 results in steam generation in the water jacket around V-140.	Likely	Process upset. Blow-down of steam into the chilled water system Z-172.	Switch over to tempered water. Procedural control over restart of system. (Check integrity of hoses)		
U-23	What if there is loss of the tempered water?	Tempered water loss. Results in difficulty in pumping bio-oil and heavy products.	Likely	Process upset. Overheating of P-182.	Procedural steps.		
U-24	What if there is a hydrogen line leak outside the enclosure?	Failure in the hydrogen line.	Very Unlikely	Flammable atmosphere -PDL. Release of hydrogen to PDL. Loss of hydrogen to reactor.	It is one piece of tubing (~17 feet) rated at maximum pressure. Located in a tray sitting in a tube holder supported across the length. It is at 13 foot elevation, in a tray, protected from edge of building. Excess flow valve on hydrogen supply (catastrophic break). Makeup air unit for enclosure. Passive PDL roof vents.		
U-25	What if there is a hydrogen line leak in the enclosure?	Failure in the hydrogen line.	Very Unlikely	Flammable atmosphere. Process impacts same as loss of hydrogen flow to reactor.	Design Hydrogen pipe system. Excess flow valve on hydrogen supply (catastrophic break). Enclosure Design – Class 1 Division 2.	C C	

Hydrotreater/Distillation Column Hazard Analysis Report

Table 3-4. What-If Hazards Analysis Results

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likeli- hood	Consequences	Hazard Controls C = Critical Control	Comments
					Enclosure Ventilation System Hydrogen monitors on skid and in enclosure. Flame detection inside enclosure. Fire suppression system in enclosure.	
U-26	What if hydrogen pressure goes down? - How to regulate	Addressed previously.				
U-27	What if temperature too high in the hi-bay?	Loss of HVAC conditioning – high temperature.	Likely	Process upset. Potential failure of PLC or instrumentation in enclosure.	Initiation of shutdown sequence based on personnel comfort temperature.	Personnel will get too hot before electronics fail
U-28	What if temperature too low in hi-bay?	Loss of HVAC conditioning – low temperature.	Likely	Process upset. Potential impact in PDL-West, freezing due to continued operation of Enclosure exhaust air. Lose ability to operate water mist system.	Initiation of shutdown sequence based on personnel comfort temperature.	
U-29	What if you have a nitrogen leak into enclosure?	Addressed previously.	Unlikely	Personnel Exposure. Potential oxygen deficient atmosphere.	Enclosure Ventilation System.	
U-30	What if nitrogen leaks into PDL-West?			Personnel Exposure Potential oxygen deficient atmosphere in PDL-West.		
U-31	What if operational upset from other PDL-West operations? (See hazardous scenario.)	Impact from Crane or load.	Likely	Flammable atmosphere. Rupture of process lines or utility lines leading to release of flammable gases. Impact to enclosure, exhaust ducts.	Operational restriction on crane use.	
U-32	What if operational upset from other PDL-West operations? (See hazardous scenario.)	Spill or leak in PDL-West results in introduction of flammable or hazardous vapors to Enclosure.	Likely	Flammable atmosphere. Flammable or hazardous vapors in Enclosure.	Flammable vapor monitor. Enclosure Design – Class 1 Div 2. MCA alarm, 20 minute bypass timer until Scenario A is initiated (unless operator bypasses).	
U-33	What if operational upset from other PDL-West operations? (See	Intake vehicle exhaust into ventilation system.	Likely	Personnel Exposure/Process upset. Impact to operations staff in PDL West and within	Administrative Control of vehicles in vicinity of building intakes (e.g., Do not park and idle)	Intakes are at ground level.

Hydrotreater/Distillation Column Hazard Analysis Report
Table 3-4. What-If Hazards Analysis Results

Utilities: Process Ventilation, Enclosure Ventilation, Compressed Air, Hydrogen, Nitrogen, Power,						
Hazard ID/ Process Step	What if:	Hazardous Scenario	Likelihood	Consequences	Hazard Controls C = Critical Control	Comments
	hazardous scenario.)			Enclosure. Inadvertent actuation of flammable vapor detection system		
U-34	What if operational upset from other PDL-West operations? (See hazardous scenario.)	Hot work in PDL-West results inadvertent flame detection, actuation of mist system.	Likely	Process upset. Inadvertent flame detection, actuation of mist system during operation (see above)	Hot Work Administrative Control.	
U-35	What if operational upset from other PDL-West operations? (See hazardous scenario.)	Future chemical fume hood operations and tie-in. Includes chemicals like acetone, sulfide agents	Likely	Flammable atmosphere. Release of flammable, hazardous vapors into exhaust system.	Exhaust flow operation. Administrative control of fume hood. Ensure future Tie-ins occur downstream of the Enclosure	

Hydrotreater/Distillation Column Hazard Analysis Report
Table 3-4. What-If Hazards Analysis Results

This page intentionally left blank

3.4 Evaluation of High Hazard Scenarios

Accident scenarios perceived as having high unmitigated consequences (energetic events with impacts outside the hydrotreater enclosure) were identified for further evaluation of the consequence and adequacy of controls. The following classes of scenarios were identified as being highly energetic and having high consequences and are further evaluated herein:

1. Boiling Liquid Expanding Vapor Explosion (BLEVE)
2. Pressure Vessel Bursts (PVB)
3. Flammable Vapor/Hydrogen leaks leading to deflagrations in the process enclosure (FA)

3.4.1 Boiling Liquid Expanding Vapor Explosion (BLEVE)

The hazard analysis identified hazard scenarios potentially resulting in BLEVEs in the hydrotreater reactor and distillation column and in several process vessels.

Of these events, consequences for the hydrotreater reactor (R-130) and distillation column (V-184) are further presented here. These components pose the highest consequences based on heat input, pressure and volume of material.

For the other pressurized process vessels, the possibility of a BLEVE is very remote as there were no identified internal heat inputs which would raise the temperature of the liquid above boiling and the vessels are insulated which would serve to protect them against the consequences of a BLEVE associated with an external fire. BLEVEs are not associated with atmospherically vented vessels unless a mechanism is identified that also results in a complete blockage of the ventilation pathway for the vessel.

3.4.1.1 BLEVE Consequence Methodology

A Boiling Liquid Expanding Vapor Explosion (BLEVE) is the result of the sudden catastrophic failure of a pressurized vessel containing liquid above its atmospheric boiling point. A BLEVE requires that the loss of containment be “sudden” and “significant” in size. Partial failures leading to two-phase jet releases would not be called a BLEVE since it does not represent a sudden loss of containment (CCPS, 2010). Depending on whether the liquid in the vessel is flammable or non-flammable, a BLEVE may include the following effects:

- blast effects (pressure wave due to the rapid vaporization of the liquid)
- missile impacts (fragment and debris throw)
- fireball (thermal hazards)

For analyzing BLEVEs, the process outlined in CCPS, 2010 was followed. Since the distillation column V-184 vessel is comprised of two sections of differing size and wall thickness, the process outlined in CCPS, 2000 was used to calculate the missile fragment range.

Blast Effects: It was conservatively assumed that the blast effects are based on the work done during an isentropic expansion process and that the energy is based on the combined energy from the liquid and vapor. The explosion energy can be written as:

$$\text{Explosion Energy, } E_{\text{ex}} = 2e_{\text{ex}}m$$

Where:

- 2 = a multiplier for ground effects.
- e_{ex} = work done, $u_1 - u_2$, the change in internal energy from state 1 (just before the failure) to state 2 (atmospheric) for both the fluid (f) and gas (g).
- m = mass of fluid released; the volume of fluid/specific volume V_1/v_1 .
- $u_{1(f,g)}$ = internal energy of the (fluid, gas) at the initial conditions. These values can be obtained directly from NIST thermodynamic data.
- $u_{2(f,g)}$ = internal energy of the (fluid, gas) in the expanded state, adjusting for the flashing fraction.

Where:

$$u_{2f} = (1 - X_f) * u_{2f} + X_f * u_{2g}$$

$$u_{2g} = X_g * u_{2f} + (1 - X_g) * u_{2g}$$

$$X_f = (s_{1f} - s_{2f}) / (s_{2g} - s_{2f})$$

$$X_g = (s_{2g} - s_{1f}) / (s_{2g} - s_{2f})$$

Energy available – Per the CCPS, 2010 methodology assuming ductile failure, the energy available is $E_{\text{ex,a}} = 0.4 * E_{\text{ex}}$. Recent work by Casal and Salla present BLEVE overpressure estimations based on superheat and state the energy available is ~ 14% (assumed to be 15%) of the superheat energy calculated by the isentropic process. Therefore; a range based on the above correlations is provided for each of the BLEVE overpressure calculations.

The scaled standoff distance, \bar{R} of the receptor is then determined by:

$$\bar{R} = R * [p_0 / E_{\text{ex,a}}]^{1/3}$$

Where:

- R = distance to receptor
- p_0 = atmospheric pressure

The scaled pressure \bar{P}_s and impulse \bar{I}_s at the receptor location are then estimated - Figures 7.6 and 7.8 of CCPS, 2010 and the final side-on pressure (P_s) and impulse (I_s) are calculated:

$$P_s = k_p * \bar{P}_s * p_0$$

$$I_s = k_i * \bar{I}_s * p_0^{2/3} * E_{\text{ex,a}}^{1/3} / a_0$$

Where:

- a_0 = speed of sound in ambient air
- $k_{(p,i)}$ scaling factor for cylindrical vessels, from Lees', 2012 - Table 17.54

Scaled dist. \bar{R}	$\bar{R} < 0.3$	$\bar{R} < 3.5$	$\bar{R} > 3.5$	Scaled dist. \bar{R}	$\bar{R} < 0.3$	$\bar{R} < 1.6$	$\bar{R} > 1.6$
k_p	4	1.6	1.4	k_i	4	1.6	1.4

Missile impacts (Hydrotreater): For missiles or rocketing fragments from a bursting vessel, CCPS, 2010 provides a simplified approach (Baum) to estimate the maximum likely range for fragments, R_{frag} . This approach is judged to be very conservative with respect to the potential for fragment travel for hydrotreater components:

- 1) The approach is derived from “open” field events (impacts of fragments with the enclosure and PDL-West building would significantly reduce the distance travelled),
- 2) The approach ignores drag associated with the fragments, and
- 3) The approach was derived for “thin-walled” vessels where the energy potential to weight ratio is much larger than that for the hydrotreater/distillation column components.

From CCPS, 2010 the maximum likely range for of the fragments, R_{frag} , meters is estimated by:

$$\text{For vessels } < 5 \text{ m}^3 \text{ the maximum likely range } R_{frag} = 90 * m^{0.333}$$

Where:

m = mass of the liquid and vapor in the vessel at the time of failure, kg

Missile impacts (Distillation Column): For missiles or rocketing fragments from the Distillation Column, a different approach was used to estimate the maximum likely range for fragments, R_{frag} . This approach was used to account for the two different sections of the vessel with varying wall thickness. This approach is judged to be very conservative with respect to the potential for fragment travel for distillation column components:

- 1) The approach is derived from “open” field events (impacts of fragments with the enclosure and PDL-West building would significantly reduce the distance travelled) and
- 2) The approach ignores drag associated with the fragments.

From CCPS, 2000 the interpolated likely range for of the fragments, R_{frag} , meters is estimated by:

$$R_{frag} = (\bar{R} * m_{frag}) / (\rho_0 * C_D * A_D)$$

Where:

\bar{R} = scaled maximal range (dimensionless)

m_{frag} = mass of the fragment, lb

ρ_0 = density of air, lb_m/ft³

C_D = drag coefficient for fragment; for sphere = 0.47

A_D = fragment surface area, ft²

g = acceleration due to gravity, length/time²

Where:

$$\bar{u} = \rho_0 C_D A_D u^2 / (m_{frag} * g)$$

$$m_{frag} = m_{vessel} / n_{frag}$$

$$A_D = A_{vessel} / n_{frag}$$

Thermal Hazards: Thermal hazards, including radiation impacts, would be limited as the hazard scenarios are enclosed within the process enclosure and PDL-West building versus an open field. As such the (maximum) fireball size and duration are calculated as a measure of the potential severity of the event with respect to close (engulfed) distances.

CCPS, 2010 provides an estimate of the fireball diameter, D_c and duration, t_c based on mass of fuel, m_f in the vessel.

$$D_c = 5.8 * m_f^{(1/3)}$$

$$t_c = 0.45 * m_f^{(1/3)} \text{ for } m_f < 30,000 \text{ kg}$$

Where:

m_f = mass of the fuel in the fireball, kg

3.4.1.2 BLEVE Results

Hydrotreater Reactor (R-130)

For the hydrotreater reactor, R-130, it is assumed the pressure in the vessel is at the PRV set point 3000 psig. This is a reasonably conservative assumption as this is a significantly higher pressure than the operating pressure (~2000 psig) and there were no events identified which would cause rapid significant pressure increases. It was conservatively assumed that the reactor contained only water and catalyst, and that the 13 liters of water volume contained 6.5 liters of liquid (water), as normally only minimal liquid is expected in the reactor and the remainder of the vapor space is steam. Accounting for hydrogen and bio-oil within the reactor would lower their potential energy due to the thermodynamic properties compared to water.

Input Assumptions:

Pressure State 1	3000 psig	20.6 MPa
Temperature State 1	368° C, saturation temperature	
Pressure State 2	14 psi	0.1 MPa
Temperature State 2	99.6° C, saturation temperature	
Volume of Reactor	26 liters	0.026 m ³
Free volume (assume 50% filled with catalyst)	13 liters	0.013 m ³
Volume of Liquid (assume 50% of free volume)	6.5 liters	0.0065 m ³
Speed of sound in air, a_0	340 m/s	

Hydrotreater/Distillation Column Hazard Analysis Report

Thermodynamic properties -Water; <http://webbook.nist.gov/chemistry/fluid/>

Temperature (°C)	Pressure (MPa)	Specific Volume, v (m ³ /kg)	Internal Energy, u (kJ/kg)	Entropy S (J/g*K)	C_v (J/g*K)	C_p (J/g*K)	Sound Spd. (m/s)	Phase
99.606	0.1	0.0010432	417.4	1.3028	3.7702	4.2152	1543.5	liquid
99.606	0.1	1.6939	2505.6	7.3588	1.5548	2.0784	471.99	vapor
368.22	20.6	0.0021291	1817.5	4.067	3.6749	31.326	383.96	liquid
368.22	20.6	0.005359	2261.5	4.8629	4.4004	65.397	373.25	vapor

Using the input assumptions and thermodynamic data provided:

The positive side-on overpressure (P_s) and positive side-on impulse (I_s) at the following receptor locations are:

Actual Receptor Distance, meters	3	7	10	30	35
scaled distance \bar{R} , m	1.6-1.2	3.8 - 2.7	5.4 – 3.9	16.3 - 11.7	19 - 13.7
P_s , kPa	45 - 70	12- 28	8 -12	2 - 3	1.4 – 2.5
I_s , Pa-s	0.09 - 0.16	0.03 - 0.06	0.02 – 0.03	<0.01 – 0.01	<0.01

The maximum likely range of fragments calculated using the CCPS, 2010 method was determined to be ~ 145 meters. As noted in Section 3.4.1.1 this distance is judged to be a very conservative estimate.

Thermal hazards were not assessed as the evaluation assumed the vessel was filled with water (liquid and vapor) to maximize the pressure and fragment impacts. Thermal hazards would be constrained by the PDL-West building and would be expected to be minimal given the steam (inerting and heat absorption) and limited quantity of flammable material. Thermal hazards are addressed in the following discussion for the distillation column and in Section 3.4.2 PVB for the reactor (assuming only hydrogen) in the vapor space.

Distillation Column (V-184)

For the Distillation Column, V-184, it is assumed the pressure in the vessel is at the PRV set point of 70 psig. This is a reasonably conservative assumption as this is a significantly higher pressure than the typical operating pressure (atmospheric to 15 psig) and there were no events identified which would cause rapid significant pressure increases. V-184 consists of two pipe sections of differing wall thickness; the smaller wall thickness (0.203 inches) was used in calculations as a conservative estimate. Due to the differing size of the sections, it was assumed that two fragments would result in the event of a BLEVE. It was conservatively assumed that the distillation column was filled ~70% (11 liters) with octane and the remaining vapor space (5.3 liters) consisting of saturated octane vapors. Accounting for treated bio-oil or heavy distillates within the distillation column would lower the potential energy of the process due to their thermodynamic properties compared to octane.

Hydrotreater/Distillation Column Hazard Analysis Report

Input Assumptions:

Pressure State 1	70 psig	0.48 MPa
Temperature State 1	193° C saturation temperature	
Pressure State 2	14 psi	0.1 MPa
Temperature State 2	126° C saturation temperature	
Volume of V-184	16.3 liters	0.0163 m ³
Volume of Liquid, octane, 70%	11 liters	0.011 m ³
Speed of sound in air, a ₀	340 m/s	
Equivalent spherical diameter	0.3145 m	
Vessel failure pressure	70 psig	482.63 kPa abs
Vessel liquid fill fraction	0.675	
Vessel wall thickness	0.203 in	0.52 cm
Vessel wall density	7800 kg/m ³	
Temperature	193°C	466.15 K
Ambient pressure	101.325 kPa abs	
Drag coefficient of fragment	0.47	
Lift to drag ratio:	0	

Thermodynamic properties -Octane; <http://webbook.nist.gov/chemistry/fluid/>

Temperature (C)	Pressure (MPa)	Specific Volume, v (m ³ /kg)	Internal Energy, u (kJ/kg)	Entropy S (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Phase
125.51	0.101	0.0016331	-0.47239	-0.00076975	2.1864	2.6481	772.03	liquid
125.51	0.101	0.27138	274.56	0.75746	2.0434	2.1426	164.49	vapor
192.93	0.48253	0.0018453	188.72	0.43715	2.4468	2.9968	525.54	liquid
192.93	0.48253	0.058767	409.58	0.96994	2.3665	2.5465	156.9	vapor

Using the input assumptions and thermodynamic data provided:

The positive side-on overpressure (P_s) and positive side-on impulse (I_s) at the following receptor locations are:

Actual Receptor Distance, meters	3	7	10	30	35
scaled distance \bar{R} , m	3.6 – 2.6	8.5 – 6.1	12 – 8.7	36 - 26	42 -30
P _s , kPa	13 - 29	4.3 - 7	3 - 4	<1.3 – 1.4	<1.3
I _s , Pa-s	0.017 - 0.04	0.007 - 0.01	0.005 - 0.009	<0.004	<0.004

The interpolated likely range of fragments calculated using the CCPS, 2000 method was determined to be ~ 84 meters. As noted in Section 3.4.1.1 this distance is judged to be a very conservative estimate.

The maximum fireball size was determined to be 10.6 meters with a duration of 0.8 seconds, not accounting for confinement provided by the enclosure or building.

3.4.2 Pressure Vessel Burst Scenarios

The hazard analysis identified scenarios as resulting in pressure vessel bursts (PVBs) in the Reactor and Distillation Columns and Process Vessels.

Of these events, consequences for the Hydrotreater Reactor (R-130) and Distillation Feed Tank (V-180) are further presented here. These vessels are pose the highest consequences based on pressure and vessel volume.

3.4.2.1 PVB Consequence Methodology

Similar to a BLEVE, a PVB accident is the result of the sudden catastrophic failure of a pressurized vessel containing gas. Depending on whether the gas in the vessel is flammable or non-flammable a PVB may include the following effects:

- blast effects (pressure wave due to the rapid expansion of the gas)
- missile impacts (fragment and debris throw)
- fireball (thermal hazards)

CCPS, 2010 notes PVBs usually do not result in ignition; therefore, thermal hazards are only addressed for the R-130 reactor under the assumption that the vessel free volume (headspace) is completely filled with hydrogen.

For analyzing PVBs, the Brode constant volume energy addition methodology, which provides an upper limit of the energy released, according to CCPS, 2010, was followed.

Blast Effects: The explosion energy can be written as:

$$\text{Explosion Energy, } E_{\text{ex,Br}} = (p_1 - p_0)V_1/(\gamma_1 - 1)$$

Where:

γ_1 = ratio of constant pressure to constant volume of specific heat of the gas in the vessel

p_0 = ambient (atmospheric) pressure to constant volume of specific heat of the gas in the vessel

p_1 = pressure in the vessel prior to burst

V_1 = Volume of vessel (gas)

Energy available – assuming ductile failure $E_{\text{ex,a}} = 0.4 * E_{\text{ex,Br}}$

The scaled standoff distance, \bar{R} of the receptor is then estimated:

$$\bar{R} = R[p_0 / E_{\text{ex,a}}]^{1/3}$$

Where:

R = distance to receptor

p_0 = atmospheric pressure

The scaled pressure \bar{P}_s and impulse \bar{I}_s at the receptor location are then determined - Figures 7.6 and 7.8 of CCPS, 2010 and the final side-on pressure (P_s) and impulse (I_s) are calculated:

$$P_s = k_p * \bar{P}_s * p_0$$

$$I_s = k_i * \bar{I}_s * p_0^{2/3} * E_{ex,a}^{1/3} / a_0$$

Where:

a_0 = speed of sound in ambient air

$k_{(p,i)}$ scaling factor for cylindrical vessels, Lees', 2012, Table 17.54

Scaled dist. \bar{R}	$\bar{R} < 0.3$	$\bar{R} < 3.5$	$\bar{R} > 3.5$	Scaled dist. \bar{R}	$\bar{R} < 0.3$	$\bar{R} < 1.6$	$\bar{R} > 1.6$
k_p	4	1.6	1.4	k_i	4	1.6	1.4

Missile impacts (rocketing fragments): For missiles or rocketing fragments from a bursting vessel, the same approach as discussed for BLEVEs was used.

Thermal Hazards: For thermal hazards from a bursting vessel, the same approach as discussed for BLEVEs was used.

3.4.2.2 PVB Results

Hydrotreater Reactor (R-130)

For the hydrotreater reactor, R-130, it is assumed the pressure in the vessel is at the PRV set point 3000 psig. This is a reasonably conservative assumption as this is a significantly higher pressure than the typical operating pressure (~2000 psig) and there were no events identified which would cause rapid significant pressure increases resulting in a common cause failure of the pressure relief valve. It was conservatively assumed that the reactor contained only hydrogen and catalyst.

Input Assumptions:

Pressure State 1	3000 psig	20.6 MPa
Pressure State 0	14 psi	0.1 MPa
Volume of Reactor	26 liters	0.026 m ³
Free volume (assume 50% filled with catalyst)	13 liters	0.013 m ³
Volume of hydrogen	13 liters	0.013 m ³
Specific Volume	0.13651 m ³ /kg	
\dot{Y}_1	1.41	
Speed of sound in air, a_0	340 m/s	

Using the input assumptions and thermodynamic data provided:

The positive side-on overpressure (P_s) and positive side-on impulse (I_s) at the following receptor locations are:

Hydrotreater/Distillation Column Hazard Analysis Report

Actual Receptor Distance, meters	3	7	10	30	35
scaled distance \bar{R} , m	1.7	4.1	5.8	17	23
P_s , kPa	46	11	7	1.7	<1.4
I_s , Pa-s	0.08	0.02	0.015	0.005	<0.005

The maximum likely range of fragments calculated using the CCPS, 2010 method was determined to be ~ 41 meters. As noted in Section 3.4.1.1 this distance is judged to be a very conservative estimate.

The maximum fireball size was determined to be 2.6 meters with a duration of 0.2 seconds.

Distillation Feed Tank (V-180)

For the Distillation Feed Tank, V-180, it is assumed the pressure in the vessel is at the PRV set point of 70 psig. This is a reasonably conservative assumption as this is a significantly higher pressure than the typical operating pressure (atmospheric to 15 psig) and there were no events identified which would cause rapid significant pressure increases resulting in a common cause failure of the pressure relief valve. It was conservatively assumed that the vessel contained only nitrogen.

Input Assumptions:

Pressure State 1	70 psig	0.48 MPa
Pressure State 0	14 psig	0.1 MPa
Volume of vessel	140 liters	0.140 m ³
Specific Volume (20°C)	0.18107 m ³ /kg	
\dot{Y}_1	1.4	
Speed of sound in air, a_0	340 m/s	

Using the input assumptions and thermodynamic data provided:

The positive side-on overpressure (P_s) and positive side-on impulse (I_s) at the following receptor locations are:

Actual Receptor Distance, meters	3	7	10	30	35
scaled distance \bar{R} , m	2.95	6.88	9.83	29.48	34.40
P_s , kPa	20.3	5.5	3.7	<1.42	<1.42
I_s , Pa-s	0.02	0.008	0.005	<0.0004	<0.0004

The maximum likely range of fragments was determined to be ~83 meters. As noted in Section 3.4.1.1 this distance is judged to be a very conservative estimate.

3.4.3 Deflagration Scenarios

The hazard analysis identified scenarios as resulting in flammable gas/vapors being released to the enclosure from the hydrogen system and process vessels and piping.

Of these events, consequences from a rupture of the hydrogen supply piping within the hydrotreater enclosure was analyzed as a bounding case. The consequences for a large release of hydrogen gas

(assumed not to be a PVB or BLEVE) from the hydrotreater reactor was also analyzed to provide a bounding case for the release of vapors from process vessels and piping.

3.4.3.1 Deflagration Consequence Methodology

Potential ignition of flammable vapors within the enclosure were modeled using the TNT Equivalency Method as evaluated in the Physical Sciences Facility Fire Hazards Analysis Report, following the approach presented in *Analytical Approach for Gas Explosions for DOE Nuclear and Non-Nuclear Facilities* (Louie and Restrepo).

The TNT approach provides a proportional relationship between the total quantity of flammable material released (whether or not it is within the flammability limits or at the stoichiometric concentration) to an equivalent weight of TNT. This weight of TNT, W_{TNT} , is then used to determine a scaled distance, \bar{R} , from which predicted overpressure can be determined using the peak side-on overpressure curve appropriate for the surface TNT equivalence method:

$$W_{TNT} = \eta_g(W_g * H_g / H_{TNT})$$

Where:

η_g = TNT equivalence factor or yield factor (dimensionless)

W_g = weight of the combustible gas (kg)

H_g = combustion energy of the combustible gas (J/kg)

H_{TNT} = TNT blast energy (J/kg)

The scaled distance, \bar{R} is then calculated by:

$$\bar{R} = R/W_{TNT}^{1/3}$$

Where:

R = distance to receptor

For TNT equivalency methods, the side-on pressure can then be taken directly from the appropriate overpressure curve.

3.4.3.2 Deflagration Results

Hydrogen Supply Line Rupture

For the hydrogen supply line rupture, it was assumed the quantity of hydrogen released equated to the volume of the hydrotreater enclosure.

Input Assumptions and thermodynamic data:

Volume of hydrogen in the enclosure	285 m ³
Density of Hydrogen at 20C	0.083191 kg/ m ³
Weight of Hydrogen	23.7 kg
TNT equivalence factor η_g	0.2 from (Louie and Restrepo)
Combustion energy, H_g	4.6E+06 J/kg
TNT blast energy, H_{TNT}	1.42E+06 J/kg

Hydrotreater/Distillation Column Hazard Analysis Report

From the TNT equivalence method:

$$\begin{aligned}W_{\text{TNT}} &= \eta_g \cdot (W_g \cdot H_g / H_{\text{TNT}}) \\ &= 1.5\text{E-}01 \text{ kg}\end{aligned}$$

The positive side-on overpressure (P_s) at the following receptor locations was then determined based on the scaled distance (Louie and Restrepo):

Actual Receptor Distance, meters	3	7	10	30	35
scaled distance \bar{R} , m	5.6	13	19	56	65
P_s , bar	0.40	0.15	0.07	0.02	0.014
P_s , kPa	40	15	7	2	1.4

Hydrotreater Reactor (R-130)

For the hydrotreater reactor, R-130, it is assumed the mass in the vessel was based on the vessel free volume and the pressure at the pressure relief valve setpoint of 3000 psig with a temperature of 368° C as was evaluated in the BLEVE case. This is a conservative assumption with respect to normal operating pressure (~2000 psig). To account for hydrogen within the supply line, the weight of hydrogen released was doubled.

Input Assumptions and thermodynamic data:

Volume of hydrogen in Vessel	0.013 m ³
Specific volume of Hydrogen v_1	0.13651 m ³ /kg
Weight of Hydrogen (V/v ₁)	0.095231 kg
TNT equivalence factor η_g	0.2 from (Louie and Restrepo)
Combustion energy, H _g	4.6E+06 J/kg
TNT blast energy, H _{TNT}	1.42E+06 J/kg

From the TNT equivalence method:

$$W_{TNT} = \eta_g(W_g * H_g / H_{TNT})$$

$$= 1.23E-03 \text{ kg}$$

The positive side-on overpressure (P_s) at the following receptor locations was then determined based on the scaled distance (Louie and Restrepo):

Actual Receptor Distance, meters	3	7	10
scaled distance \bar{R} , m	28	65	93
P _s , bar	.025	0.01	< 0.01
P _s , kPa	2.5	1	< 1

3.4.4 Calculation Summary

Comparing the calculated overpressures from the above conservative analyses to the damage estimates of Table 3-5 shows that a failure of the hydrotreater/distillation column enclosure would result in the event of a BLEVE, PVB, or explosion of hydrogen within the enclosure. However, only for a BLEVE of the reactor (R-130) could significant overpressures (greater than 21 kPa) be developed which would challenge the PDL-West building structure itself. There were no cases in which overpressures sufficient to result in greater than minor damage (7 kPa) reached at the nearest analyzed location (PDL-East).

For missile generation, the CCPS, 2010 methodology conservatively estimates missile ranges out to ~145 meters for the hydrotreater. As noted, this ignores several physical properties associated with the event. DOE-TIC 11268, Figure 6.17 identifies that the 90th percentile fragment range as being less than ~24 meters (80 feet) for an energy level of 2.2E+07 joules (1.6E+07 foot-pounds) which is more than 10 times greater than calculated energy available for the R-130 BLEVE limiting case.

For all events analyzed, the robust design of the hydrotreater/distillation column systems make the overpressure and missile generation events very low likelihood scenarios.

Table 3-5. Damage Estimates for Common Structures Based on Overpressure

Pressure		Damage
kPa	psig	
2.07	0.3	“Safe distance” (probability 0.95 of no serious damage below this value); projectile limit; some damage to house ceilings; 10% window glass broken.
3.4-6.9	0.5 - 1	Large and small windows usually shattered; occasional damage to window frames.
13.8 - 20.7	2 - 3	Concrete or cinder block walls, not reinforced, shattered
20.7 ⁽¹⁾ - 27.7	3 - 4	Frameless, self-framing steel panel building demolished; rupture of oil storage tanks
34.5	5	Wooden utility poles snapped; tall hydraulic press (40,000 lb) in building slightly damaged
34.5 - 48.2	5 - 7	Nearly complete destruction of houses
68.9	10	Probable total destruction of buildings; heavy machine tools (7000 lb) moved and badly damaged; very heavy machine tools (12000 lb) survive

AICHe/CCPS, Guidelines for Chemical Process Quantitative Risk Analysis, New York: AICHe, 2000

(1) Assumed threshold for serious damage from Lees’ 2012.

“Table 17.28- Typical Values of Failure Pressures in Building Structures

	Failure Pressure (kN/m ²) [kPa]
Windows (normal)	3-4.6
Windows (strained)	1, or even 0.2
Chipboard (19mm)	7
Brick wall (114mm)	Survived at 23, destroyed at 35
Brick wall (228mm)	Survived at 70, destroyed at 105

It has been suggested by Buckland (1980) that the explosion pressure should not exceed 21 kN/m² if the building is to avoid serious damage.”

4.0 HAZARD CONTROLS

4.1 Critical Controls

This section describes the attributes of the critical controls (Table 4-1) specifically identified in the hazard analysis as mitigating against the higher consequence hazards associated with the hydrotreater/distillation column process as addressed in Section 3.4.

Table 4-1 Critical Hazard Controls

Hazard Control	Event Type	Hazard ID
Vessel Design per ASME Section VIII and ASME B341.3	BLEVE	H.4-6; H.4-7; H.4-9; H.7-1; H.2-10; H.4-11; H.4-18; H.1-19; H.2-20; D.2-7; D.4-3; D.4-4; D.4-5; U-9
	PVB	H.1-16; H.2-7; H.4-17; H.4-18; H.4-22; H.4-29; H.4-31; H.7-4; D.1-6; D.1-7; D.4-13
	FA	H.4-8; H.4-15; H.4-20; H.7-8; D.1-10; D.2-3; D.4-11; D.4-9;
Relief Valve Sizing and Flowpath Design	BLEVE	H.1-19; H.2-10; H.4-6; H.4-7; H.7-1; D.2-7; D.4-3;
	PVB	H.1-11; H.1-15; H.1-16; H.1-21; H.2-7; H.2-10; H.4-1; H.4-17; H.4-22; H.4-29; H.4-31; H.7-4; D.1-6; D.1-7; D.1-14; D.4-13
	FA	D.1-10; U-8
Piping Design per B31.3 and NFPA 55	FA	H.5-2; H.6-1; H.7-7; D.1-10
Hydrogen Piping and Excess Flow Valve Design per IFC	BLEVE	H.4-10; U-10
	FA	U-25
Reactor and Distillation Column High-High Temperature Interlock	BLEVE	H.2-20; H.3-6; D.2-17
Enclosure Design as Class 1 Division 2 environment	BLEVE	D.4-5
	FA	H.1-8; H.1-12; H.1-14; H.4-23; H.4-26; H.4-28; H.4-8; H.5-2; H.7-5; H.7-9; D.5-7
Enclosure Ventilation System Design	FA	H.1-8; H.1-12; H.1-14; H.1-17; H.2-1; H.2-2; H.2-3; H.4-23; H.4-28; H.4-8; H.7-5; H.7-9; D.1-8; D.2-1; D.2-2; D.2-3; D.4-7; D.4-9; D.5-7
Hydrogen Monitor	FA	H.1-8; H.1-12; H.1-14; H.1-17; H.2-1; H.2-2; H.2-3; H.4-8; H.4-26; D.1-8
Flammable Vapor Monitor	FA	H.1-8; H.1-12; H.1-14; H.2-1; H.2-3; H.4-8; D.2-3
Pressure Test Procedure	BLEVE	H.4-9; H.4-11; D.4-4
	PVB	H.4-18; D.4-13
	FA	H.1-8; H.1-12; H.1-17; H.1-18; H.4-8; H.4-15; H.4-20; H.4-28; H.7-8; D.1-8; D.1-13; D.2-1; D.2-2; D.2-3; D.4-9; D.4-11

4.1.1 Vessel and Piping Design

The robust design of vessels, components, and piping (tubing) ensures the pressure integrity of the process boundary for normal operations and upset conditions.

Vessel Design: The R-130 reactor vessel and V-184 distillation column are designed, fabricated, welded, inspected, and tested in accordance with ASME B31.3 and augmented consistent with the ASME *Boiler and Pressure Vessel Code* (ASME B&PV Code), Section VIII.

All vessels with a diameter greater than 6 inches and a design pressure greater than 15 psi are designed, fabricated, welded, inspected, and tested in accordance with the ASME B&PV Code, Section VIII.

Relief Valve Sizing: All relief valves and pressure relief flowpaths are sized for the worst-case flow rates, including any backflow from high to low pressure areas, per API 521. This includes the addition of vessel insulation on vessels where required to support flow rates (CTI 12-631).

PSE-2005 upstream of Check Valve CK-2012 protects against backflow through P-121A/B from the reactor.

Piping Design: All pressure piping is designed, installed (approved fittings, quick disconnects, appropriate support distances, etc.), and leak tested in accordance with ASME B31.3 and NFPA 55. The new valve, HV-2018, upstream of HV-2009 provides positive pressure boundary from the reactor R-130 when draining bio-oil/acetone from the P-121A/B pumps during the shutdown flushing modes.

Hydrogen Utility (supplied) Design: All hydrogen piping is installed in accordance with the International Fire Code (IFC), which includes an appropriately sized excess flow control valve. Maximum hydrogen pressure – limited by compressor (3000 psi) and protected by pressure relief valve.

Table 4-2 Vessel and Piping Design Summary

Component	Vessel Design Pressure ⁽¹⁾⁽²⁾ psig	Vessel Design Temperature ⁽³⁾ °C	Pressure Relief Setpoint Psig ⁽¹⁾	Insulation ⁽¹⁾
V-120	135	148	70	Yes
V-125	155	148	100	No
R-130	3000	426 (heads) 537 (shell)	3000	No
V-140	3000	454	3000	No
LG-142	3000			
LG-147	100	148	Atm ⁽⁴⁾	NR
V-160A/B	155	148	70	Yes
V-161A/B	155	148	70	Yes
V-162	180 ⁽⁴⁾	148	Atm ⁽⁵⁾	NR
V-163	180 ⁽⁴⁾	148	Atm ⁽⁵⁾	NR
V-180	135	148	70	Yes
V-184	100 ⁽⁵⁾	454	70	Yes
V-191 & V-193	135	148	70	Yes
V-192 & V-194	135	148	70	Yes
1/4"-T035-316	5100 ⁽⁶⁾		-	
3/8"-T049-316	4800 ⁽⁶⁾			
1/2"-T049-316	3700 ⁽⁶⁾		-	

(1) From CTI 12-631, unless otherwise noted.

(2) Maximum Allowable Working Pressure

(3) From Project Drawings: 782-4-100 through 782-4-190

(4) Note: additional pressure relief provided by PSV-4016 upstream DWG-782-4-140

(5) From Project Drawing: 782-4-160

(6) Swagelok Tubing Data (R10) accessed at

<http://www.swagelok.com/downloads/WebCatalogs/EN/MS-01-107.PDF>

4.1.2 Reactor and Distillation Column Temperature Critical Controls

The high-high temperature interlock (500° C) for each of the eight zones of the R-130 vessel removes power to its respective heater. This eliminates the source of external heat to that zone and provides adequate margin below the vessel (shell) design temperature of 537°C (Table 4-2).

The high-high temperature interlocks (425° C) remove power to the V-184 distillation column reboiler and bottom section heaters to provide adequate margin below the vessel design temperature of 454°C (Table 4-2).

The ten (10) critical temperature controls (eight associated with R-130 and two associated with V-184) use safety circuitry, independent of the control circuitry, to fulfill their shutdown functions {within the HTDC documentation (e.g., P&IDs, Cause and Effect Diagram), TAHH-xxxxA denotes a control circuit; TAHH-xxxxB denotes a safety circuit}. These safety and control circuits utilize independent

thermocouples and PLCs to ensure safety system response is not compromised by failure of a control system. These temperature critical controls (designated as “P3” in the Supplemental HARs) receive their own credit in the quantitative risk assessment (see Appendices D and E).

4.1.3 Enclosure Design and Ventilation

The enclosure design and ventilation system reduce the potential for deflagrations resulting from the release of flammable vapors from the hydrotreater/distillation process pressure boundary.

Enclosure Design Class 1 Division 2: All exposed electrical in the enclosure is Class 1 Division 2 (explosion proof) or contained in air purged cabinet (Z-Purge) to prevent the introduction of flammable vapors/gases. This minimizes the potential for an ignition source.

Enclosure Ventilation System: The enclosure is normally ventilated at 6 air changes per hour, which is consistent with standard laboratory flow rates at PNNL. The ventilation is well mixed due to the inlet being toward the bottom of the enclosure and the outlet near the top. This minimum ventilation rate meets the requirements of NFPA 55 and the IFC and reduces the concentration of flammable vapors to below lower flammability limits. Loss of enclosure ventilation shuts off the hydrogen supply and initiates Shutdown Scenario A (heaters, pumps, and hydrogen shutoff) from the hydrotreater/distillation column process controller (see Appendix B, “Key Design Information Reviewed,” – Interlock Matrices).

4.1.4 Hydrogen Monitors

There are three hydrogen monitors; one is installed high on the reactor skid and two are installed near the ceiling in the enclosure. The ceiling detectors alarm at 10% of the LEL resulting in a fire alarm control panel (FACP) supervisory alarm, and alarm at 25% of the LEL which results in an FACP supervisory alarm, isolates the hydrogen supply, and initiates Shutdown Scenario A. The reactor skid detector is interlocked to isolate the hydrogen supply at 25% of the LEL and also initiates Shutdown Scenario A.

4.1.5 Flammable Vapor Monitors

Flammable vapor monitors (one H₂S and two combustible gas detectors) are installed on the reactor and distillation skids. The H₂S detector alarms at 5 ppm resulting in an FACP supervisory alarm, and alarms at 40 ppm which results in an FACP supervisory alarm and initiates Shutdown Scenario B. The two combustible gas detectors alarm at 10% of the LEL and at 25% of the LEL initiate Shutdown Scenario A.

4.1.6 Safe Operating Procedures (SOPs)

The system will be operated via approved procedures. Per the SOPs:

- Trained operators: Each shift will have two operators (experienced with similar equipment) trained per the approved operating procedures. The system will not operate unattended.
- Pressure testing: Prior to the initiation of each run, the system is leak checked with nitrogen to ensure any re-assembly or cycling does not create a leak.
- System shutdown: This will ensure the system has been placed in a non-Class I/Div 2 status.

4.2 Other Controls (Non-Critical)

This section describes the attributes of the other non-critical controls (Table 4-3) identified as providing significant benefit in further reducing the event frequency for higher consequence hazards associated with the hydrotreater/distillation column process as addressed in Section 3.4.

Table 4-3. Other Non-Critical Controls.

Hazard Control	Event Type	Hazard ID
Flame Detectors	BLEVE	D.4-5; H.4-10; H.4-11; U-9; U-10; U-25
Fire Suppression System	BLEVE	D.4-5; H.4-10; H.4-11; U-9; U-10; U-25
Temperature and Pressure Controls/Alarms Prompting Operator Response	BLEVE	D.4-3; H.1-1; H.1-2; H.1-5; H.1-6; H.1-19; H.2-10; H.2-15; H.2-20; H.3-6; H.4-2; H.4-6; H.4-7; H.7-1; H.7-7
	PVB	H.4-17; H.4-27; U-1; U-7
Check Valves	PVB	H.4-1
Facility Configuration	FA	U-24; U-30

4.2.1 Flame Detectors

There are two flame detectors located in the enclosure; activation of either results in the following:

- FACP alarm,
- Isolation of the hydrogen supply,
- Shutdown of the enclosure exhaust ventilation,
- Activation of the water mist system,
- Deactivation of power to the enclosure (after 5 second delay),
- Opening the reactor purge (vent) valve (after 60 second delay), and
- Initiation of Shutdown Scenario C.

4.2.2 Fire Suppression System

There are both sidewall wet-pipe sprinklers and a mist system located in the enclosure. The mist system is activated when the flame detector is activated.

4.2.3 Temperature and Pressure Controls/Alarms Prompting Operator Response

There are numerous high temperature and pressure alarm and control set points that provide the operator an opportunity to identify and correct an off-normal occurrence and to prevent/mitigate potential problems; many of these instruments will automatically control the system to limit potential problems in the unlikely event that prompt operator action is not taken. The high-high pressure interlocks (2700 psig) for the R-130 reactor vessel and the V-140 HP separator stop the flow of hydrogen and nitrogen and feed of bio-oil into the reactor. This eliminates the sources of pressure input and limits any exothermic reaction once the hydrogen is consumed thus protecting the pressure boundary of the reactor. These temperature and pressure alarms and controls would further reduce the frequency of a hazardous event.

4.2.4 Check Valves

Check valves are in place throughout the hydrotreater system to protect against backflow.

4.2.5 Facility Configuration

The configuration of the facility housing the hydrotreater and distillation column skids will aid in ventilation of the system. PDL-West facility is equipped with a passive ventilation system. In the event of loss of enclosure ventilation, the large size of the PDL-West facility and passive ventilation system would further reduce the frequency of hazardous event scenarios.

4.3 Safety Management Programs

In addition to the critical controls described above, institutional Safety Management Programs (SMPs) are integrated into the PNNL requirements management infrastructure and delivered to staff members through the “How Do I...?” (HDI) work flows and work controls. HDI deploys the Laboratory-level requirements and procedures to PNNL staff. SMPs that are directly related to the Hydrotreater/Distillation project are identified below.

4.3.1 Worker Safety and Health

The Worker Safety and Health programs include the Chemical Hygiene Program, Hazard Communication Program, Hazard Assessment Program, Chemical Management System, and Integrated Safety Management System. Specific standards and procedures related to the operations of the hydrotreater/distillation project (*Working with Chemicals, Compressed Gases, Pressure and Vacuum Systems*, etc.) are provided in HDI, and implemented through Integrated Operations System (IOPS), and other implementing procedures.

IOPS helps managers and staff to identify and mitigate operational risks of experimental work in PNNL-operated workspaces. The processes involve identifying and managing risks and hazards associated with activities performed in each IOPS workspace, continually assessing ongoing or changing work risks, and controlling access so that only trained and authorized people are working in the workspace.

The IOPS tool delivers automated processes to support implementation of the IOPS program workflows that IOPS Administrators, Cognizant Space Managers, workers, and others use to achieve a safe workplace and efficient operations. The processes are designed to support the following:

- Configuration of IOPS buildings
- Establishing and maintaining IOPS workspaces
- Providing tailored controls
- Authorizing activities
- Performing work and monitoring work for changes.

4.3.2 Fire Protection Program

PNNL has established and maintains a Fire Protection Program that implements the applicable requirements of DOE O 420.1B, *Facility Safety*. This SMP applies to DOE facilities operated by PNNL

including the PDL-West facility. The program affords a level of protection by providing the following services:

- Management of combustible materials and flammable liquids and gases
- A permit process for hot work
- Proper workspace housekeeping; facility and equipment modification design reviews and approvals; and periodic facility inspections and assessments
- Engineered features that minimize the potential for fire and the propagation of fires, including:
 - Facility fire walls and barriers
 - Fire detection and alarm systems
 - Automatic suppression systems including the mist suppression system within the enclosure
 - Portable fire extinguishers
- Emergency services (e.g., fire, medical) for PDL-West are provided by the City of Richland
- Implementation of applicable NFPA 101 requirements
- Inspection and maintenance of fire alarm, detection, and suppression systems
- Outages and impairments impacting fire protection systems are controlled and tracked through formal, documented systems to minimize the fire risks while systems are out of service.

The fire protection program is intended to ensure an available means of egress for personnel during a fire, minimize damage to property, and minimize the potential for DOE programs to suffer unacceptable delays or effects as a result of fire.

4.3.3 Training and Qualification

The training and qualification function establishes Laboratory-wide policies and standards and maintains a system for training delivery and documentation. Training and qualification requirements are implemented to ensure that personnel responsible for facility operations, process operations, vehicle operation, maintenance, and technical support are trained and qualified, as applicable, to accomplish their safety-related responsibilities. Line management makes sure that personnel are trained to work safely, effectively, and in accordance with DOE requirements and PNNL policies. PNNL training requirements and standards provide a uniform method for identifying, performing, and documenting the required indoctrination and training of PNNL staff.

4.3.4 Maintenance and Testing Program

This section discusses initial (startup) testing and maintenance programs for the PDL-West facility, including the Hydrotreater/Distillation Column project.

4.3.4.1 Initial Testing

PNNL facility design procedures require testing to verify proper operation of equipment and systems prior to their installation or return to service following facility modifications. Documents that implement installation and post-modification testing are developed based on operational and equipment functional requirements. Documents implementing installation, modifications, and associated tests

(plans, permits, procedures, etc.) are prepared and peer reviewed by technical disciplines and line-management, as appropriate.

4.3.4.2 Maintenance

The PNNL facility operations function establishes a maintenance program that implements applicable maintenance requirements, including equipment vendor specifications and recommendations; and applicable national, state, local, and DOE codes and standards. PNNL facility procedures require testing to verify proper operation of specific safety equipment and systems (e.g., ventilation, cranes/hoists, fire alarm/detection/suppression) prior to returning them to service following preventive/corrective maintenance activities. Documents based on operational requirements; equipment functions; manufacture recommendations; operational restrictions; and/or applicable national, state, local, and DOE codes and standards implementing preventive/corrective maintenance actions and post-maintenance testing are prepared and peer reviewed by technical disciplines and line management, as appropriate.

5.0 CONCLUSION

Two What-If hazard analyses were performed by PNNL to support the Hydrotreater/Distillation Process operation. These hazard analyses postulated off-normal or upset conditions including the release of the hazardous material or energy. For all events involving the release of material or energy, the hazard analyses identified the hazard controls which would prevent or mitigate the release. For high-energy events which could breach the hydrotreater and distillation column enclosure, the analyses were supplemented by calculations documenting the potential magnitude of the bounding case unmitigated consequences. The critical controls which are relied on to prevent the occurrence of these events are identified (see Table 4-1). Additional hazard controls identified for these events provide defense-in-depth by reducing either the potential for or consequences of the postulated events (See Table 3-4, *What-If Hazards Analysis Results*). In addition, two supplemental hazard analyses were conducted and quantitative risk assessments performed for the Distillation Column and Hydrotreater units (see Appendices D and E).

With the identified hazard controls applied and operations performed within the envelope of the PNNL Safety Management Programs, the risks posed from operation of the hydrotreater and distillation columns are adequately mitigated, and these systems can be operated safely, consistent with PNNL control of other laboratory operations.

6.0 REFERENCES

AIChE, 1992, *Guidelines for Hazard Evaluation Procedures – With Worked Examples, 2nd Edition*, American Institute of Chemical Engineers, New York.

Casal, Joaquim and Salla, Josep, *Using Superheating energy for a quick estimation of overpressures in BLEVEs and similar explosions*, Journal of Hazardous Materials, A137, 2006 pp. 1321-1327

CCPS, 2000, Center for Chemical Process Safety, *Guidelines for Chemical Process Quantitative Risk Analysis*, American Institute of Chemical Engineers, New York.

CCPS, 2010, Center for Chemical Process Safety, *Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards*, American Institute of Chemical Engineers, New York

DOE-HDBK-1100-2004, *Chemical Process Hazards Analysis*, U.S. DOE

DOE/TIC-11268, *A Manual for the Prediction of Blast and Fragment Loadings on Structures*, Change 1, 15 August 1981, U.S. DOE Albuquerque Operations Office

CTI 12-631, Rev 2, *Pressure Relief Vent Header and KO Vessel Sizing for PNNL Hydrotreater Facility*, January 2013, Centaurus Technology Inc. Simpsonsville KY 40067

Lees' Loss Prevention in the Process Industries. (Fourth Edition) Elsevier 2012,
DOI: <http://dx.doi.org/10.1016/B978-0-12-397189-0.00017-3>

Louie, David L.Y. and Restrepo, Louis F., *Analytical Approach for Gas Explosions for DOE Nuclear and Non-Nuclear Facilities*.

Appendix A: Attendees

Hydrotreater/Distillation Column Hazard Analysis Report

Attendees

Name		Affiliation	Role
Brawn	David	PNNL	Building Engineer
Brooks	Shirley	PNNL	Hazards Analysis
Carlson	Jeff	PNSO	
Clark	Pat	PNNL	Facilities and Operations
Coles	Garril	PNNL	Hazards Analysis
Cuello	Rob	PNNL	Operations
Dotson	Paul	PNNL	Facility PM
Edwards	Dan	PNNL	ES&H
Elliot	Doug	PNNL	CBPDG
Elliot	Mike	PNNL	
Evans	Brad	PNNL	Nuclear Safety and Facility Authorization
Hart	Todd	PNNL	Hydrotreater Project Operator
Hastings	David	PNSO	
Lowry	Pete	PNNL	Hazards Analysis
McGaughy	Renee	PNNL	WS&H
McMullin	Ken	PNNL	Building Manager
Minister	Andrew	PNNL	Fire Protection
Neuenschwander	Gary	PNNL	Hydrotreater Project Operator
Olarte	Mariefel V	PNNL	Hydrotreater Project Operator
Orth	Rick	PNNL	Line Manager
Paulsen	Sam	PNNL	Pressure Safety
Rohrig	David	PNNL	ES&H - Pressure Safety
Rotness	L.J.	PNNL	Hydrotreater Project Operator
Sauve	Gerald	PNSO	
Short	Steve	PNNL	Hazards Analysis
Stephens	Vicki	PNNL	Operations
Wagner	Dan	PNNL	Building Engineer
Wyatt	David	PNNL	WS&H – Fire Protection
Xuan	Vic	PNSO	
Zacher	Alan	PNNL	Hydrotreater Project-PM

Note: Personnel who attended 1 or more meetings.

Appendix B: Key Design Information Reviewed

Design Information Reviewed

HYDROTREATER/DISTILLATION SYSTEM Calculations

CTI 12-631, Rev 2, Pressure Relief Vent Header and KO Vessel Sizing for PNNL Hydrotreater Facility

HYDROTREATER/DISTILLATION SYSTEM Drawings³

PNNL HYDROTREATER – DISTILLATION PROCESS SKETCH	 hydro_process.pdf
782-4-100 PNNL BIO-OIL HYDROTREATER BIO-OIL BATCH FILTRATION	 Zeton Redlines.pdf
782-4-110 PNNL BIO-OIL HYDROTREATER GAS FEED	
782-4-120 PNNL BIO-OIL HYDROTREATER LIQUID FEED	
782-4-130 PNNL BIO-OIL HYDROTREATER REACTOR	
782-4-140 PNNL BIO-OIL HYDROTREATER GAS/OIL/WATER SEPARATION	
782-4-150 PNNL BIO-OIL HYDROTREATER PRODUCT GAS MEASUREMENT	
782-4-160 PNNL BIO-OIL HYDROTREATER LIQUID PRODUCT COLLECTION	
782-4-170 PNNL BIO-OIL HYDROTREATER WATER RECIRCULATION	
782-4-180 PNNL BIO-OIL DISTILLATION COLUMN	
782-4-190 PNNL BIO-OIL DISTILLATION COLUMN CUT COLLECTION	

ENCLOSURE/FACILITY Drawings³

A2.0 PNNL HYDROTREATER ENCLOSURE DESIGN PDLW FLOOR PLAN	 A2.0_PLDW_FLOOR _PLAN[2].pdf
A3.1 PNNL HYDROTREATER ENCLOSURE DESIGN Exterior Elevations PLAN	 A3.1_Hydrotreater - Enclosure.pdf
M2.0 PNNL HYDROTREATER ENCLOSURE - Enclosure P&ID	 M2.0 Enclosure P&ID.pdf
M2.1 PNNL HYDROTREATER ENCLOSURE - Enclosure P&ID	 M2.1 Enclosure P&ID.pdf
M2.3 PNNL HYDROTREATER ENCLOSURE - Enclosure P&ID	 M2.3 Enclosure P&ID.pdf

³ These drawings are historical documents and subject to change. See the Hydrotreater/Distillation Column SharePoint site for current drawings.

Hydrotreater/Distillation Column Hazard Analysis Report

INTERLOCK MATRICES⁴

Cause/Effect Matrix	 Cause and Effect Rev 2_24Jan_2013_F
FACP Hydrotreater Logic	 3030 Logic-Hydrotreater-R2

⁴ These documents are historical and subject to change. See the Hydrotreater/Distillation Column SharePoint Site for current versions.

**Appendix C: November 2012 Hydrotreater / Distillation Column Project
Hazard and Risk Analysis Report**

November 2012 Hydrotreater / Distillation Column Project Hazard and Risk Analysis Report



Hydrotreater HA Nov
2012.pdf

Appendix D: Supplemental Hazard Analysis and Risk Assessment – Distillation Column

Supplemental Hazard Analysis and Risk Assessment – Distillation Column



Supplemental HAR -
Distillation Column

Appendix E: Supplemental Hazard Analysis and Risk Assessment - Hydrotreater

Supplemental Hazard Analysis and Risk Assessment - Hydrotreater



Supplemental HAR -
Hydrotreater



Pacific Northwest
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)
www.pnnl.gov



U.S. DEPARTMENT OF
ENERGY