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Hydrothermal Liquefaction Treatment Hazard Analysis Report

Revision 3

September 2016

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Executive Summary

Hazard analyses were performed to evaluate the modular hydrothermal liquefaction treatment system. The hazard assessment process was performed in 2 stages. An initial assessment utilizing Hazard Identification and Preliminary Hazards Analysis (PHA) techniques identified areas with significant or unique hazards (process safety-related hazards) that fall outside of the normal operating envelope of PNNL and warranted additional analysis. The subsequent assessment was based on a qualitative What-If analysis. The analysis was augmented, as necessary, by additional quantitative analysis for scenarios involving a release of hazardous material or energy with the potential for affecting the public.

The following selected hazardous scenarios received increased attention:

- Scenarios involving a release of hazardous material or energy, controls were identified in the What-If analysis table that prevent the occurrence or mitigate the effects of the release.
- Scenarios with significant consequences that could impact personnel outside the immediate operations area, quantitative analyses were performed to determine the potential magnitude of the scenario.

The set of “critical controls” were identified for these scenarios (see Section 4) which prevent the occurrence or mitigate the effects of the release of events with significant consequences.

Additional guidance to the design organization (Appendix D) was provided in July 2015 to provide considerations to minimize the likelihood of subsequent BLEVE events (domino failures) during the detailed design phase. Analyses show that domino failures are << 1E-06; based on the failure rates of the identified vessels and the likelihood of impacting and subsequently failing a target vessel, and thus pose minimal concern.

RECORD OF REVISION		
Revision	**Description of Changes**	**Comments**
0	Initial issue	
1	Incorporated Appendix D Guidance to Support the Evaluation of Secondary Impacts from High Consequence Low Frequency Events in HTL. Editorial Corrections	Significantly affected pages denoted Rev 1.
2	Revised for Design Changes Review.	
3	Revised per July Hazard Analysis in support of Operations.	

Table of Contents

Acronyms and Abbreviations

AIChE	American Institute of Chemical Engineers
BLEVE	boiling liquid expanding vapor explosion
C	Celsius
CCPS	Center for Chemical Process Safety
f	frequency
FH	Flammability Hazard
FS	flashing spray release
HH	Health Hazard
I_s	positive side-on impulse
IR	Instability / Reactivity
kPa	kilo-Pascal
L/h	liters per hour
lbs	pounds
m	meters
m/s	meters per second
MAWP	Maximum Allowable Working Pressure
MAWT	Maximum Allowable Working Temperature
MHTLS	modular hydrothermal liquefaction system
MPa	Mega-Pascal
P_s	positive side-on overpressure
PAC	Protective Action Criteria
PHA	Preliminary Hazards Analysis
PPE	personnel protective equipment
psig	pound per square inch gauge
PVB	Pressure Vessel Burst

1.0 INTRODUCTION

The modular hydrothermal liquefaction system (MHTLS) is an engineering-scale process system being designed to support scale-up of process parameters for converting various wet biomass sources to a biocrude. Candidate biomass feedstocks for evaluation with the MHTLS include algae, lignocellulosic materials (wood, wheat, straw, stover, agriculture residuals), and wastewater treatment sludges.

The system is being designed utilizing a modular approach and individual process skids to allow for re-locatable operation at third-party sites.

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. As part of the conceptual design process, the hazards associated with the MHTLS processes have been reviewed and controls and design assumptions critical to supporting safe operations identified. The purpose of this report is to document the hazards and key controls and assumptions associated with the MHTLS and the potential interactions of these hazards with respect to supporting systems and the facilities.

1.2 Scope

The Hazard Evaluation process for the significant review cycles (Revision 0 and Revision 3) was performed in 2 stages. An initial assessment utilizing Hazard Identification and Preliminary Hazards Analysis (PHA) techniques identified areas with significant or unique hazards (process safety-related hazards) that fall outside of the normal operating envelope of PNNL and warrant additional analysis.

For the hazard identification phase the MHTLS was parsed into several evaluation areas based upon the processing area and key unit operations/components. Within each evaluation area, the inventory and primary process parameters (pressure, temperature) were evaluated to determine if unique or significant hazards were posed by the operation. If a processing area was determined to have a unique or significant hazard, a subsequent hazard analysis was performed.

The hazard analysis utilized a qualitative What-If analysis for those portions on the MHTLS which were identified as having unique or significant hazards.

The What-If hazard analysis used for the MHTLS 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 What-If analysis focused on the 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 consistent with the design information available at this time.

The hazard evaluation postulated scenarios involving random 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 the MHTLS immediate operations area.

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

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

Section 4, *Hazard Control*s, describes the "critical controls" for the high consequence hazards. The critical controls are those required to prevent or mitigate significant consequences associated with the MHTLS process hazards.

Section 5, *Conclusions*, provides a summary of the analysis and the critical controls identified in the analysis.

Appendix A contains the meeting participant information for the hazards analysis meetings.

Appendix B contains the design information as reviewed during the latest hazards analysis meetings.

Appendix C contains the result of the Hazard Identification and Preliminary Hazard Assessment.

Appendix D provides design guidance considered to support the evaluation of secondary impacts for high consequence low frequency events.

2.0 FACILITY AND PROCESS DESCRIPTION

2.1 Site and Facility Layout

The MHTLS processes are mounted on three relocatable skids. The HA identified siting related concerns and system interfaces required to ensure operations of the MHTLS safety. These considerations were inputs into the operating location and acceptability.

2.2 MHTLS Processes

The MHTLS is being designed to demonstrate engineering-scale conversion of various wet biomass sources to a biocrude. Candidate biomass feedstocks for evaluation with the MHTLS include algae, lignocellulosic materials (wood, wheat, straw, stover, agriculture residuals), and wastewater treatment sludges. All feedstocks shall be tested at the bench scale before being evaluated in the MHTLS. The MHTLS allows testing at line velocities relevant to pilot- and commercial-scale plants. The recent advancements in HTL at the bench scale with plug-flow reactors design serve as the basis for the design of the scaled modular system.

The MHTLS consists of the following major operational areas as shown in Figure 2-1. Note that the operational areas are located on separate skids.

Feed Preparation, Staging, and Delivery Area (unit operations for feed formatting, including size reduction, shearing, and mixing to prepare a homogeneous and pumpable feed; feed tanks; and feed delivery pumps)

HTL Processing Area (feed delivery to HTL conditions, slurry heating, reactors, solids removal, and pressure letdown)

Product Collection Area (separations and product storage)

The MHTLS shall be designed to safely process biomass feedstocks at a nominal rate of 12 liters per hour (L/h) in runs of 120-hour nominal duration (380 gallons/week).

More-detailed requirements for the overall process and subsystems are presented in Section 4.0 of the Functional Design Criteria for Modular Hydrothermal Liquefaction System (MHTLS-RPT-001).

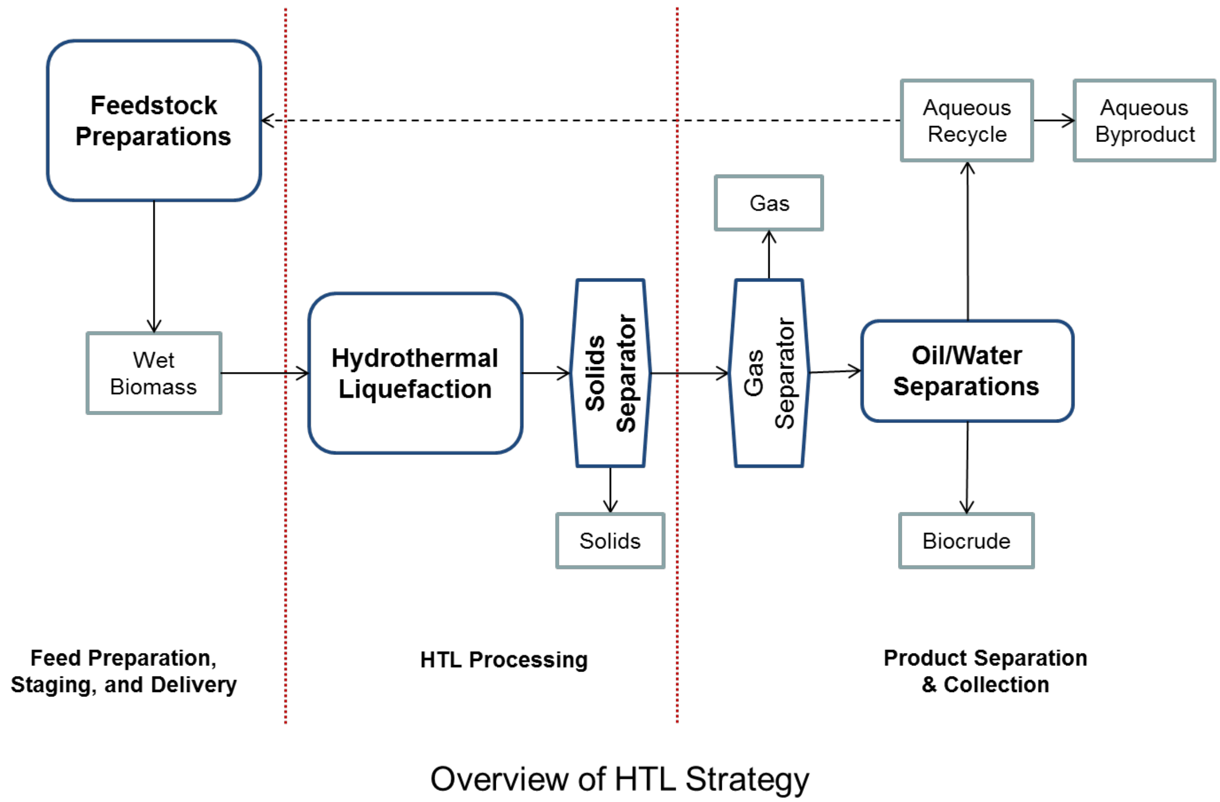

Figure 2-1. –MHTLS Process Overview.

3.0 HAZARD ASSESSMENT

A series of facilitated hazard analysis sessions were conducted in February 2015. A follow-on hazard analysis session was conducted in July 2016 and included review of significant design changes and consideration of operational activities and sequences. The PNNL teams involved in the hazard analysis sessions included R&D operations and engineering; Fire Protection; Pressure Systems; Environmental, Safety and Health; and hazard and safety analysts. Observers from DOE's Pacific Northwest Site Office also attended the sessions. Appendix A lists the attendees at each of the hazards analysis sessions.

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

3.1 Hazard Identification and Preliminary Hazards Assessment

The first step of the hazard analysis process was to identify the form, quantities, and characteristics of the hazards, including chemicals associated with the major process components (Hazard Identification).

For the initial assessment, the MHTLS was parsed into several evaluation areas based upon the processing areas and key unit operations/components. Within each evaluation area, the inventory and primary process parameters (pressure, temperature) were evaluated to determine if unique or significant hazards were posed by the operation. To aid in this determination the process parameters were categorized as having a hazard potential as identified in Tables 3-1 and 3-2. Other potential hazards/hazardous situations were identified and captured as appropriate.

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 operations assessment the same parsing of system was used. In addition, key operational activities and skid interfaces were identified, by individual skid:

Skid 1 activities
<u>Operations</u>
Stage Feed Materials
Load Feed Material into cutting mill (Z-1), if used for the test and/or wet immersion mill (Z-2)
Grind/Mill dry (Z-1)
Establish cooling water flow to immersion mill.
Transfer Feed to Mill Wet (Z-2)
Grind to form a pumpable slurry/paste
Transfer prepped slurry to Feed Staging Tank (T-1).

Skid 1/Skid 2 interface activities
<u>Operations</u>
Transfer prepped slurry from Feed Staging tank (T-1, Skid 1) to Feed Day Tank (T-2, Skid 2) (~ once every 12 h)
<u>Post run Activities</u>

Cleanout flush of vessel contents on Skid 2 will be transferred to the bulk liquid collection tank (skid 1)

Skid 2 activities

Precursors

Establish configuration for system
Make hard pipe connection for selected configuration.
Pressure check (N2) for leaks, with open pathway to blowdown vessels, BD-1. BD-2; (Valves XV-2225, XV-2401, XV-2402 open).
Close valves to blowdown vessels (Valves XV-2225, XV-2401, XV-2402).
Set badger control valve and begin pressurization.
Start CSTR Agitator (if testing in configuration 2)
Pump water in the vessels and tubing.
Establish cooling water flow
Engage cooling fan.
Initiate vessel heating

Operations

Complete heat up with water flow
Engage Feed Pumps (P4 A/B)

Expected Evolutions

Refill Feed Day Tank (T2)
Blow Down (Lines, Filters)
Empty Blowdown Receipt Tank (T-3)
Change over BPR (plugging)

Skid 2/Skid 3 interface activities

Operations

Product slurry continuously flows to Skid 3 (ambient pressure, <100C)

Skid 3 activities

Precursors

Configure valve HV-3004 (based on the oil being heavier or lighter than water).
Pre-Filter (F-3) Coalescer (V-8) in or bypassed.
Aqueous Byproduct in T-6 may be transferred to Z-2 (for wood recycle runs)

Operations

Adjustments to temperature to Gas Separator (V-6), Oil/Water Separator (V-7), aqueous buffer tank (V-7), and Coalescer (V-8)
Adjustments to outlet elevation in Gas Separator
Sample collection of product, aqueous phase and biocrude phase. HV-3001, HV-3210, HV-3211, and HV-3302)

Appendix C contains the results of the Hazard Identification. For the MHTLS processes, significant hazards requiring further evaluation via the What-If hazards analysis process included portions of the system with high pressure processes and the presence of high temperature liquids and gases. Table 3-3 lists the process areas identified as having significant hazards during the Hazard Identification process.

Table 3-1. Inventory Hazard Potential[1]

Hazard Potential	Health Hazard (HH)	Flammability Hazard (FH)	Instability / Reactivity (IR)
Low	HH 0, 1, 2	FH 0, 1, 2	IR 0, 1
High	HH 3, 4	FH 3, 4	IR 2, 3, 4

1. Based on NPFA 704 or equivalent consensus rating system

Table 3-2. Processing (Parameter) Hazard Potential

Hazard Potential	Temperature °C	Pressure, psig
Ambient	~ 30	<15
Low	< 100	<100
Moderate	100-200	100-200
High	>200	>200

Table 3-3. MHTLS Process Areas with the Potential for Significant Hazards (See Appendix C)

AREA	Key Components	Volume (Vessels)	Process Function
HTL-3	**Back Flush Line**		**Back Flush Line:** Allows blow down of H-1 or H-2 to remove line blockage by providing routing to blowdown tank 2 (BD-2). Manual operation of line.
HTL-4a	**H-1**		**H-1 Feed/Product Heat Exchanger:** Configuration 1 only. Heat pressurized slurry from room temperature to 300 to 325 °C, through heat exchange with filtered product stream (counter-current tube-in-tube heat exchanger). MAWP 3500 psig 425 C
HTL-4b	**H-2** **CSTR**	 **2 L**	**H-2 Feed Preheater:** Configuration 2 only. Heat feed slurry from 25 to 150 °C to reduce heating load on CSTR. MAWP 3500 psig 425 C **CSTR (Vessel) and Associated Heating System:** Configuration 2 only. Provide aggressive mixing and heating to aid in transition from slurry to liquefied product. Provide capacity to heat slurry from 140 to 325 °C. MAWP 3500 psig 425 C
HTL-5	**H-3** **H-4**		**H-3 Trim Heater**: Configurations 1 and 2. Heat slurry from 300 to 350 °C. Heat skid components during startup. Final heat-up. 2x12 ft long tubes 3/8 OD 0.049 wall 316 SS encased in Aluminum block heater. MAWP 3500 psig 425 C **H-4 Tubular Reactor Section**: Provide requisite residence time at reaction temperature (350 °C) and pressure (3000 psig, nominal) while maintaining slurry at a velocity sufficient to minimize particulate settling. Heat slurry as necessary and maintain slurry at 350 °C. 12x12 ft long tubes ½ OD 0.065 wall 316 SS MAWP 3500 psig 425 C encased in Aluminum block heater.
HTL-6	**F-1** **F-2**	**5 L** **5 L**	**F-1&F-2 Filter/Housing for Solids Removal**: F-1 is operated for all runs and F-2 operation is optional. Remove solids/precipitate from liquefied stream, down to 20 microns. MAWP 3500 psig 425 C
HTL-7	**R-2**	**5 L**	**Separator Vessel (R-2)**: Provide for potential separation of aqueous phase organic compounds. Maintain temperature of HTL product stream at 350 °C. Reducing carbon content in aqueous phase. MAWP 3500 psig 425 C
HTL-8	**BD-1** **BD-2** **TK-3** **TK-4**	**3 L** **3 L** **12L** **15 Gal**	**Filter Blowdown Vessel (BD-1) & (BD-2)**: Receive solids from the filter element/filter housing (F1) during the filter blowdowns while being isolated from blowdown slurry receipt tank (TK-3). Reduce blowdown slurry temperature (≤80 °C). Provide means/logic to discharge cooled slurry to blowdown slurry receipt tank (TK-3) while isolated from the filter housing (F1). BD-2 will be configured to receive flow from either F-2 or from the Back Flush Line. MAWP 3500 psig 425 C **TK-3 Blowdown Receipt Tank:** Remain isolated from the blowdown vessel (BD-1) during normal operation. Receive slurry (≤80 °C) from the blowdown vessel (BD-1) when it is emptied/flashed to atmospheric pressure. Provide means to offload tank to portable accumulation vessel (e.g., tank, drum, bucket). Vessel may be tipping drum. MAWP

Table 3-3. MHTLS Process Areas with the Potential for Significant Hazards (See Appendix C)

AREA	Key Components	Volume (Vessels)	Process Function
			Atmospheric , 80C **TK-4 Pressure Relief Vent Header and Knock-out Vessel**: All pressure release systems will be routed to TK-4 for safe receipt/containment of steam/water/slurry surge in event of activation of a pressure relief line. Protect vessel from overpressure by a vent to atmosphere. MAWP 440 psig, 200C
HTL-9a	**H-1**		**H-1 Feed/Product Heat Exchanger:** Configuration 1 only. Heat pressurized slurry from room temperature to 300 to 325 °C, through heat exchange with filtered product stream (counter-current tube-in-tube heat exchanger). Addressed in Evaluation Area 4a.
HTL-9b	**C-2**		**Product Cooler (C-2)**: Primary cooling unit for Configuration 2. Provide required cooling of product stream from 350 to 100 °C.
HTL-9c	**C-1** **BPRs**		**Product Trim Cooler (C-1):** Provide cooling/temperature control of product steam to optimize operation of the backpressure regulator (i.e., cool product from about 100 to 50 °C). **BPR Back Pressure Regulators:** Provide stable operating pressure for the MHTLS. Reduce HTL operating pressure to atmospheric or near atmospheric pressure. Normal Operation 2 in parallel with 1 in operation.

3.2 What-If Analysis

The What-If analysis technique is a structured brainstorming method of determining 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…”.

Facilitated hazard analysis sessions were held in February 2015 in support of the conceptual design development and statement of work preparation. The What-If sessions focused on the MHTLS processes identified as having significant hazards and interfaces with necessary support “facility” systems. Revision 2 focused on important design changes from preliminary to final design and operational sequences for the process. A subsequent hazard analysis session was held in July 2016 in support of the operation of the MHTLS. This hazard evaluation (Revision 3) re-affirmed the scope of the detailed hazard evaluation (Skid 2) and focused on important design changes from preliminary to final design and the operational sequences for the process.

As part of the What-If analysis, a qualitative likelihood was assigned to all unmitigated hazardous scenarios. This reflects the likelihood of an initiating event coupled with a postulated upset condition, absent 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 upset condition (Table 3-4).

Each hazardous scenario was further defined by qualitative evaluations of the potential unmitigated consequences such as: process upset; energetic release events from a vessel pressure boundary (boiling liquid expanding vapor explosion [BLEVE] or pressure vessel burst [PVB]), flashing spray releases; and spray or spill of material. The unmitigated consequences identified during the analysis represent bounding outcomes in most instances, rather than a more likely but less significant outcome.

Table 3-4. Likelihoods Used for the MHTLS 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 [numerical guidance: frequency (f) > 1E-01]
Unlikely	Conditions involving failure of two or more of the above, mechanical failures of active systems (e.g., pump/motor failures) [numerical guidance: 1E-01 ≥ f > 1E-03]
Very Unlikely	Multiple failures (more than 2), failures of robust passive systems [numerical guidance: 1E-03 ≥ f > 1E-05]
Extremely Unlikely	Many concurrent, independent failures [numerical guidance: 1E-05 ≤ f]

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 in the hazard analysis table which will prevent the occurrence or mitigate the effects of the release.

A postulated event involving a heat exchanger pressure tube leak impacting the outer tube (shell side) resulting in a spray of oil posing a potential flammability concern was eliminated as part of final design activities by use of an air cooled heat exchanger.

Several highly energetic releases (i.e., BLEVE/PVB) having High consequence levels to the Worker were identified, See Table 3-5. For these events, additional analyses were performed (Section 3.4) to determine the likelihood and potential magnitude of the impacts from the event to receptor locations for bounding scenarios of each type. Critical Controls were identified to reduce the risk or protect assumptions such that these events are shown to be Risk Bin III or less.

Flashing spray (FS) releases assumed to have the potential for Moderate consequence level to a Worker were also identified. These events can have serious impacts to MHTLS workers due to direct steam impingement but would not extend beyond an immediate work area. The hazard controls identified in the hazards analysis are also supplemented via PNNL work control processes as such most events are evaluated to be in the Very Unlikely range (requires multiple failures and enabling assumptions including failure of the pressure boundary, orientation of the break in an adverse direction, presence of personnel, and lack of protective guards and PPE). Note: events resulting in a BLEVE (complete sudden rupture of a vessel) also have the potential to result in a flashing spray release, but are adequately protected by the controls for the BLEVE.

Table 3-5. Consequence Thresholds

Consequence Level	Public (P)	Co-located Staff (CS)	Worker (W)
High	**Irreversible or other serious health effects that could impair the ability to take protective action**. <u>Supplemental Guidance:</u> Chemical: ≥PAC*-2, Physical: ≥2 psi overpressure	**Life-threatening health effects.** <u>Supplemental Guidance:</u> Chemical: ≥PAC-3 Physical: ≥5 psi overpressure	**Prompt death, multiple serious injuries, or significant radiological and chemical exposure.** [1]
Moderate	**Transient health effects** <u>Supplemental Guidance:</u> Chemical: ≥PAC-1 Physical: ≥ 1 psi overpressure	**Irreversible or other serious health effects that could impair the ability to take protective action** <u>Supplemental Guidance:</u> Chemical: ≥PAC-2 Physical: ≥2 psi overpressure	**Serious injuries**
Low	**No appreciable risk of health effects.** <u>Supplemental Guidance:</u> Chemical: <PAC-1 Physical: < 1 psi overpressure	**Transient health effects.** <u>Supplemental Guidance:</u> Chemical: <PAC-2 Physical: <2 psi overpressure	No distinguishable threshold [2]

* Protective Action Criteria (PAC); http://orise.orau.gov/emi/scapa/chem-pacs-teels/default.htm

1. High concentrations of radioactive or chemically toxic materials in areas where a facility worker could be present;

   Explosions or over-pressurizations within process equipment or confinement/containment structures or vessels, where serious injury or death to a facility worker is expected to result; or

   Unique hazards that could result in asphyxiation or significant chemical/thermal burns
2. Typically identified as Low Consequence to the worker.

Table 3-6. Risk Ranking Bins

Consequence Level	Extremely Unlikely	Very Unlikely	Unlikely	Likely
High Consequence	IV	II	I	I
Moderate Consequence	IV	III	II	I
Low Consequence	IV	IV	IV	III
I = Combination of conclusions from hazard analysis that identify situations of major concern II = Combination of conclusions from hazard analysis that identify situations of concern III = Combination of conclusions from hazard analysis that identify situations of minor concern IV = Combination of conclusions from risk analysis that identify situations of minimal concern				

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
HTL-PRE.1	What if path closed?	Failure to open valves (Valves XV-2225, XV-2401, XV-2402) during prestart; results in not pressure checking pressure blowdown vessel 1 & 2	L	Pre-existing leak not detected. Worst Case: flashing spray release of process fluid during subsequent blowdown during operations.	Administrative Controls (check pressure)	V	L	L	M	III
HTL-PRE.2	What if valves left open?	Failure to close valves	L	Process upset Pressure does not increase as expected; no consequence from nitrogen	Close valve		-	-	-	-
HTL-PRE.3	What if agitator left off?	Failure to start agitator	L	Process upset failure to heat appropriately	Indicator on agitator speed		-	-	-	-
HTL-PRE.4	What if no flow (plug)?	Extended loss of flow condition	L	Process upset (loss of flow); Reach boiling conditions	Temperature/pressure indication		-	-	-	-
HTL Processing-4a / 4b (See 782-10-122)										
HTL-4a.1	What if loss of pressure boundary? (Inner Tube)	Failure of pressure boundary, inner tube, results in mixing of process streams	V	Process upset; Product contamination with feed; Plugging of BPRs	Inner and Outer Pipe (Pipe in Pipe heat exchanger) designed for High Pressure.		-	-	-	-
HTL-4a.2	What if loss of pressure boundary? (Outer Tube)	Failure in pressure boundary outer tube results in a release to environment	U	Flashing spray release of process fluid	Pressure boundary; Skid design provides spray protection for operators.	V	L	L	M	III
HTL-4a.3	What if mis-batched material?	Processing outside of feed specifications	L	Process upset; Degradation of heat transfer coefficient; Possible precipitates	Administrative controls		-	-	-	-
HTL-4a.4	What if no flow (plug)?	Plugged line; Expected design condition	L	Process upset, loss of production until resolved	Heat design option (post-run)		-	-	-	-
HTL-4a.5	What if high pressure?	Pumps set at or run at higher than expected pressures results in pressure boundary failure (tubing) and release with fluid temperature range 60 to 350 °C	L	Flashing spray release of process fluid	PSE-2207/PSV-2224 High – High Pressure Interlock Process Pressure Switch/Indicators/Alarm ISCO Automatic pump shut-off ISCO shear pin at 3750 psig Skid design provides spray protection for operators.	V	L	L	M	III
HTL-4a.6	What if poor performance (heating)?	Process fluid is not heated appropriately	L	Process upset; Pressure drops across filter			-	-	-	-
HTL-4a.7	What if poor	Process fluid is not cooled appropriately	L	Process upset	Controls will be discussed		-	-	-	-

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
	performance (cooling)?				in HTL Processing-9-BPR					
HTL-4b1.1	What if loss of pressure boundary? (Inner Tube)	Failure of inner pressure boundary allows mixing of hot process fluid and cold fluid. Entire system is at pressure.	U	Process upset	Pressure boundary; robust design inner and out tubes both design for maximum pressure.		-	-	-	-
HTL-4b1.2	What if loss of pressure boundary? (Outer Tube)	Failure of outer tube pressure boundary releases process fluid (see HTL-7.1a)	U	Flashing spray release of process fluid	Pressure boundary; Skid design provides spray protection for operators.	V	L	L	M	III
HTL-4b1.3	What if no flow (plug)?	Plugged; Expected design condition	L	Process upset	Heat design option (post-run)		-	-	-	-
HTL-4b1.4a	What if high pressure?	Pumping at higher than expected pressures results in Failure (at HE-2). Line failure resulting in flashing spray release with fluid temperature range 60 to 150 °C.	L	Flashing spray release of process fluid	PSE-2207/PSV-2224; High – High Pressure Interlock Process Pressure Indicators/Alarm ISCO Automatic pump shut-off; ISCO shear pin at 3750 psig Skid design provides spray protection for operators.	V	L	L	M	III
HTL-4b1.4b	What if high pressure?	Pumping at higher than expected pressures results in failure of (CSTR) vessel pressure boundary.	L	BLEVE	PSE-2219 at 3500 psig; High – High Pressure Interlock Process Pressure Indicators/Alarm ISCO Automatic pump shut-off; ISCO shear pin at 3750 psig	EU <1E-6	L	L	H	IV
HTL-4b1.5	What if poor performance (heating)?	Process fluid is not heated appropriately	L	Process upset; Pressure drops across filter			-	-	-	-
HTL-4b2.1	What if loss of pressure boundary?	Failure of pressure boundary at gasket	L	Smoke type release/odor	Startup procedures; Design of flange and clamping system prevents		L	L	L	III

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
					direct spray.					
HTL-4b2.2	What if loss of pressure boundary?	Catastrophic failure of (CSTR) vessel pressure boundary (material failure)	V	BLEVE	Design of pressure boundary	EU <1E-6	L	L	H	IV
HTL-4b2.2a	What if loss of pressure boundary?	Failure in piping.	U	Flashing spray release of process fluid	Pressure boundary; Skid design provides spray protection for operators.	V	L	L	M	III
HTL-4b2.3	What if too much power (over heat)?	Overheat (CSTR) vessel wall resulting in Failure of pressure boundary; Heat transfer decreases; Agitator may stop; Potential impacts to rupture disks releasing at lower pressure	L	BLEVE	Controls on heater; Independent temperature control on vessel wall; Over-temp shut-off; 2 TCs	EU <1E-6	L	L	H	IV
HTL-4b2.4	What if no flow (plug)?	Plugged line	L	Process upset	Procedural blow down sequences		-	-	-	-
HTL-4b2.5	What if loss of mixing?	Loss of agitation results in Temperature reduction; Building of char; Generation of solids resulting in plugging	L	Process upset			-	-	-	-
HTL-4b2.6	What if poor performance (heating)?	Process fluid is not heated appropriately	L	Process upset			-	-	-	-
HTL-4b2.7	What if you add cold water to heated system during startup?	Cold water added, resulting to shock to the vessel at temperature 300 °C	L	Seal failure/leak (steam vapor) is expected	Administrative controls		L	L	L	III
HTL-4b2.8	What if over mixing?	Too much agitation/ process upset	L	Process upset; Impeller falls off leads to loss of mixing	Magnetically coupled; Design of impeller					
HTL Processing-5 (See 782-10-123)										
HTL-5.1	What if loss of pressure boundary?	Catastrophic failure of vessel pressure boundary (material failure)	U	Flashing spray release of process fluid	Pressure boundary; Skid design provides spray protection for operators.	V	L	L	M	III
HTL-5.2	What if loss of pressure boundary?	Loss of pressure boundary at connections (flange leak)	L	Dripping or small leak; Smoking; Odor	Pressure checks preoperational; Design of swag lock		L	L	L	III
HTL-5.3	What if too much power (over heat)?	Overheating results in Loss of pressure boundary	L	Flashing spray release of process fluid Potential Electrical Hazard due to	Temperature controls; Thermo-couples between block and tube	V	L	L	M	III

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
				shorting.						
HTL-5.4	What if poor performance (heating)?	Process fluid is not heated appropriately.	L	Process upset			-	-	-	-
HTL Processing-6 (See 782-10-124)										
HTL-6.1	What if loss of pressure boundary?	Failure of pressure boundary (Filter)	V	BLEVE	Design of vessel	EU <1E-6	L	L	H	IV
HTL-6.1a	What if loss of pressure boundary?	Failure in piping.	U	Flashing spray release of process fluid	Pressure boundary; Skid design provides spray protection for operators.	V	L	L	M	III
HTL-6.2	What if loss of flow (plug)?	Plugged filter	L	Process upset	Timed blow down frequency anticipated based on feed stock; Operational controls		-	-	-	-
HTL-6.3	What if break through?	Breakthrough of filter results in particle entering downstream components (R-2/BPR).	L	Process upset; Send particles downstream –potential blockage of BPR	See HTL-8 See HTL-9					
HTL-6.5	What if fluid is the wrong temperature?	Process fluid too hot	L	Process Upset; Less viscous process fluid; collect fluid quicker	Filter designed for maximum pressure		-	-	-	-
HTL-6.6	What if fluid mis-batched (more solids)?	Processing outside of feed specifications	L	Process upset; Possible precipitates; More frequent plugging	Administrative controls		-	-	-	-
HTL-6.7	What if too much power (over heat)?	Overheating of filter vessel results in failure of pressure boundary; Heat transfer decreases; Potential impacts to rupture disks releasing at lower pressure	L	BLEVE	Controls on heater; Independent temperature control on vessel wall; Over-temp shut-off; 2 TCs	EU <1E-6	L	L	H	IV
HTL-6.8	What if loss of pressure boundary?	Loss of pressure boundary at connections (flange leak)	L	Dripping or small leak; Smoking; Odor	Pressure checks preoperational; Design of swag lock		L	L	L	III
HTL-6.11	What if open offline vessel?	Opening valve (XV-2415) results in fluid in F-2. Compresses whatever is in F-2	L	Process upset	F-2 designed for pressure, is open on back end, and has Pressure relief.		-	-	-	-
HTL Processing-7 (See 782-10-124)										
HTL-7.1	What if loss of	Failure of pressure boundary Separator	V	BLEVE	Design of vessel	EU	L	L	H	IV

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
	pressure boundary?	Vessel (R- 2)				<1E-6				
HTL-7.1a	What if loss of pressure boundary?	Failure in piping.	U	Flashing spray release of process fluid	Pressure boundary; Skid design provides spray protection for operators.		L	L	M	II
HTL-7.2	What if loss of flow (plug)?	Plugged line results is blocked flow and overpressure of Separator vessel or piping	L	BLEVE if failures occurs in vessel Flashing spray release of process fluid if failure occurs in line	Design of vessel Pressure boundary; Skid design provides spray protection for operators. Pressure relief	EU <1E-6	L	L	H	IV
HTL-7.3	What if break through (separations particles)?	Internals fail	U	May send particles downstream –plug BPR	See HTL-9					
HTL-7.4	What if separations do not work?	No separations occur and product is not changed	L	Process Upset: Decreased product quality			-	-	-	-
HTL-7.5	What if too much power (over heat)?	Overheating of separator vessel (R-2) failure of pressure boundary; Heat transfer decreases; Potential impacts to rupture disks releasing at lower pressure	L	BLEVE	Controls on heater; Independent temperature control on vessel wall; Over-temp shut-off; 2 TCs	EU <1E-6	L	L	H	IV
HTL-7.6	What if inadvertent operation of separator?	Process fluid passed through separator inadvertently	L	No consequence; thermal impacts similar to F-2			-	-	-	-
HTL Processing-9a / 9b / -9c (See 782-10-122, 782-10-126)										
HTL-9a	H-1 Feed Heat Exchanger Addressed in Evaluation 4a.									
HTL-9b.1 (782-10-126)	What if pressure boundary loss?	Failure of pressure boundary	V	Flashing spray release of process fluid	Design of the pressure system; Skid design to protect personnel from steam	V	L	L	M	III
HTL-9b.2	What if air loss?	Loss of (HVAC) air resulting in loss of cooling	L	Larger thermal load on Cooler C-1	Loss of flow alarm;		-	-	-	-
HTL-9b.3	What if the line	Plugged line	L	Process upset	Pressure relief		-	-	-	-

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
	plugs?									
HTL-9c1.1 (782-10-126)	What if loss of inner pressure boundary?	Failure of pressure boundary at moderate temperature results in mixing of moderate temperature fluid with cold fluid; Blow back to open tank (Operations during FAT show temperature <100C)	U	Flashing spray release or steam release (160 C process fluid mixing with Water)	Pressure Boundary (inner)	V	L	L	M	III
HTL-9c1.2	What if loss of outer pressure boundary?	Failure of outer pressure boundary results in spill of water to operating area. Fluid not cooled into BPR, which will lead to BPR failure over extended time (see HTL-9c2.4)	L	Process Upset;			-	-	-	-
HTL-9c1.3	What if loss of flow (plug)?	Plugged line	L	Process upset			-	-	-	-
HTL-9c2.1	What if loss of flow (plug)	Plugged line	L	Process upset			-	-	-	-
	Due to loss of pressure upstream?	Plugged line due to loss of pressure upstream	L	Process upset; No real impact			-	-	-	-
	Due to separator screen failure?	Plugged line due to separator particles; failure in **closed** position	U	Process upset; plug			-	-	-	-
	Due to separator screen failure?	Plugged line due to separator particles; failure in **open** position	U	Process upset; Erosion of BPR diaphragm; Lose fine control of pressure			-	-	-	-
HTL-9c2.3	What if failure (full open) of BPR?	Failure of BPR results in high pressure in S-1;	U	Process upset; Loss of fine pressure control	BPR design limits pressure downstream (fail full open). Provide pressure relief (rupture disk PSE-2623)		-	-	-	-
HTL-9c2.4	What if process fluid is not cooled upstream?	Hot process fluid to BPR. Steam, Boiling, and pressure; wear out BPR system, (Operations during FAT show temperature <100C)	L	Process upset (premature wear out of BPR)			-	-	-	-
Operation Blowdown line (See 782-10-122, 782-10-125)										
HTL-3.1	What if valve opens too soon?	Unintentional (early) blowdown in to BD-2. Would have to have additional valves open to result in exposure to personnel	U	Flashing spray release of process fluid if open pathway to TK-3.	BD-2 designed to contain full system pressure.	V	L	L	M	III

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Af[1]	P	CS	W	Risk
				Process upset; harder on valves if opened out of sequence 2 – 1 instead of 1 – 2. Lose option for recovery if valve fails.	BD-2 is isolated from TK-3					
HTL-3.2	What if valve stays opens too long?	Failure to close valve results in filling blow down vessel 2.	L	Process upset; Pressure will decrease further than expected and BD-2 will be filled.	BD-2 designed to contain full system pressure.		-	-	-	-
HTL-3.3	What if you get a back flow of N2?	Back flow of high pressure nitrogen into system results in failure of MHTLS Components due to High Pressure Nitrogen (above system Design Pressure).	U	Flashing spray release of process fluid and release of nitrogen.	Overpressure protection on Nitrogen System (PSV-4301) 3500 psig. Pressure Regulation of Nitrogen System. Rupture disk (downstream of Trim Heater) (PSE-2304) Skid design provides spray protection for operators.	V	L	L	M	III
HTL-3.4	What if loss of pressure boundary?	Failure in blowdown lines results in release of process fluid at elevated temperature due to blowdown of entire system.	U	Flashing spray release of process fluid	Pressure Boundary Skid design provides spray protection for operators.	V	L	L	M	III
HTL-3.5	What if no flow (plug)?	Inability to unplug system	L	Process upset	Alternate methods of operation including filter blow down		-	-	-	-
Operation Blowdown Filter (See 782-10-124, 782-10-125)										
HTL-6.4	What if blowdown too early (inadvertently)?	Blow down initiated too early	L	Process upset; Lose use of blow down operation; Loss of product	BD vessels designed for system pressure		-	-	-	-
HTL-6.9	What if N2 valve opens early?	Opening of N2 valve early, resulting in process fluid entering into N2 system	L	Process upset; Fouling of the N2 system	Overpressure protection on nitrogen line		-	-	-	-
HTL-6.10	What if N2 high pressure?	Filter pressure too high resulting in loss of (F-1/F-2) pressure boundary	U	BLEVE; Potential to blow through BPRs	Pressure Regulation of Nitrogen System. Overpressure protection on Nitrogen System Filter overpressure protection set at 3500 psi	EU <1E-6	L	L	H	IV
HTL-6.11	What if N2 low	Potential backflow from the process	U	Process upset; Contamination of N2	Check Valve CK-2403		-	-	-	-

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	A_f[1]	P	CS	W	Risk
	pressure?	through check valve CK-2403		supply line						
HTL-8.1-1	What if blowdown too early with drain line open (BD-1/BD-2)?	Blow down occurs during run with drain line open ; flashing steam into TK-3; Boiling, loss of pressure within system	U	Flashing spray release of process fluid if pressure boundary breached, potential for PVB Burst <100 psig if vent plugged or overwhelmed	Interlock design of valves (blowdown , nitrogen, and drain to TK-3); TK-3 vented	V	L	L	M	III
HTL-8.1-2	What if loss of pressure boundary?	Failure of pressure boundary (Blow Down Vessel, BD-1, BD-2)	U	BLEVE	BD Vessel designed for system pressure	EU <1E-6	L	L	H	IV
HTL-8.1-3	What if loss of flow (plug)?	Plugged line	L	Process upset; loss of production	Pressure indication to notify operator		-	-	-	-
HTL-8.1-4	What if blow down with low pressure N2 system open to BD-1? (or BD-2)	Blow down with N2 open to BD-1/2, Less effective blow down;	L	Flashing spray release due to failure in low pressure nitrogen line	LP nitrogen normally isolated from BD vessels Check valves Nitrogen Line Designed to full system pressure BD-1/2 Designed as Pressure Vessel with overpressure protection	V	L	L	M	III
HTL-8.2-1	What if blowdown too early with drain line open to TK-3 (XV-2501/2502 open)?	Blow down occurs during run with drain line open. flashing steam into TK-3; Boiling, loss of pressure within system	U	Flashing spray release if pressure boundary breached, potential for PVB Burst <100 psig if vent plugged or overwhelmed	Interlock design of valves (blowdown , nitrogen, and drain to TK-3); TK-3 vented	V	L	L	M	III
HTL-8.2-2	What if too hot (transfer early)?	Process fluid from BD Vessel transferred to TK-3 when too hot but < 100 C.	L	Process upset; Flashing into TK-3	TK-3 vented;		-	-	-	-
HTL-8.2-3	What if failure in pressure boundary (TK-3)?	Material Failure results in release of fluid to environment (assuming no other failure material is < 80 C).	U	Spill hot liquid to environment.	TK-3 Design 316 SS Atmospheric Vessel		L	L	L	IV
HTL-8.2-4	What if BD vessel is not isolated for TK-3, and HV-2505 open during blow down?	Failure to isolate TK-3 pressure boundary following draining results in open pathway to environment during blowdown. Requires additional failure of BD-2 drain valve.	V	Flashing spray release of process fluid. Potential failure of pressure boundary.	Interlock design of valves (nitrogen and drain to TK-3); TK-3 vented TK-3 isolated (HV-2505 closed and Capped.	V	L	L	M	III
HTL--8.2-6	What if demister plugs (TK-3)?	Potential higher than expected pressure	U	Bound by HTL-8.1- 1						
Utilities/Facilities Interface										

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	A_f[1]	P	CS	W	Risk
FU-1	What if loss of power (short–term power bump)?	Power bump resulting in electronics shutting off	L	Process upset; All electronics need to be powered on; Plug if system off for more than 5 minutes; Pressurized quiescent state; Valves fail closed	Stored memory of temperature controls		-	-	-	-
FU-1	What if loss of power (short–term power bump)?	Power bump resulting in water chiller shutting off/flow stopping	L	Process Upset; Low consequence	Stored memory of temperature controls					
FU-2a	What if loss of ventilation? Skid 1	Nuisance odors not ventilated on Skid 1	L	Nuisance odors/ low consequence	Facility Operating requirements		L	L	L	IV
FU-2b	What if loss of ventilation? Skid 2	Loss of ventilation on Skid 2	L	Possible build-up of H2S in 15-20 min; potential to heat up skid 2 due to loss of heat eject	Facility Operating requirements		L	L	L	IV
FU-2c	What if loss of ventilation? Skid 3	Same as Skid1	L	Nuisance odors/ low consequence	Facility Operating requirements		L	L	L	IV
FU-2d	What if loss of ventilation at Vessel S-1?	Loss of ventilation at Vessel S-1	L	Nuisance odor (possible H2S)	Facility Operating requirements		L	L	L	IV
FU-3a	What if loss of building water?	Loss of process water	L	Process Upset; Lose ability to operate (startup)	Possibly recycle water if already passed startup or have a standby water tank		-	-	-	-
FU-3b	What if loss of chilled water?	Loss of cooling	L	Process Upset; Hot process fluid to BPR results in boiling of cooling water in shell side of C-1	Flow indicator					
FU-3b	What if flashing cooling water then restart with shell hot?	Run with hot water	U	Shocking system results in shell failure. Steam (water) release	Flow indicator/temperature System with glycol helps	V	L	L	M	III
FU-3b	What if loss of chilled water at BD-1/BD-2?	Loss of cooling	L	Process Upset. Hot process fluid/ buildup of solids	Run water to cool process fluid		-	-	-	-
FU-4	What if loss of N2?	Loss N2 system resulting in loss of ability to blowdown or re-pressurize system after attempting blowdown	L	Process Upset. Plugging; removes plugging mitigation tools			-	-	-	-
FU-5	What if loss of building air?	Loss of building air, resulting in loss of low pressure pumps. Blow down valves won't open; Inability to blow down filter; Shut down condition	L	Process Upset. Can't operate valves			-	-	-	-
FU-6	What if building	Building emergency resulting in	L	Process Upset. Unattended operations.	Emergency Stops located					

Table 3-8. What-If Hazards Analysis Results

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	A_f[1]	P	CS	W	Risk
	emergency (evacuation)?	evacuation. Would stop operations		No release unless subsequent failure occurred.	on Skid 1 and Skid 3 Shutdown from HMI.					

1. A_f = Accident Frequency, if used provides updated accident frequency estimations for Risk Binning based on additional failure information or enabling failures and assumptions required for the event to result in the identified consequences. If "Blank" the original Likelihood identified in the HA was used for Risk Binning.

3.4 Evaluation of High Hazard Scenarios

Accident scenarios perceived as having high unmitigated consequences 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)

3.4.1 Boiling Liquid Expanding Vapor Explosion (BLEVE)

The hazard analysis identified hazard scenarios potentially resulting in BLEVEs in the MHTLS in the following process vessels:

- R-1 Continuous Stirred Reactor (2 liter)
- F-1/F-2 Filter Vessels (5 liter)
- R-2 Separator Vessel (5 liter)
- BD-1/BD-2 Blowdown vessels (3 liter)

Of these events, consequences for the Filter Vessel (F-1, F-2) are further presented here. These components pose the highest consequences based upon assumed temperature, pressure and volume of material.

Events which could result in BLEVE were also assumed to have the possibility of resulting in a PVB (due to the use of Nitrogen to purge and back pulse the system).

BLEVEs and PVBs are not associated with atmospherically vented vessels unless a mechanism is identified that also results in a blockage of the vent pathway for the vessel. There were no mechanisms identified in this analysis, which would result in a concurrent blockage of a vent system or of a more severe event than those analyzed.

3.4.1.1 BLEVE Consequence Methodology

For analyzing the consequence of BLEVEs, the process outlined in CCPS, 2010 was followed. 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) -not relevant for this system

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

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

Where:

- 2 = a multiplier for ground effects.
- e_{ex} = work done, u1-u2, 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:

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

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

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

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

Where:

$s_{(f,g)(1,2)}$ = entropy (J/g°K) of the fluid and gas at state 1 and 2 respectively

$X_{(f,g)}$ = mass fraction of the fluid and gas

Energy available – Per the CCPS, 2010 methodology assuming ductile failure, the energy available is $E_{ex,a} = 0.4* E_{ex}$. 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, $\overline{R}$ of the receptor is then determined by:

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

Where:

R= distance to receptor

p_0 = atmospheric pressure

The scaled pressure $\overline{P}_s$ and impulse $\overline{I}_s$ 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:

$$P_S =k_p*\overline{P}_s* p_0$$

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

Where:

a_0 = speed of sound in ambient air

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

Scaled dist. $\overline{R}$	$\overline{R}$< **0.3**	$\overline{R}$< **3.5**	$\overline{R}$> **3.5**
k_P	4	1.6	1.4

Scaled dist. $\overline{R}$	$\overline{R}$< **0.3**	$\overline{R}$< **1.6**	$\overline{R}$> **1.6**
k_I	4	1.6	1.4

Missile impacts (rocketing fragments): 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 MHTLS components:

1) The approach is derived from "open" field events; impacts of fragments with the skid structure, other components, and any building enclosure 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 for that that for the MHTLS components.

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

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

Where:

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

Thermal Hazards: Based on the process fluid's low combustibility, entrained water content, and use of inert gases no fireball hazards were postulated.

3.4.1.2 BLEVE Results

For evaluation, it is assumed the pressure in the filter vessel is at the maximum system pressure 3500 psig (MHTLS-RPT-001, Rev. 0 Table 4). It is also assumed that the system is at a supercritical fluid temperature of 425°C. These are conservative assumptions as these conditions are at higher pressures and temperatures than the operating pressure (~2800-3000 psig) and temperature (350 °C) and would require multiple upsets and failures to achieve. It was conservatively assumed that the filter vessel contained 5 liters of liquid (water), ignoring any volume taken up by the filter internals. Accounting for the slurry mixture (solids, bio-oil and water) would lower the potential energy due to the thermodynamic properties compared to water.

<u>Input Assumptions:</u>

Pressure State 1	3500 psig	24.127 MPa
Temperature State 1	425 °C, supercritical fluid	
Pressure State 2	14 psi	0.1 MPa
Temperature State 2	99.6 °C, saturation temperature	
Volume of Reactor	5 liters	0.005 m^3
Speed of sound in air, a_0	340 m/s	

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

Temperature (°C)	Pressure (MPa)	Specific Volume, *v* (m3/kg)	Internal Energy, u (kJ/kg)	Enthalpy h (kJ/kg)	Entropy S (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Phase
100	0.1	0.0010435	419.06	419.17	1.3072	3.7682	4.2157	1543.2	liquid
100	0.1	1.6959	2506.2	2675.8	7.361	1.5535	2.0766	472.28	vapor
425	22.4	0.0095826	2671.7	5.6198	5.6198	2.5561	5.5884	529.68	Super critical liquid
425	24.12	0.0084264	2630.5	5.5222	5.5222	2.6599	6.3511	517.82	Super critical liquid

Thus from above:

$E_{ex,a}$ = 0.15* E_{ex}. (Casal and Salla) = 135E+03 joules

= 0.4* E_{ex}. (CCPS, 2010) = 360E+03 joules

Using the input assumptions and thermodynamic data, the positive side-on overpressure (P_s) and positive side-on impulse (I_s) at the following receptor locations are:

Actual Receptor Distance, meters (m)	3	5	7	10	15
scaled distance $\overline{R}$, m	**2.0-2.7**	**3.3 – 4.5**	**4.6 – 6.4**	**6.6 – 9.1**	**9.8–13.6**
P_s, kPa	**25.3 – 33.9**	**10.3-15.7**	**6.4 -10**	**4-6.1**	**1.8-3.7**
I_S, Pa-s	**0.041-0.056**	**0.020-0.027**	**0.012-0.017**	**0.009- 0.02**	**<0.008**

The maximum likely range of fragments calculated using the CCPS, 2010 method was determined to be ~ 76 meters. As noted in Section 3.4.1.1 and 3.4.3, this distance is judged to be a very conservative estimate.

3.4.1.3 BLEVE Likelihood

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). For a catastrophic failure of pipe, (all HTL components subject to BLEVEs are essentially piping systems) pipe failure data was taken from CCPS [2] page 183. 3.2.1.1 Piping systems – Metal – Straight sections. For this evaluation the mean failure rate as a function of the in service time: $0.0268/10^6$ mile-hours = 2.68E-02 *(8760 hours/year) / 10^6 hours) = 2.35E-04/mile- year. For a section of pipe 5 foot in length (~ length of the filter vessel) this results in an estimated failure rate of:

= 2.35E-04 /mile- year * (5 feet/5280 feet/mile) = 2.22E-07 / yr.

Note: This use of the mean failure data for this evaluation is adequately conservative as the exposure time (in service time) is set to an entire year versus the actual operating time (expected to be significantly less). Further, with the exception of the CSTR, the components are fabricated out of Schedule 160 pipe whereas the failure rate data is representative of all pipe schedules.

The likelihood of events resulting in more severe accident conditions than analyzed (higher temperatures and pressures) require additional process upsets and failures and are thus bound by this likelihood. Similarly upset events would have to greatly exceed the maximum allowable working pressure or temperature to result in a catastrophic failure; these events are protected by overpressure and over temperature controls, thus are thus bound by this likelihood.

3.4.2 Pressure Vessel Burst Scenarios

The hazard analysis identified scenarios as resulting in pressure vessel bursts (PVBs) in the MHTLS process vessels.

Of these events, consequences for the Filter Vessels are further presented here. These vessels 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)

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:

Explosion Energy, $E_{ex,Br} = (p_1-p_0)V1/(\acute{Y}_1 -1)$

Where:

$\acute{Y}_1$ = 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 $E_{ex,a} = 0.4 * E_{ex,Br}$

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

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

Where:

R= distance to receptor
p_0 = atmospheric pressure

The scaled pressure $\overline{P}_s$ and impulse $\overline{I}_s$ 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:

$$P_S = k_p * \overline{P}_s * p_0$$

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

Where:

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

Scaled dist. $\overline{R}$	$\overline{R}$< **0.3**	$\overline{R}$< **3.5**	$\overline{R}$> **3.5**
k_P	4	1.6	1.4

Scaled dist. $\overline{R}$	$\overline{R}$< **0.3**	$\overline{R}$< **1.6**	$\overline{R}$> **1.6**
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.

3.4.2.2 PVB Results

For the filter vessel, it is assumed the nitrogen pressure is at the maximum system pressure, 3500 psig (MHTLS-RPT-001, Rev. 0, Table 4). This is a reasonably conservative assumption as this is a higher pressure than the typical operating pressure (~2800 -3000 psig). It was further assumed that the filter vessel contained only nitrogen (the presence of incompressible fluids would reduce the consequences) and the nitrogen temperature was ambient (22.5 °C) which maximizes the energy potential.

<u>Input Assumptions:</u>

Pressure State 1	3500 psig	24.127 MPa
Pressure State 0	14 psi	0.1 MPa
Temperature of gas	73°F	22.5°C
Volume of Filter	5 liters	0.005 m^3
Specific Volume	0.00395 m^3/kg	
$Ý_1$	1.40	
Speed of sound in air, a_0	340 m/s	

Thus from above:

$$E_{ex,a} = 0.4 * E_{ex,Br} = 240E+03 \text{ joules}$$

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 (m)	**3**	**5**	**7**	**10**	**15**

scaled distance $\overline{R}$, m	**2.3**	**3.0**	**5.25**	**7.5**	**11.3**
P_s, kPa	**30.4**	**12.3**	**8.1**	**5.1**	**2.6**
I_S, Pa-s	**0.036**	**0.019**	**0.013**	**0.009**	**0.006**

The maximum likely range of fragments calculated using the CCPS, 2010 method was determined to be ~ 97 meters. As noted in Section 3.4.1.1 and 3.4.3 this distance is judged to be a very conservative estimate.

3.4.3 Calculation Summary

Comparing the calculated overpressures from the above conservative analyses to the damage estimates of Table 3-9 shows that a failure of the filter vessel resulting in a BLEVE or PVB could have significant impacts. However, significant overpressures which could challenge a building structure (greater than 21 kPa) are only developed at distances of less than 5 meters. Overpressures sufficient to result in greater than minor damage (7 kPa) were only reached at distances of less than10 meters.

For missile generation, the CCPS, 2010 methodology conservatively estimates missile ranges out to ~97 meters, for the limiting case. As noted, this calculation ignores several physical properties associated with the event. Further, DOE/TIC-11268, Table 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 (1.7E+07 foot-pounds) which is ~60 times greater than calculated energy available for the limiting case.

For all events analyzed, the design of the MHTLS components (use of corrosion resistant ductile material, tubing, and thick wall vessels) makes the catastrophic failure and missile generation very low likelihood scenarios.

Table 3-9. Damage Estimates for Common Structures Based on Overpressure

Pressure		
kPa	psig	Damage
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, as presented below

Lees' 2012 **"**Table 17.28- Typical Values of Failure Pressures in Building Structures"

	Failure Pressure (kN/m2) [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 at70, destroyed at 105

It has been suggested by Buckland (1980) that the explosion pressure should not exceed 21 kN/m^2 if the building is to avoid serious damage.**"**

4.0 HAZARD CONTROLS

4.1 Critical Controls

This section describes the attributes of the controls (Table 4-1) identified in the hazard analysis required to provide protection against the high consequence hazards associated with the MHTLS process as addressed in Section 3.3

Table 4-1 Initial Critical Hazard Controls

Hazard Control	Event Type	Representative Event ID
Vessel Design	BLEVE /PVB	4b2.2, 6.1, 7.1, 7.5, 8.1-2, 8.1-4,
Overpressure Protection	BLEVE /PVB	4b1.4, 6.10, 9c2.3
Process High-High Temperature Protection	BLEVE /PVB	4b2.3, 5.3, 6.7, 7.5

4.1.1 Vessel Design

<u>Safety Function:</u>

The following vessels are designed with a Maximum Allowable Working Pressure (MAWP) of 3500 psig to ensure the pressure integrity of the process boundary for normal operations and upset conditions.

Vessel		Volume (liters)	Over Pressure	Over Temperature	Comments
BD-1	Blowdown Vessel 1	3	PSV-2509	NA	
BD-2	Blowdown Vessel 2	3	PSV-2510	NA	
F-1	Solids Removal Filter 1	5	PSE-2404	TIS-2407B	
F-2	Solids Removal Filter 2	5	PSE-2405	TIS-2408B	
R-1	CSTR	2	PSE-2219	TIS-2220B	
R-2	Separator Vessel	5	PSE-2409	TIS-2410B	

<u>System Evaluation and Configuration Control:</u>

Sizing (volume) of the vessels as identified above and MAWP of 3500 psig provides assurance that the accident analysis is adequately conservative.

The vessel design in accordance with ASME Section VIII and use of ductile and corrosion resistant material for construction of the vessels reduces the likelihood of catastrophic failure and provides consistency with the assumptions underlying the frequency evaluation in the accident analysis.

Inspection of the vessel shall be in accordance with PNNL HDI Pressure and Vacuum Systems requirements to provide consistency with the assumptions underlying the frequency evaluation in the accident analysis.

4.1.2 Overpressure Protection

Safety Function:

All vessels identified in Section 4.1.1 are provided overpressure protection at a setpoint equal to the MAWP of 3500 psig or less to ensure the pressure integrity of the process boundary for upset conditions.

System Evaluation and Configuration Control:

The overpressure protection systems design in accordance with ASME Section VIII and API 521 and setpoint, equal to the maximum allowable working pressure (MAWP) for the vessel, of 3500 psig provides assurance that the vessel pressure boundary is protected. The accident analysis is sufficiently conservative to account for normal acceptance tolerances in the setpoint determination and any pressure relief overpressure.

Inspection and calibration of overpressure protection devices shall be in accordance with PNNL HDI Pressure and Vacuum Systems requirements to provide consistency with the assumptions underlying the frequency evaluation in the accident analysis.

4.1.3 Process High-High Temperature Protection

Safety Function:

On each vessel identified in Section 4.1.1 that is provided with an external (non-process) heat source, an independent high-high temperature interlock (425 °C) is provided to isolate power to the external heater to ensure the pressure integrity of the process boundary for upset temperature conditions.

System Evaluation and Configuration Control:

The vessel high-high temperature interlock protection setpoint, equal to the maximum allowable working temperature (MAWT) for the vessel, of 425 °C, measured on the heater block boundary, provides assurance that the vessel pressure boundary is protected from elevated temperatures. The use of the heater block versus the vessel skin for the shutoff temperature and conservative accident analysis provide additional margin against exceeding the vessel MAWT.

Calibrated thermocouples are used for the independent high-high temperature protection system and the output is compared with process thermocouples output to provide additional assurance of proper operation.

5.0 CONCLUSION

What-If hazard analyses were performed to support the MHTLS process. The hazard analysis 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 analysis identified the hazard controls which would prevent or mitigate the release. For high-energy events which could have high unmitigated consequences outside immediate operating area (e.g., high energetic events), the analysis was 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 and other hazardous 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*) are identified in the hazard analysis tables.

The identified critical hazard controls provide assurance of the safety of the design of the MHTLS consistent with PNNL Safety Management Program expectations. Analysis of the risks posed from operation of the MHTLS demonstrates that the system can be operated safely and is consistent with the risk posed by 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.

American Petroleum Institute (API), Standard 521, *Pressure-relieving and Depressuring Systems*

American Society of Mechanical Engineers (ASME), *Boiler and Pressure Vessel Code*, Section VIII, *Rules for Construction of Pressure Vessels*, New York, NY.

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.

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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.

MHTLS-RPT-001, *Functional Design Criteria for Modular Hydrothermal Liquefaction System*, Rev. 0 Table 4, *Process Operating Specifications*. Chemical and Biological Process Development Group, Pacific Northwest National Laboratory

Appendix A: Attendance

Modular Hydrothermal Liquefaction System
Hazard Analysis

Pacific Northwest NATIONAL LABORATORY
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Sign Up Sheet

Tuesday February 17, 2015

Name	Role	Organization	Phone Number
Pete Lowry	Lead	R&DS	2-6573
Erick Flieger	LSD	PNSO	2-4606
Dan Anderson	PM	PNNL	5-4406
Tyler Gilmore	PMOD	PNNL	1-7171
David Rohrig	Pressure Safety	PNNL	1-2690
Vicki L. Stephens	EEDOps.	PNNL	5-3883
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Renee McGaughy	WS+H	PNNL	5-2971
Sharon Bailey	Design team	PNNL	5-2243
Scott S. ALLEN	EED TECH OPS	PNNL	1-7053
Todd Hart	EED - operator	PNNL	1-6509
Ross Cuello	EED Ops	PNNL	5-2848
Andrew Schmidt	Lead Eng	PNNL	5-2280
Rick Orth	TGM	PNNL	5-6709
Katie Wagner	Scribe	PNNL/EA	5-2387

Modular Hydrothermal Liquefaction System
Hazard Analysis

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Thursday February 19, 2015

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Modular Hydrothermal Liquefaction System
Hazard Analysis

Sign Up Sheet

Friday February 20, 2015

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Modular Hydrothermal Liquefaction System
Hazard Analysis

Sign Up Sheet

Thursday July 28, 2016

Name	Role	Phone Number
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Vicki Stephens	EED Ops. O&E	375-3883
Mike Elliott	PNNL	372-4324
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Appendix B: Key Design Information Reviewed

Key Design Information Reviewed
(July 2016 HA Meeting)

HTL SYSTEM Block Diagrams **(Includes Business Sensitive Information)**	PFDs for Ops HA_7_27.pptx
HTL SYSTEM P&IDs **(Includes Business Sensitive Information)**	782-10 PnIDs REV 0_ppla.pdf
Functional Design Criteria for Modular Hydrothermal Liquefaction System	MHTLS-RPT-001, revision 0
Vessel Design Drawings: (G.A and Details) **Filter Vessels** **Separator Vessel** **Blowdown Vessels** **CSTR**	 782-10-F-1 & F-2, Rev 1 782-10-V-2, Rev 1 782-10-V-4/V-5, Rev 1 QW16051-01

Appendix C: Preliminary Hazard Assessment

MHTLS Initial Hazard Identification – Major Components

	Component	Volume	Comments
ML-1	Cutting Mill		
HS-1	Homogenizer Vessel	50 gal	
ML-2	Immersion Mill	32 gal	The mill itself will likely be less than 5 gal
P-1	LP Pump		4 gpm, 60 psi
TK-1	Feed Staging Tank	250 gal	
P-2	LP Pump		0.9 gpm, 60 psi
TK-2	Feed Day Tank	55 gal	
P-3	LP Pump		
P-4A/B	HP Pump		(510 ml cylinder) 24 L/hr , 5000 psig
P-5A/B	HP Pump		(510 ml cylinder) 24 L/hr , 5000 psig
H-1	Feed Product Heat Exchanger		0.5 in. tubing inside 0.75 in shell x 1-5 ft
H-2	Feed Preheater **Configuration 2 only**		0.375- in tubing encased in block heater
R-1	Continuous Stirred-Tank Reactor **Configuration 2 only**	2 L	
H-3	Reactor #2 Trim heater		4 - 4 ft long 1/2- in (0.065 wall) tubing encased in block heater.
H-4	Plug Flow Reactor		12 – 12 ft long 1/2- in (0.065 wall) tubing encased in block heater
F-1	Filter 1	5 L	3-in Schedule 160
F-2	Filter 2	5 L	3-in Schedule 160
R-2	Separator	5 L	3-in Schedule 160
BD-1/ 2	Blowdown Vessel	3 L	3-in Schedule 160
TK-3	Blowdown Receipt Tank	16 L	
C-1	Product Trim Cooler		0.5 in. tubing inside 0.75 in shell x 15 ft
C-2	Cooler **- Configuration 2 only**		Air cooled heat exchanger
TK-4	Relief Knock Out Vessel	15 gal	
S-1	Gas Separator	7.5 L	10 psig
S-2	Product (Oil/Water) Separator	24 L	10 psig
V-3	Aqueous Byproduct Buffer	5 L	10 psig
TK-5	BioCrude Storage Tank	55 gal	HDPE drum
S-3	Oil Recovery Separator	1.6 L	2-in Schedule 10, 24-in. long.
TK-6	Aqueous Byproduct Storage	500 gal	
P-7	Pump to Coalescer		1 gpm
TK-7	Bulk Liquid Collection (Drain Waste) Tank	275 gal	
P-8	Aqueous Byproduct Pump		8 gpm, 60 psig
C-3	Vent Cooler		10 psig
V-9	H2S Scrubber	30 gal	

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Feed Prep -1			
ML-1 Cutting Mill: Size-reduce dry or wet particles from 20 mm to < 1 mm			
Interface: The cutting mill will be manually loaded and the milled output stream will be manually collected and transferred to other operations in the Feed Preparation, Staging, and Delivery area.			
Inventory (material):	Low	low-moisture particulate solids (e.g., wood chips, corn stover, wheat straw, dried algae, etc.)	No
Pressure:	Ambient	No pressurization mechanism identified	
Temperature:	Low	No mechanism for rapid temperature excursion	
(other)	Dust explosion	Using existing cutting mill with shop vac for dust control (5-6 yrs operational experience); larger particles will be contracted out (Idaho –feed stock logistics); if mill is scaled up, will implement additional NFPA 654 controls	
	Noise	105 decibels @ 10 feet, – post hearing protection sign	
Location		existing one in high bay	

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Feed Prep -2			
HS-1 Homogenizer Vessel: Disintegrate larger agglomerates to form pumpable slurry. Homogenize feedstock through high-shear mixing			
ML-2 Immersion Mill: Wet-grind the feed stream to produce a pumpable and stable suspended slurry. The particle size will be reduced from ~1000 microns to a volume-mean particle size of 20 to 50 microns.			
P-1 Pump 1 and Piping for Homogenizer/Immersion Mill Recirculation: Recirculate slurry during homogenizing/immersion milling. Transfer milled slurry to Feed Staging Tank. Discharge Pressure 60 psig.			
Interface: Sodium carbonate addition; water or HTL aqueous product (from aqueous product storage tank TK-6)			
Inventory (material):	Low	Feedstock Wet Slurry (may add Na2CO3 manually – may be dissolved prior)	No
Pressure:	Low	Vessels operated at Ambient – Low – Output Pump 1 **(60 psig**)	
Temperature:	Low	No mechanism for rapid temperature excursion	
(other)		Moving/rotating parts – guards/posting signs	
		Manually moving/loading material (5 gal buckets; ~40 lbs) – repetitive lifting criteria	
		Outdoor electrical; wet/damp locations	
		Noise (unknown decibels)	
Location		Utilities; 55 gal drums on wheels; wet/damp locations; solid surface to roll drums or port on bottom of tanks so they don't have to be moved	

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Feed Prep -3			
TK-1 Feed Staging Tank: Provide capacity to contain nominally or 220 gal of feed from Homogenizer vessel. Provide batches of slurry to Feed Day Tank (TK-2). Located on Skid 1.			
P-2 Pump 2 and Piping for Feed Staging Tank: Transfer milled slurry to Feed Day Tank. Discharge Pressure 60 psig. (functionality may be combined into Pump 1)			
Interface: Vent to (outside environs) Sodium carbonate addition; water			
Inventory (material):	Low	Feedstock Slurry	No
Pressure:	Low	Vessels operated at Ambient – Low – Output Pump 1 **(60 psig**)	
Temperature:	Low	No mechanism for rapid temperature excursion	
(other)		Tank will need venting for non-hazardous (nuisance) odors (hook up to system with snorkel/mechanical ventilation)	
Location		Need ventilation utility; if no active ventilation, nuisance odor	

Preliminary Hazard Assessment

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Evaluation Area: HTL Processing-1			
Feed Day Tank (TK-2): Provide capacity to contain nominally 38 gal of feed. Provide slurry feed to low-pressure pump.			
Low Pressure Feed Pump (P-3) and Piping: Provide slurry to high-pressure pump. Recirculate/mix slurry in feed tank. Empty feed day tank at termination of run. Discharge Pressure 60 psig.			
Interface: Vent to (outside environs). Sodium carbonate addition (at the feed skid preparation).			
Inventory (material):	Low	Feedstock Slurry	See prior evaluation
Pressure:	Low	Vessels operated at Ambient – Low – Output Pump 1 **(60 psig**)	
Temperature:	Low	No mechanism for rapid temperature excursion	
(other)			
Location			

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Evaluation Area: HTL Processing-2			
P-4 High-Pressure Pump for Feed and Piping: Pressurize liquid slurry from atmospheric pressure to 2900 psig. Provide means to measure rate of pressurized feed delivery.			
P-5 High-Pressure Pump for Water: Pump water to Feed/Product Heat Exchanger. Provide redundant capability to high-pressure feed pump (P-4). Provide means to measure rate of pressurized feed delivery.			
Interface: Building Water, Low Pressure Feed Pump, Back Flush Line			
Inventory (material):	Low	Process Slurry (volume-mean particle size of 20-50 micron) , water	No
Pressure:	High	Interface Low/high pressure; PRV system downstream of the pump; pump set to auto shutoff at nominal 3100 psig.	
Temperature:	Low	No mechanism for rapid temperature excursion; jacketed cylinder with recirculated water to heat if needed ~60C water h	
(other)			
Location		No need for physical boundary; building water source needed; minimal odor	

Preliminary Hazard Assessment

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Evaluation Area: HTL Processing-3			
Back Flush Line: Allows blow down of H-1 or H-2 to remove line blockage by provided routing to blowdown tank 2 (BD-2). Manual operation of line.			
Interface: HP Pump/Feed Preheater and Blow Down Tank. Nitrogen System			
Inventory (material):	Low	Process Slurry, water, nitrogen	Yes – similar to filter blow down
Pressure:	High		
Temperature:	High		
Nitrogen		Interface is located upstream of BPR	
(other)			
Location		Coupled as closely as possible with blow down tank	
Evaluation Area: HTL Processing-4a			
H-1 Feed/Product Heat Exchanger: Configuration 1 only. Heat pressurized slurry from room temperature to 300 to 325 °C, through heat exchange with filtered product stream (counter-current tube-in-tube heat exchanger).			
Interface: Low temperature (25 °C) to high temperature (300 to 325 °C)			
Inventory (material):	Low	Process Slurry	Yes
Pressure:	High	PRV located on front end of pump	
Temperature:	High	Jacketed insulation on main body	
(other)			
Location		Having good straight runs of tubing to minimize plugs;	

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**

Evaluation Area: HTL Processing-4b

H-2 Feed Preheater: Configuration 2 only. Heat feed slurry from 25 to 150 °C to reduce heating load on CSTR.

CSTR and Associated Heating System: Configuration 2 only. Provide aggressive mixing and heating to aid in transition from slurry to liquefied product. Provide capacity to heat slurry from 140 to 325 °C.

Interface: Addition of oil

Inventory (material):	Low	Process Slurry Liquefied product – aqueous bio-oil mixture; inorganic salts precipitating out (Calcium phosphate/calcium sulfate) – condensed CO_2	Yes
Pressure:	High		
Temperature:	High		
(other)		CSTR is electrically heated; 750 rpm (magnetically coupled)	
Location			

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: HTL Processing-5			
H-3 Trim Heater: Configurations 1 and 2. Heat slurry from 300 to 350 °C. Heat skid components during startup. Final heat-up.			
H-4 Tubular Reactor Section: Provide requisite residence time at reaction temperature (350 °C) and pressure (3000 psig, nominal) while maintaining slurry at a velocity sufficient to minimize particulate settling. Heat slurry from 340/350 °C and maintain slurry at 350 °C			
Interface: Thermal expansion of materials			
Inventory (material):	Low	Process Slurry/ Liquefied product – aqueous bio-oil mixture; inorganic salts precipitating out (Calcium phosphate/calcium sulfate) – condensed CO_2	Yes
Pressure:	High		
Temperature: (other)	High	Electrical resistance heating	
Location		Same as previous area	

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Evaluation Area: HTL Processing-6			
F-1&F-2 Filter/Housing for Solids Removal: F-1 is operated for all runs and F-2 operation is optional. Remove solids/precipitate from liquefied stream, down to 20 microns. Promote particle settling. Provide capability to maintain product slurry temperature at 350 °C. Provide means to address ΔP increases across filter element. Provide means for removal of accumulated solids, with filter remaining online. Run with single or two filters in parallel; depends on ash content. Centered screen filter.			
Interface: Blowdown vessels			
Inventory (material):	Low	Liquefied product – aqueous bio-oil mixture; inorganic salts precipitating out (Calcium phosphate/calcium sulfate) – condensed CO_2	Yes
Pressure:	High	Positive isolation for F-2 filter if not in use.	
Temperature:	High		
(other)		Electrical heating capability	
Location			
Evaluation Area: HTL Processing-7			
Separator Vessel (R-2): Provide a device for the separation of aqueous phase from organic compounds. Maintain temperature of HTL product stream at 350 °C. Reducing carbon content in aqueous phase.			
Interface:			
Inventory (material):	Low	Liquefied product	Yes
Pressure:	High		
Temperature:	High		
(other)		Electrical resistance heating	
Location			

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**

Evaluation Area: HTL Processing-8

Filter Blowdown Vessel (BD-1) & (BD-2): Receive solids from the filter element/filter housing (F1) during the filter blowdowns while being isolated from blowdown slurry receipt tank (TK-2). Reduce blowdown slurry temperature (≤80 °C). Provide means/logic to discharge cooled slurry to blowdown slurry receipt tank (TK-2) while isolated from the filter housing (F1). BD-2 will be configured to receive flow from either F-2 or from the Back Flush Line.

TK-3 Blowdown Receipt Tank: Remain isolated from the blowdown vessel (BD-1) during normal operation. Receive slurry (≤80 °C) from the blowdown vessel (BD-1) when it is emptied/flashed to atmospheric pressure. Provide means to offload tank to portable accumulation vessel (e.g., tank, drum, bucket).

TK-4 Pressure Relief Vent Header and Knock-out Vessel: All pressure release systems will be routed to TK-4 for safe receipt/containment of steam/water/slurry surge in event of activation of a pressure relief line. Protect vessel from overpressure by a vent to atmosphere. Vessel may be tipping drum.

Interface: High pressure and temperature to atmospheric pressure and low temperature (≤100 °C). Nitrogen purge. Manual loading of TK-3.

Inventory (material):		Process Slurry Liquefied product Some gas	Yes
Pressure:	High		
Temperature:	High		
Nitrogen (other)			
Location		Blow down receipt tank (TK-3) routed to skid vent system	

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Evaluation Area: Evaluation Area: HTL Processing-9a			
H-1 Feed/Product Heat Exchanger: Configuration 1 only. **Addressed Evaluation Area 4a**			
Interface			
Inventory (material):			
Pressure:			
Temperature:			
(other)			
Location			
Evaluation Area: HTL Processing-9b			
Product Cooler (C-2): Primary cooling unit for Configuration 2. Provide required cooling of product stream from 350 to 100 °C.			
Interface: High temperature (350 °C) to moderate temperature (100 °C); Oil, Building Water, Air			
Inventory (material):	Low	Liquefied product	Yes
Pressure:	High		
Temperature:	High		
(other)		Uses forced air cooling.	
Location			

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**

Evaluation Area: Evaluation Area: HTL Processing-9c

Product Trim Cooler (C-1): Used in Configuration 1 and Configuration 2. Provide cooling/temperature control of product steam to optimize operation of the backpressure regulator (i.e., cool product from about 100 to 50 °C).

BPR Back Pressure Regulator: Provide stable operating pressure for the MHTLS. Reduce HTL operating pressure to atmospheric or near atmospheric pressure.

Interface: Building water

Low	Liquefied product		
High			
Moderate			
	Stand alone chiller unit		

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**

Evaluation Area: Product Separations-1

Gas Separator (S-1): Provide volume and residence time to separate gases from liquids. Provide means to knock down foam and capture aerosol from the gas phase.

Pump to Oil/Water Separator (P-6) (optional): Continuously transfer liquids from gas separator to oil/water separator. Depends on staging; prefer gravity feed

Interface: Carbon Dioxide, Foam (mostly dissipates in 1 minute), Demister, Gas Vent

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Inventory (material):	Low	Biocrude liquids; aqueous by-product (water) , gases (CO2)	Interface boundary defined at BPR (impact of BPR failures considered)
Pressure:	Low		
Temperature:	Low		
Carbon Dioxide		High percentage of all feed stocks (>90%); reduces flammability concern	
Oil Foam		Can be carried over to off gas line	
H2S		Generated when significant sulfur in feed (algae); feed strains not run on large scale without bench testing? (0.5%)	
VOCs		Varies based on feed stock	
(other)		m	
Location		Located on Skid 3; pressure relief prior to system. Capability of H2S abatement	

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Product Separations-2			
Oil/Water Separator (S-2): Separate biocrude from aqueous byproduct via differences in density, viscosity, surface tension. Ability to control temperature to manipulate physical properties that affect oil/water separation.			
Aqueous Byproduct buffer (Zeton ID V-3): Separate aqueous byproduct and gas to maintain proper leves in Oil/ Water Separator			
Interface: Gas Vent			
Inventory (material):	Low	Biocrude; aqueous byproduct	No- will be addressed upstream
Pressure:	Ambient		
Temperature:	Low		
(other)		Some gas evolution potential (CO2)	
Location			
Evaluation Area: Product Separations-3			
Pump to Coalescer (P-7): Continuously transfer aqueous phase with disbursed oil from oil/water separator to coalescer.			
Oil Recovery Separator/Coalescer (S-3): Capture dispersed/emulsified biocrude from aqueous stream, when needed.			
Interface: Biocrude will be manually collected and moved to the Biocrude Storage Tank (TK-5); bypass line to aqueous collection tank (TK-6)			
Inventory (material):	Low	Biocrude; aqueous byproduct	No
Pressure:	Low		
Temperature:	Low		
(other)	Low	Option to heat line – heat trace (<100C)	
Location			

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Product Separations-4			
Biocrude Storage Tank (TK-5): Provide capacity to contain all biocrude generated during a 120-h run at the 70% fill level.			
Interface: Vent to (outside environs), Electrically bonded/grounded, Secondary Containment			
Inventory (material):	Low	Bio-oil high flash point (>100C)	No
Pressure:	Ambient		
Temperature:	Low to Moderate		
(other)			
Location			
Evaluation Area: Product Separation-5			
Aqueous Byproduct Storage Tank (TK-6): Provide capacity to contain all aqueous byproduct during a 120-h run, 70% fill level. Provide routing to feed preparation area, to allow recycle of aqueous product in feed makeup. **Aqueous Byproduct Pump (P-8)**: Transfer aqueous byproduct to milled slurry to Feed Staging Tank in 20- to 30-gal batches. Transfer aqueous product into container for final disposition.			
Interface: Vent to (outside environs), Optional Load Cell			
Inventory (material):	Low	Aqueous Byproduct	No
Pressure:	Low		
Temperature:	Ambient		
(other)			
Location			

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Product Separation-6			
Clean-out Storage Tank (TK-7): Provide capacity to contain tank and equipment flushes during set up and clean up after a 120-h run, 70% fill. Clean-out post operations.			
Interface: Vent to (outside environs)			
Inventory (material):	Low	Equipment flushes (water, slurry, biocrude, aqueous byproduct)	No
Pressure:	Ambient		
Temperature:	Ambient		
(other)			
Location			

Appendix D: Design Guidance to Support the Evaluation of Secondary Impacts from High Consequence Low Frequency Events in MHTL

This appendix provides guidance which addresses the effects associated with successive system failures due to a BLEVE event within an MHTLS vessel. For the purpose of this evaluation a process vessel includes major process equipment with significant volumes (CSTR reactor, filters, separator and blowdown vessels,); piping, tubing, and pumps are not included. The estimated likelihood of a BLEVE failure in the MHTLS is expected to be extremely low 2.2E-07 per yr (much less than 1E-5/yr, as discussed in the risk assessments for the Hydrotreater and Distillation Columns). However, to ensure there are no “cliff edge” effects, where the consequences significantly increase, due to subsequent impacts of the BLEVE on other MHTLS components, the following additional scenario was considered:

- BLEVE failure of a vessel resulting in the BLEVE failure of a second vessel due to shrapnel or pressure impacts

Implementation of this guidance by the design organization will increase the confidence that a multiple BLEVE event is significantly less likely to result in additional subsequent damage or adverse effects compared to the events analyzed in Section 3.4 of the main body of the report.

D.1 BLEVE Resulting in a Subsequent BLEVE

Several instances of a BLEVE initiating a subsequent BLEVE event have been documented in Case Histories[1]. Most multiple BLEVE accidents involve flammable material; however, in this evaluation, no distinction was typically made if impacts (missile), pressure, or thermal degradation was the primary failure mechanism. Impacts of missiles from flammable storage vessels have been identified as resulting in subsequent fires as well as the direct damage caused by the impact energy.

For a vessel containing non-flammable material, the blast effects (overpressure and missile generation) from a secondary BLEVE are expected to act as an independent event from the first BLEVE. From Serrano[2], for a railcar analysis, propane may have different release behaviors. It may be released as a jet fire, vapor cloud explosion, BLEVE, or flash fire. Jet fire and BLEVE events should be considered only for one car because their effects cannot be combined when more than one car is involved. However, pool fire, vapor cloud explosion, and flash fires depend on the number of cars released, which means, if two cars are involved in the accident and they are releasing the content as a pool fire, the area affected would be greater than if only one car is involved."

For the MHTL, a liquid filled system, the time following the initial BLEVE, including missile generation and travel, impact and failure of the secondary vessel and then subsequent flashing of the liquid would be expected to be on the order of 50 ms to > 1 second, depending upon the superheat within the system (Birk[3]). Note: This requires the missile impact to catastrophically fail the tank such that it is fully opened to release its contents nearly instantaneously. For less damaging events, (cracks, partial failures), the timeframe to BLEVE could be on the order of 3 seconds. From Birk "… very long-duration BLEVEs of stronger tanks are possible, and these are driven by violent boiling or possibly superheat limit-type explosive boiling in the tank after initial tank failure." These events represent the transition from a BLEVE to a non-BLEVE, and are representative of the conditions for the MHTL.

Additional mitigating factors reducing the consequences of a secondary BLEVE in the MHTLS would include the reduction in pressure in the system due to the initial BLEVE (release of liquid through the transfer piping) and the conservative nature of the calculation used for the BLEVE. Analysis of the secondary vessel consequence at reduced parameters (3000 psi and 368 °C, critical temperature) would reduce the energy available by approximately 50%.

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[1] Abbasi, S.A, and Tasneem Abbasi, *The boiling liquid expanding vapour explosion (BLEVE): Mechanism, consequence assessment, Management,* Journal of Hazardous Materials, 1*41 (2007)*

[2] **TRB 14-5296**, *Methodology to Evaluate the Consequence of Hazardous Material Releases from Multiple Tank Cars Involved in Train Accidents*, Jesus Aguilar Serrano et al, Rail Transportation and Engineering Center Department of Civil and Environmental Engineering University of Illinois at Urbana-Champaign *Submitted for Presentation at the 93rd Annual Meeting of the Transportation Research Board 7 and Publication in Transportation Research Record,* August 1, 2014

[3] Birk, A.M. and M.H. Cunningham, *The boiling liquid expanding vapour explosion*, Journal of Loss Prevention in the Process Industries 1994. Volume 7, Number 6.

Thus, from a determination of maximum overpressure and the potential for missile generation and travel, the initial BLEVE is the limiting event; however, the additional impacts of a secondary "domino" event are also considered. Therefore, design guidance has been developed to reduce the probability of a secondary BLEVE and subsequent impacts given a BLEVE in the initial (primary) vessel.

Given a primary event (BLEVE) the probability of a secondary (domino) BLEVE can be expressed as[1,5]:

$$Pdomino = P_{gen} * P_{imp} * P_{rup}$$

where

- P_{gen} is the probability of the fragment (with defined mass, shape and initial velocity) to be generated in the primary event;
- P_{imp} is the probability of impact between the fragment and a target;
- P_{rup} is the probability of target damage given the impact with the fragment.

Design considerations for each of the above areas of concern follow.

D.1.1 Primary Vessel Fragment Generation

For fragment (missile) generation, a key design consideration is material selection (strength ductility). Ductile materials will generally result in the formation of fewer larger fragments; whereas, brittle material will tend to form smaller and more fragments. High strength materials also serve to reduce the number of fragments as well as the likelihood of the BLEVE, as the pressure will have time to relieve as the crack develops. In one study of 30 propane tanks, in which the tanks were deliberately subjected to fire sufficient to generate local failures (cracks), only about 50% of the ruptured tanks resulted in a BLEVE[2].

The following design considerations are provided:
The use of high-strength, ductile, materials of construction for process vessels is recommended. Further, as crack growth and propagation has been demonstrated in areas of residual stress associated with welding and over working materials, limiting these actions or providing stress relief should be considered.

D.1.2 Fragment Impact with Target

Multiple studies have shown that orientation of cylindrical vessels and separation between the initiating vessel and target vessel is important in determining the likelihood of a secondary vessel BLEVE. For cylindrical vessels, the potential for missile generation has been shown to be the greatest in the axial direction, with approximately 50% of the missile fragments occurring within a 30° degree cone along the axial direction of the vessel[3]. Simplified models[4] for the assessment of the impact probability of fragments have also been developed. The probability of an impact based on distance to the target vessel is given in terms of "equivalent" vessel

[1] G. Gubinelli et al. *Journal of Hazardous Materials A116 (2004) 175–187*
[2] A. M. Birk and M. H. Cunningham, *The boiling liquid expanding vapour explosion*: J. Loss Prev. Process Ind., 1994, Volume 7, Number 6
[3] T. Abbasi, S.A. Abbasi, *Journal of Hazardous Materials* 141 (2007) 489–519
[4] D. Sun et al. *Journal of Loss Prevention in the Process Industries* 35 (2015) 211-223

diameters. For a cylindrical vessel the equivalent diameter is the diameter of a spherical vessel having the same volume. The study is based on vessels in use in the process industry which are much larger in size, and is considered conservative with respect to the key attributes of the MHTLS. The study was based on larger vessels expected to generate more fragments; with larger volumes of flashing liquids - equating to higher initial velocities; ignores the directional bias of cylindrical vessels, and includes larger target vessels.

Bounding probabilities from this study are presented below.

Target Distance	Impact Probability
D	0.09837
2D	0.03155
3D	0.02334
4D	0.01945
5D	0.0185
6D	0.01536
7D	0.00928
8D	0.00649
9D	0.00571
10D	0.00461

D is primary vessel equivalent diameter.

The following design considerations are provided:
Do not locate pressurized process vessels within a 30° cone in the axial direction of pressurized vessels, unless otherwise protected.

Provide sufficient distance "e.g., 2D-3D" or other protective measures between process vessels to significantly reduce the probability of an impact.

D.1.3 Target Rupture

Sun[1] provides an assessment of the rupture probability of an impacted target. Rupture probabilities are shown to be relative to the distance (source size) from the independent vessel until approximately 14 vessel diameters. However, the source orientation is also a factor with vertical cylindrical vessels resulting in the greatest risk of rupture of an impacted target vessel of approximately 50%.

The following design considerations are provided:
Similar to the generation of missiles, the use of high-strength, ductile materials will reduce the likelihood of rupture given a strike.

[1] D. Sun et al. *Journal of Loss Prevention in the Process Industries* 35 (2015) 211-223