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Hydrothermal Liquefaction Treatment Preliminary Hazard Analysis Report

August 2015

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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.

Executive Summary

A preliminary hazard assessment was completed during February 2015 to evaluate the conceptual design of the modular hydrothermal liquefaction treatment system. The hazard assessment 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. This 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:

- For 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. For 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.
- For energetic releases (BLEVE/PVB, flashing spray release), the initial set of “critical controls” were identified in Section 4 to prevent the occurrence or mitigate the effects of the release.

Additional guidance to the design organization was provided in July 2015, Appendix D, to provide considerations in order to minimize the likelihood of subsequent BLEVE events (domino failures) during the detailed design phase.

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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. For PNNL operations, a Siting Evaluation will be conducted as part of the design effort to determine the preferred location of the MHTLS on the PNNL campus and to identify interfaces associated with the facility/site systems and utilities.

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 as evaluated during the Preliminary and What-If hazard analysis sessions held in February 2015.

1.2 Scope

The Hazard Assessment 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 warranting additional analysis.

For the initial assessment 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 assessment was performed.

The subsequent assessment included 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 conceptual design information available at this time. The hazard evaluation postulated scenarios involving both single-point/event failures and common-cause initiators. The upset conditions with the potential to result in highly energetic releases or potential deflagrations were evaluated using quantitative analysis to determine the potential magnitude of the scenario, including the potential to affect the environment outside 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.

Appendices A and B contain the meeting participant information and design information reviewed during the hazards analysis meetings.

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

2.0 FACILITY AND PROCESS DESCRIPTION

2.1 Site and Facility Layout

The MHTLS processes will be conducted on mobile skids. The HA identified siting related concerns and system interfaces required to ensure operations of the MHTLS safety. These considerations are inputs into the final selection of the PNNL operating location and acceptability offsite locations.

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 designs will serve as the basis for the design of the scaled modular system.

The MHTLS consist of the following major operational areas as shown in Figure 2-1. Note that the operational areas may be 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).

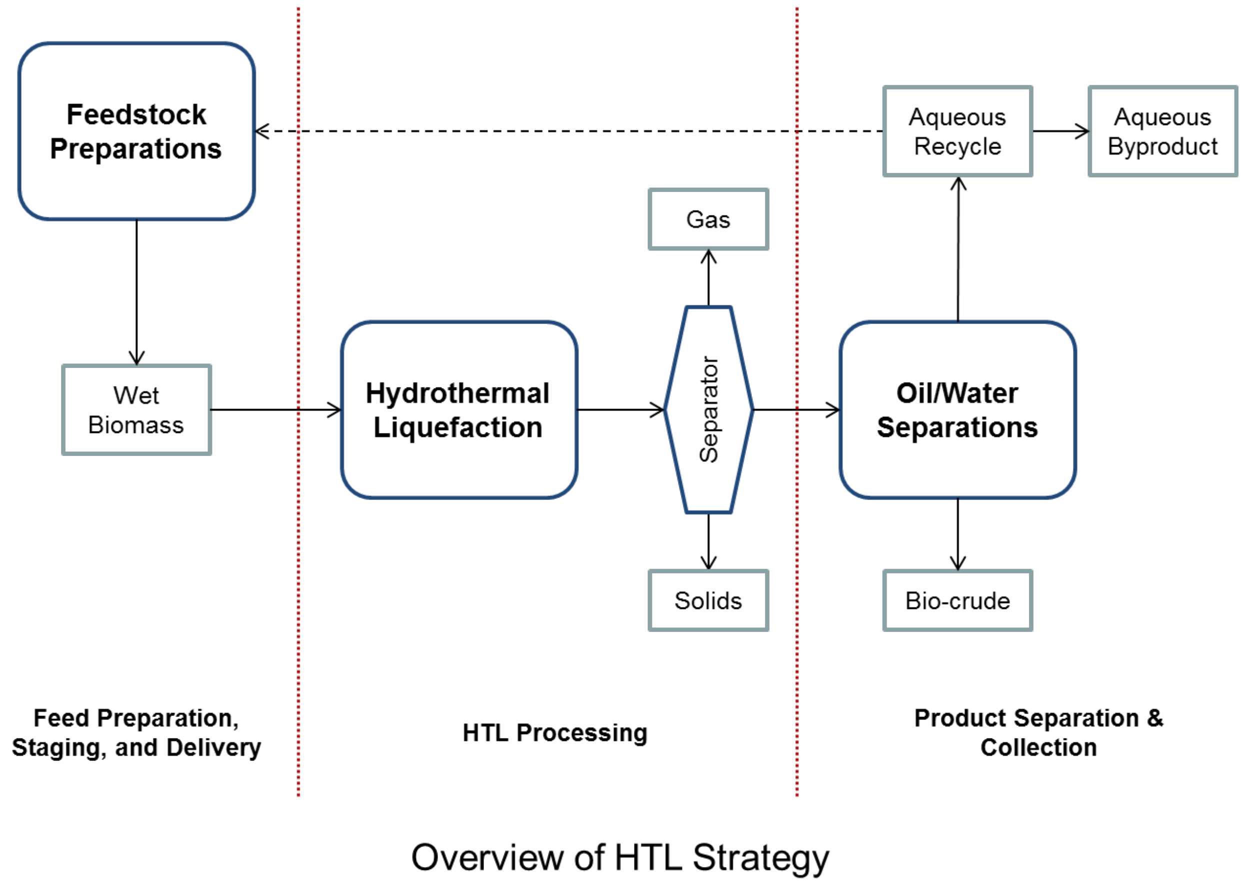

Figure 2-1. –MHTLS Process Overview.

3.0 HAZARD ASSESSMENT

A series of facilitated hazard analysis sessions were conducted in February 2015. The PNNL team assembled for the hazard analysis sessions included R&D operations and engineering; Fire Protection; Pressure Systems; Environmental, Safety and Health; and hazard and safety analysts. PNSO observers also attended the sessions. Appendix A lists the attendees at 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 in this table 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.

Appendix C contains the results of the Hazard Identification and Preliminary Hazards Assessment sessions. 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 Preliminary Hazards Analysis process.

Table 3-1. Inventory Hazard Potential

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

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 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 provided routing to blowdown tank 2 (BD-2). Manual operation of line.
HTL-4a	**H-1**	**1.8 L**	**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).
HTL-4b	**H-2** **CSTR**	**1 L** **2 L**	**H-2 Feed Preheater:** Configuration 2 only. Heat feed slurry from 25 to 150 °C to reduce heating load on CSTR. **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.
HTL-5	**H-3** **H-4**	**0.5 L** **3 L**	**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.
HTL-6	**F-1** **F-2**	**4L** **4L**	**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. .
HTL-7	**R-2**	**3L**	**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.
HTL-8	**BD-1** **BD-2** **TK-3** **TK-4**	**1.5 L** **1.5 L** **12L** **5-20 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-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). Vessel may be tipping drum. **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.
HTL-9a	**C-1**		**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).

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

AREA	Key Components	Volume (Vessels)	Process Function
			BPR Back Pressure Regulator: Provide stable operating pressure for the MHTLS. Reduce HTL operating pressure to atmospheric or near atmospheric pressure.
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.
PS-1	**S-1**	**6 L**	**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. **Included within the scope of WHAT-IF (Processing Area HTL-9a) for to failures in BPR.**

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…”.

As noted in Section 3.0, facilitated hazard analysis sessions were held in February 2015 in support of the conceptual design development and SOW preparation. The What-If sessions focused on the MHTLS processes identified as having significant hazards and interfaces with necessary support “facility” systems.

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 3-5).

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
Unlikely	Conditions involving failure of two or more of the above, mechanical failures of active systems (e.g., pump/motor failures)
Very Unlikely	Multiple failures (more than 2), failures of robust passive systems
Extremely Unlikely	Many concurrent, independent failures

3.3 Analysis Results

The results of the What-If analysis are provided in Table 3-4. For all releases of hazardous material or energy, controls were identified in the hazard analysis table which will prevent the occurrence or mitigate the effects of the release.

Several highly energetic releases (i.e., BLEVE/PVB) were identified. For these events, additional analysis was performed (Section 3.3) to determine the potential magnitude of the impacts from the event to receptor locations for bounding scenarios of each type.

In addition, a number of flashing spray (FS) releases were identified. Note: events resulting in a BLEVE (complete sudden rupture of a vessel) also have the potential to result in a flashing spray release. These events can have serious impacts to MHTLS workers due to direct steam impingement.

A postulated event involving a heat exchanger pressure tube leak impacting the outer tube (shell side) resulted in a spray of oil posing a potential flammability concern.

One action affecting control selection was identified during the What-If analysis for scenarios HTL-4b2.7. This action addresses the potential for thermal shock to the system due to cold water addition or impingement on heated components.

Table 3-4. What-If Hazards Analysis Results

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).

Interface: HP Pump/Feed Preheater and Blow Down Tank. Nitrogen System

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
HTL-3.1	What if valve opens too soon?	Unintentional (early) blowdown in to BD-1. Would have to have additional valves open to result in exposure to personnel	U	Process upset; harder on valves if opened 2 – 1 instead of 1 – 2. Lose option for recovery if valve fails	BD-2 design to contain full system pressure. BD-2 is normally isolated from other vessels with rupture disk to TK-4.	
HTL-3.2	What if valve stays opens too long?	Failure to close valve results in overfilling blow down vessel 2.	L	Pressure will not decrease as 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 MHTL Components due to High Pressure Nitrogen (above system Design Pressure).	U	Flashing spray release	Pressure Regulation of Nitrogen System. PRV 13 Rupture disk (downstream of Trim Heater) Skid design provides spray protection for operators.	
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	Pressure Boundary Skid design provides spray protection for operators.	
HTL-3.5	What if no flow (plug)?	Inability to unplug system	L	Process upset	Alternate methods of operation including filter blow down	

Table 3-4. What-If Hazards Analysis Results

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)

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
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.	Recommendation: Consider skid ventilation provision for nuisance odors.
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	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	PRV-13; 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.	
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 performance (cooling)?	Process fluid is not cooled appropriately	L	Process upset	Controls will be discussed in HTL Processing-9- BPR	

Table 3-4. What-If Hazards Analysis Results

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

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
HTL-4b1.1	What if loss of pressure boundary? (Inner Tube)	Failure of inner pressure boundary pressurizes oil system resulting in loss of pressure boundary; spray release of heated oil plus process fluid up to 160 °C; back flow of warmer material	V	Spray release of heated oil potential - Flammable Atmosphere Flashing Spray Release	Pressure boundary; robust design Skid design provides spray protection for operators.	**Consider Pressure relief on Shell side (located on shell) with relief to appropriate vent path.**
HTL-4b1.2	What if loss of pressure boundary? (Outer Tube)	Failure of outer tube pressure boundary releases oil;	V	Spill of oil. Process upset due to loss of heating	Design of system; 15 psig; System startup operations	
HTL-4b1.3	What if no flow (plug)?	Plugged; Expected design condition	L	Process upset	Heat design option (post-run)	
HTL-4b1.4	What if high pressure?	Pumping at higher than expected pressures results in Failure (upstream of Trim Heater, H-3). Line failure resulting in flashing spray release with fluid temperature range 60 to 150 °C or BLEVE if in CSTR	L	BLEVE Flashing Spray Release	PRV-13; 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.	
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 direct spray.	

Table 3-4. What-If Hazards Analysis Results

HTL-4b2.2	What if loss of pressure boundary?	Catastrophic failure of vessel pressure boundary (material failure)	V	BLEVE	Design of pressure boundary	
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.	
HTL-4b2.3	What if too much power (over heat)?	Overheat 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	
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		Same as HTL-4a
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	Shock to the vessel needs to be addressed.
HTL-4b2.8	What if over mixing?	Too much agitation/ process upset	L	Impeller falls off leads to loss of mixing	Magnetically coupled; Design of impeller	

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.

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

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
HTL-5.1	What if loss of pressure	Catastrophic failure of vessel	U	Flashing spray release of	Pressure boundary;	

Table 3-4. What-If Hazards Analysis Results

	boundary?	pressure boundary (material failure) H-3		process fluid	Skid design provides spray protection for operators.	
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	
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 shorting.	Temperature controls; Thermo-couples between block and tube	
HTL-5.4	What if poor performance (heating)?	Process fluid is not heated appropriately	L	Process upset		Understand design constraints in low temperature conditions

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. During blowdown sequence, N2 gas will automatically be introduced (downstream side of filter) to provide motive force for cleaning filter and to maintain system pressure.

Interface:

Hazard ID	**What if:**	**Hazardous Scenario**	**Likeli-hood**	**Consequences**	**Hazard Controls**	**Comments**
HTL-6.1	What if loss of pressure boundary?	Failure of pressure boundary (Filter)	V	BLEVE	Design of vessel	similar to CSTR
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.	
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?	Break through of filter results in particle entering downstream	L	Send particles downstream –potential	See HTL-8 See HTL-9	

Table 3-4. What-If Hazards Analysis Results

		components (R-2/BPR).		plugging		
HTL-6.4	What if blowdown too early (inadvertently)?	Blow down initiated too early	L	Lose use of blow down operation; Loss of product	Design for system pressure	
HTL-6.5	What if fluid is the wrong temperature?	Process fluid too hot	L	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 vessel 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	May be precluded by Heater design.
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	
HTL-6.9	What if N2 valve opens early?	Opening of N2 valve early, resulting in process fluid entering into N2 system	L	Fouling of the N2 system	Pressure relief on line	
HTL-6.10	What if N2 high pressure?	Filter pressure too high resulting in loss of pressure boundary	U	BLEVE; Potential to blow through BPRs	Pressure Regulation of Nitrogen System. PRV on Nitrogen System Filter PRV or rupture disk to not exceed 3500 psi	
HTL-6.11	What if open offline vessel?	Opening valve (HV-20) results in fluid in F-2. Compresses whatever is in F-2	U	Process upset	Design of vessel	Note: If not in use F-2 will be physically isolated (e.g., locked valve or blank flange) from system.

Table 3-4. What-If Hazards Analysis Results

Evaluation Area: HTL Processing-7

Separations Vessel (R-2): Provide a device for the separation of aqueous phase from organic compounds. Maintain temperature of HTL product stream at 350 °C.

Interface:

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
HTL-7.1	What if loss of pressure boundary?	Failure of pressure boundary (R-2)	V	BLEVE	Design of vessel	Similar to CSTR and filters
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.	
HTL-7.2	What if loss of flow (plug)?	Plugged line	L	Blocked flow		
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 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	
HTL-7.6	What if inadvertent operation of separator?	Process fluid passed through separator inadvertently	L	No consequence; thermal impacts similar to F-2		

Table 3-4. What-If Hazards Analysis Results

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). Vessel may be tipping drum.

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.

Interface: High pressure and temperature to atmospheric pressure and low temperature (≤80 °C). Nitrogen purge. Manual loading of TK-3.

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
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 if pressure boundary breached Process upset;	Interlock design of AV-10 and AV-11 (V-13 and AV-14); TK-3 vented to either TK-4 or rupture disk header	
HTL-8.1-2	What if loss of pressure boundary?	Failure of pressure boundary (Blow Down Vessel)	U	BLEVE	Design BD Vessel	BD-1/BD-2 will see thermal pressure cycling
HTL-8.1-3	What if loss of flow (plug)?	Plugged line	L	Process upset	P-19 pressure transducer to notify operator	
HTL-8.1-4	What if blow down with N2 system open to BD-1?	Blow down with N2 open to BD-1, Less effective blow down;	L	Flashing spray release	Check valves and pressure relief on N2 line BD-1 Design as Pressure Vessel PRV on BD-1	
HTL-8.2-1	What if blowdown too early with drain line open to TK-3 (AV-11/AV-14 open)?	Blow down occurs during run with drain line open. flashing steam into TK-3; Boiling, loss of pressure within system	L	Flashing spray release if pressure boundary breached Process upset;	Interlock design of AV-10 and AV-11 (V-13 and AV-14) TK-3 vented to either TK-4 or rupture disk header	Same event as t HTL-8.1-1

Table 3-4. What-If Hazards Analysis Results

HTL-8.2-2	What if too hot (transfer early)?	Process fluid from BD Vessel transferred to TK-3 when too hot	L	Process upset; Flashing into TK-3	TK-3 vented to TK-4, which is also vented to atmosphere ; Interlock design of AV-10 and AV-11 (V-13 and AV-14)	Not expected to fail pressure boundary as liquid has already flashed in BD vessel and pathway to TK-4 is open.
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 < 80 C).	U	Spill hot liquid to environment.	TK-3 Design 316 SS Atmospheric Vessel	
HTL-8.2-4	What if not isolated AV-10, AV-11, and HV-18 or AV-12, AV-14, and HV-18 open during blow down?	Valves not closed during run Hot process fluid into TK-7 (poly tank);	V	Flashing spray release Failure of pressure boundary	AV-10 and AV-11 (AV-12 and AV-14) are interlocked. Pressure check on BD-1 and BD-2 for AV-11 and AV-14	Consider if in processing area of skid 1 or skid 3
HTL-8.2-5	What if HV-31 open?	Valves not closed during run hot process fluid into TK-7 (poly tank) on activation of pressure relief.	U	Flashing spray release Failure of pressure boundary TK-7	TK-4 is vented; Admin control on valve position	

Evaluation Area: Evaluation Area: HTL Processing-9a

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

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
HTL-9a1.1	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	U	Flashing Spray or Steam release (100 C process fluid mixing with Water)	Pressure Boundary (inner)	**Consider Pressure relief on outer tube with relief to appropriate vent path.**
HTL-9a1.2	What if loss of outer pressure boundary?	Failure of outer pressure boundary results in spill of water to operating area.	L	Process Upset;		

Table 3-4. What-If Hazards Analysis Results

		Fluid not cooled into BPR, which will lead to BPR failure over extended time				
HTL-9a1.3	What if loss of flow (plug)?	Plugged line	L	Process upset		
HTL-9a2.1	What if loss of flow (plug)					
	a. Due to loss of pressure upstream?	Plugged line due to loss of pressure upstream	L	Process upset; No real impact		
	b. Due to separator screen failure?	Plugged line due to separator particles; failure in closed position	U	Process upset; plug		
	c. 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-9a2.2	What if keep first stage, but lose second?	Loss of second BPR	L	No real impact		
HTL-9a2.3	What if failure of both BPRs?	Failure of both BPRs results in high pressure and temperature process fluid enters S-1;	U	BLEVE	Design S-1 for Full pressure Provide pressure relief (PRV or rupture disk)	
HTL-9a2.4	What if process fluid is not cooled upstream?	Hot process fluid to BPR. Steam, Boiling, and pressure; wear out BPR system	L	Process upset (premature wear out of BPR)		

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

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
HTL-9b.1	What if pressure boundary loss?	Failure of pressure boundary (c-2)	V	Flashing spray release	Design of the pressure system; Skid design to protect personnel from steam	Recommendation: Consider skid ventilation provision for nuisance odors.
HTL-9b.2	What if air loss?	Loss of (HVAC) air resulting in	L	Larger thermal load on	Loss of flow alarm;	Operating procedure

Table 3-4. What-If Hazards Analysis Results

		loss of cooling		Cooler C-1		will address shut down if long term loss of fan
HTL-9b.3	What if the line plugs?	Plugged line	L	Process upset	Pressure relief	See above

Evaluation Area: Facility/Utility-1

Hazard ID	What if:	Hazardous Scenario	Likeli-hood	Consequences	Hazard Controls	Comments
FU-1	What if loss of power (short–term power bump)?	Power bump resulting in electronics shutting off	L	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	Low consequence	Stored memory of temperature controls	
FU-2	What if loss of ventilation? Skid 1	Nuisance odors not ventilated on Skid 1	L	Nuisance odors/ low consequence	Facility Operating requirements	
FU-2	What if loss of ventilation? Skid 2	Loss of ventilation on Skid 2	L	Possible build-up of H2S in 15-20 min	Facility Operating requirements	
FU-2	What if loss of ventilation? Skid 3	Same as Skid1	L	Nuisance odors/ low consequence	Facility Operating requirements	
FU-2	What if loss of ventilation at Vessel S-1?	Loss of ventilation at S-1	L	Nuisance odor (possible H2S)	Facility Operating requirements	
FU-3a	What if loss of building water?	Loss of process water	L	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	Hot process fluid to BPR; 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	System with glycol helps	Possible flow indicator/temperature	Consider adding closed loop chiller to system
FU-3b	What if loss of chilled water at BD-1/BD-2?	Loss of cooling	L	Hot process fluid/ buildup of solids	Run water to cool process fluid	Consider adding closed loop chiller to system

Table 3-4. What-If Hazards Analysis Results

FU-4	What if loss of N2?	Loss N2 system resulting in loss of ability to repressurize	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.	
FU-6	What if building emergency (evacuation)?	Building emergency resulting in cease of operations	L	Process upset	Define emergency shutdown sequence

3.4 Evaluation of High Hazard Scenarios

Accident scenarios perceived as having high unmitigated consequences (energetic events with impacts outside of immediate operating area) 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 several process vessels.

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

Events which could result in BLEVE were also assumed to have the possibility of resulting in a pressure vessel burst (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 further mechanisms identified in this preliminary analysis, which would result in a more severe event than those analyzed.

3.4.1.1 BLEVE Consequence Methodology

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

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

For analyzing BLEVEs, the process outlined in CCPS, 2010 was followed.

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.
$u1_{(f,g)}$	= internal energy of the (fluid, gas) at the initial conditions. These values can be obtained directly from NIST thermodynamic data.
$u2_{(f,g)}$	= internal energy of the (fluid, gas) in the expanded state, adjusting for the flashing fraction.

Where:

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

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

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

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

Energy available – Per the CCPS, 2010 methodology assuming ductile failure, the energy available is $E_{ex,a} = 0.4 * E_{ex}$. 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 thermal hazards were postulated.

3.4.1.2 BLEVE Results

Filter Vessel (F-1, F-2)

For this calculation, it is assumed the pressure in the vessel is at the maximum system pressure 3500 psig (MHTLS-RPT-001, Rev. 0 [Draft F], Tables 3&4). This is a reasonably conservative assumption as these conditions are at higher pressures and temperatures than the operating pressure (~2800-3000 psig) and temperature (350 °C). It was conservatively assumed that the filter vessel contained 4 liters of liquid (water), ignoring any volume taken up by the filter internals. Accounting for the slurry mixture (solids, bio-oil and water) lower the potential energy due to the thermodynamic properties compared to water.

Input Assumptions:

Pressure State 1	3500 psig	24.12 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	4 liters	0.004 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)	Entropy S (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Phase
99.606	0.1	0.0010432	419.1	1.303	3.7702	4.2152	1543.5	liquid
99.606	0.1	1.6939	2505.6	7.36	1.5548	2.0784	471.99	vapor
425	22.4	0.0095826	2671.7	5.6198	2.5561	5.5884	529.68	Super critical liquid
425	24.12	0.0084264	2630.5	5.5222	2.6599	6.3511	517.82	Super Critical liquid

Thus from above:

$E_{ex,a}$ = 0.15* E_{ex}. (Casal and Salla) = 107E+03 joules

= 0.4* E_{ex}. (CCPS, 2010) = 287E+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	**3**	**5**	**7**	**10**	**15**
scaled distance $\overline{R}$, m	**0.1-2.9** **2.1-2.9**	**3.5 – 4.9**	**4.9 – 6.9**	**7.1 – 9.8**	**10.6–14.7**
P_s, kPa	**21.1 – 30.9**	**9.4-13**	**5.7-8.9**	**3.6-5.4**	**1.4-2.8**
I_S, Pa-s	**0.022-0.041**	**0.011-0.022**	**008-0.015**	**<0.006- 0.01**	**<0.006** **<0.0065**

The maximum likely range of fragments calculated using the CCPS, 2010 method was determined to be ~ 70 meters. As noted in Section 3.4.1.1 and 3.4.3, this distance is judged to be a very conservative estimate.

3.4.2 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**
$\mathbf{k_P}$	4	1.6	1.4

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

<u>Filter Vessel (F-1, F-2)</u>

For the filter vessel, it is assumed the pressure in the nitrogen pressure in the vessel is at the maximum system pressure 3500 psig (MHTLS-RPT-001, Rev. 0 [Draft F], Tables 3&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.

Input Assumptions:

Pressure State 1	3500 psig	24.12 MPa
Pressure State 0	14 psi	0.1 MPa
Volume of Filter	4 liters	0.004 m^3
Specific Volume	0.00395 m^3/kg	
$\acute{Y}_1$	1.40	
Speed of sound in air, a_0	340 m/s	

Thus from above:

$$E_{ex,a} = 0.4 * E_{ex,Br} = 187E+03 \text{ joules}$$

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	3	5	7	10	15
scaled distance $\overline{R}$, m	**2.4**	**4.0**	**5.7**	**8.1**	**12.1**
P_s, kPa	**29.7**	**11.3**	**7.4**	**4.8**	**2.8**
I_S, Pa-s	**0.031**	**0.015**	**0.011**	**0.009**	**0.005**

The maximum likely range of fragments calculated using the CCPS, 2010 method was determined to be ~ 90 meters. As noted in Section 3.4.1.1 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 3-5 shows that a failure of the filter vessel resulting in a BLEVE or PVB could have significant impacts. However, only for a Filter vessel would significant overpressures (greater than 21 kPa) be developed which would challenge a building structure at greater than 4 meters. There were no cases in which overpressures sufficient to result in greater than minor damage (7 kPa) reached at a distance of 10 meters.

For missile generation, the CCPS, 2010 methodology conservatively estimates missile ranges out to ~67 meters. As noted, this 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 ~75 times greater than calculated energy available for the Filter Vessel BLEVE 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 3-5. 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 Initial Critical Controls

This section describes the attributes of the critical controls (Table 4-1) recommended in the hazard analysis as providing protection against the higher consequence hazards associated with the MHTLS process as addressed in Section 3.3. Note: all controls are not currently included with the as part of the design information (P&IDs, Functional Design Criteria) reviewed during the HA but reflect additional recommendations made from the hazards analysis. Temperature and pressure set points are considered preliminary and subject to change. Significant changes in these set points should be reviewed for possible safety implications.

Table 4-1 Initial Critical Hazard Controls

Hazard Control	Event Type	Representative Event ID
Vessel Design	BLEVE /PVB	4b2.2, 5.1, 6.1, 7.1, 7.5, 8.1-2, 8.1-4, 9a.2-3
	FS	3.3,
Piping Design per B31.3 and NFPA 55	FS	3.3, 3.4, 4a.2, 4b1.1, 4b1.4, 4b2.2a, 6.1a, 7.1a, 9a1.1, 9b.1
	FA	4b1.1, 5.1a
Relief Valve Sizing and Flowpath Design	BLEVE /PVB	6.10, 9a.2-3, 4b1.4
	FS	3.3, 3.4, 4a.2, 4b1.1, 4b1.4, 8.1-1, 8.1-4, 8.2-1
	FA	4b1.1, 9a1.1
Nitrogen Supply System Design (Pressure Regulation)	BLEVE /PVB	6.10
	FS	3.3, 8.1-4
Process High-High Temperature Interlock	BLEVE	4b2.3, 5.3, 6.7, 7.5
Process High-High Pressure Interlock	BLEVE /PVB	4b1.4
	FS	4a.5, 4b1.4
Process Valve (Position) Interlock	FS	8.1-1, 8.2-1, 8.2-4
Skid Design as Shield against Steam Spray	FS	3.3, 3.4, 4a.2, 4a.5, 4b1.1, 4b1.4, 4b2.2a, 6.1a, 7.1a, 9a1.1, 9b.1
Operating Area (Stand off distance)	BLEVE /PVB	4b2.2, 5.1, 6.1, 7.1, 7.5, 8.1-2
HV-31 position	FS	8.2-5

4.1.1 Vessel and Piping Design

The design of vessels, components, and piping (tubing) should ensure the pressure integrity of the process boundary for normal operations and upset conditions. Design should utilize corrosion resistant and ductile material to minimize catastrophic failure potential. The design should address the potential for thermal shock of the system as identified in Section 3.3 assuming a minimum water temperature

(Tmin) of 10°C. **For Example**: See Thermal Shock Cracking: Design and Assessment Guidelines pages 125 -132, Journal of Pressure Vessel Technology, Vol 129, February 2007.

Piping connections should utilize Swagelok® or other fittings/protection preventing a direct release path to the environment in the event of a gasket or other failure at the connection.

4.1.2 Relief Valve Sizing

Relief Valve Sizing: All relief valves and pressure relief flow paths should be sized for the worst-case flow rates, including any backflow from high to low pressure areas, see API 521.

4.1.3 Nitrogen Supply Design

Maximum nitrogen pressure –should be limited by a regulator (3000 psig, system pressure) and protected by pressure relief valve (3500 psig).

4.1.4 Temperature Control (Independent)

On each component provided with an external (non-process) heat source, a high-high temperature interlock (425 °C) should be provided to isolate power or stop the external heat thus, protecting the pressure boundary of the component from seeing excessive temperatures.

4.1.5 Pressure Control (Independent)

The high-high pressure interlock (3500 psig) should stop or isolate pressure sources (ISCO Pump and nitrogen) and external heat sources to the system thus, protecting the pressure boundary of the MHTLS components from seeing excessive pressures.

4.1.6 Valve Interlock Controls

The valve interlock system should prevent concurrent opening of multiple valves in the blowdown path protecting against a direct flow path from high pressure to non-rated components.

4.1.7 Skid Design

The skid design should incorporate provisions of a spray shield for protecting operators from flashing spray releases events. Spray shield should be shatter -resistant (FEMA 426), and capable of withstanding steam jet pressure of and temperatures of associated with system failure.

Recommendation: The Skid 2 design should provide provisions for mitigation of “nuisance” odors due to spills, leaks and off gases from the process.

4.2 Safety Management Programs

4.2.1 Operating Area

An administratively controlled operating area should encompass an area with a radius no less than 4 meters for protection of public and non-MHTLS related hazardous material storage.

4.2.2 Valve Position

An administrative program for positive control of valve position (HV-31) closed during normal operations should be established.

4.3 Safety Management Programs

To be completed at a later time.

5.0 CONCLUSION

A What-If hazard analysis was performed by PNNL to support the MHTLS design 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 (energetic events with impacts outside immediate operating area), 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 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*).

The identified initial hazard controls provide assurance of the safety of the design of the MHTLS consistent with PNNL Safety Management Program expectations. Further analysis of the risks posed from operation of the MHTLS is expected as part of design maturity, to demonstrate operation of the MHTLS can be performed safely, consistent with PNNL control of other laboratory operations.

6.0 REFERENCES

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Appendix A: Attendance

Modular Hydrothermal Liquefaction System
Hazard Analysis

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

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
ROBERT YASEK	PNSO (FR)	PNSO	2-4023
Renee McGaughy	WS+H	PNDL	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 Cirello	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

Pacific Northwest NATIONAL LABORATORY

Sign Up Sheet

Thursday February 19, 2015

Name	Role	Organization	Phone Number
Erick Flieger	PNSO LSD	DOE	372-4606
Pete Lowry	HA Lead	R&DS	372-6573
Dan Anderson	PM	PNNL	5-4406
Brad Evans	PSB Rep	NOD	1-7386
ROB YASEK	FR	PNSO	2 4023
David Rohrig	WS&H	PNNL	1-7690
Sharon Bailey	proj. team	PNNL	5-2243
TODD HART	Yes	PNNL	1-6509
Scott S. Allen	EED	PNNL	1-7053
Gerald Sauve	PNSO	PNSO	372 4083
Rob Cuello	EED	PNNL	5-2848
Andy Minister	FP	PNNL	371-7902
Tyler Gilmore	PMOD	PNNL	371-7171
Andrew Schmidt	PNNL	PNNL	375-2280
Katie Wagner	HA Scribe	EA	5-2387

Modular Hydrothermal Liquefaction System
Hazard Analysis

Sign Up Sheet

Friday February 20, 2015

Name	Role	Organization	Phone Number
Tyler Gilmore	PMOD	PNNL	371-7171
Pete Lowry	HA Lead	R&DS	2-6573
Andrew J Schmidt	Engr	PNNL	~~2-35~~ 375-2280
Sharon Bailey	proj.	PNNL	5-2243
Erick Flieger	PNSO CSD	DOE	5-4606
David Rohrig	WS+H	PNNL	5-6298
Don Anderson	PM	"	5-4406
Gerald Sauve	PNSO	DOE	372 4083
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Scott S. Allen	EED	PNNL	1-7053
Rick Orth	TGM	PNNL	5-6709
Todd Hart	Yes	PNNL	1-6509
Katie Wagner	Scribe	EA	5-2387

Appendix B: Key Design Information Reviewed

Design Information Reviewed

MHTLS-RPT-001 **Functional Design Criteria for Modular Hydrothermal Liquefaction System,** Revision 0 [Draft F**]** **(Includes Business Sensitive Information)**	
HTL SYSTEM Block Diagrams **(Includes Business Sensitive Information)**	MHTLS-RPT-001 Rev 0 Draft E 2015-01-23_
HTL SYSTEM P&IDs **(Includes Business Sensitive Information)**	PID Skids 2-12-15REV_PHA Draf
MHTL Overview **(Includes Business Sensitive Information)**	MHTLS Overview for PHA 2-17-15...
Slide of N2 to Filter **BPR control scheme**	HTL3 addition of N2 at 2800 psi...

Appendix C: Preliminary Hazard Assessment

MHTLS Initial Hazard Identification – Component Volumes

	Component	Volume	Comments
ML-1	Cutting Mill		
HS-1	Homogenizer Vessel	50 gal	
ML-2	Immersion Mill	5 - 10 gal	The mill itself will likely be less than 5 gal
P-1	LP Pump		
TK-1	Feed Staging Tank	220 gal	
P-2	LP Pump		
TK-2	Feed Day Tank	54 gal	
P-3	LP Pump		
P-4	HP Pump	0.5 L	(510 ml cylinder)
P-5	HP Pump	0.5 L	(510 ml cylinder)
H-1	Preheater	2 L	inner tube – 3/8-in. ID, 0.049-in. wall outer tube - 3/4-in. ID, 0.083-in. wall
H-2	Preheater **Configuration 2 only**	0.5 L	~40 ft of 3/8 in inner tube Can be tube in tube, with hot oil on outer tube at 15 psig, or can be coiled tubing inside a 4.25 in. shell (shell at 15 psig)
R-1	Continuous Stirred-Tank Reactor **Configuration 2 only**	2 L	
H-3	Trim heater	0.5 L	20 ft of 1/2- in (0.065 wall) tubing.
H-4	Plug Flow Reactor	3 L	Tubing
F-1	Filter 1	4 L	2 in. x 60 in. = 3L free volume
F-2	Filter 2	4 L	2 in. x 60 in. = 3 L free volume
R-2	Separator	3-L	Space velocity of 4 L/L/h L/D ration of ≥ 10, 2 in x 60 inch.
BD-1/ BD-2	Blowdown Vessel	1.5L	Number of blow down vessels (1 or 2) – TBD..
TK-3	Blowdown Receipt Tank	12 L	API 520 Calculation ~ 8x(BD-1)=
C-1	Cooler	1 L	Tubing: 0.5 in. x 40 ft unless a shell-and-tube design.
C-2	Cooler **- Configuration 2 only**		
BPR (a/b)	Back Pressure Reducer		
TK-4	Knock Out Vessel	5 to 20 gal	API 520 Part I for Sizing
S-1	Gas Separator	6 L	
	Vent		
S-2	Product (Oil/Water) Separator	17 L	
TK-5	BioCrude Storage Tank	40-50 gal	
P-6	Pump to Oil/Water Separator		Optional
S-3	Oil Water Separator		
TK-6	Aqueous Byproduct Storage	500 gal	

	Component	Volume	Comments
P-7	Pump to Coalescer		
TK-7	Drain Waste Tank	275 gal	
P-8	Aqueous Byproduct Pump		
	Back Flow Line		

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 – post hearing protection sign	
Location		10 feet, 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			

Preliminary Hazard Assessment			
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 (3400) of the pump – make sure maintenance program in place to handle slurry fluid for PRVs; pump set to auto shutoff at 3100	
Temperature:	Low	Will need to confirm if upset (high temperature) is credible/relevant. No mechanism for rapid temperature excursion; want to have feature to heat if needed ~60C water bath	
(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;	

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 CO2	Yes
Pressure:	High		
Temperature:	High		
(other)		Oil – Dynalene 600; shell = 15 psi (CC Flash Point 160°C; Fire Point 193°C)	
		CSTR is electrically heated; 750 rpm (magnetically coupled)	
Location		Standard equipment	

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 CO2	Yes
Pressure:	High		
Temperature:	High	Electrical resistance heating	
(other)			
Location		Same as previous area	

Preliminary Hazard Assessment			
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

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
Inventory (material):	Low	Liquefied product – aqueous bio-oil mixture; inorganic salts precipitating out (Calcium phosphate/calcium sulfate) – condensed CO2	Yes
Pressure:	High	Positive isolation for F-2 filter if not in use.	
Temperature:	High	Start losing heat	
(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:

Parameter	Hazard Potential	Evaluation	Unique or Significant Hazard
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 (≤80 °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) needs to be connected to vent system; may need active ventilation	

Preliminary Hazard Assessment			
Parameter	**Hazard Potential**	**Evaluation**	**Unique or Significant Hazard**
Evaluation Area: Evaluation Area: HTL Processing-9a			
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			
Inventory (material):	Low	Liquefied product	Yes
Pressure:	High		
Temperature:	Moderate		
(other)			
Location		Access to building water (10-40 psi); can be standalone chiller	
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)		Most likely will use forced air or oil to cool; won't use chilled water to cool; air cooling on water	
Location			

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			
Inventory (material):	Low	Biocrude liquids; aqueous by-product (water) , gases (CO2)	Yes – within the scope of pressure consideration and design considerations (skid 2/3) and H2S
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)		Should this be on Skid 2 or Skid 3; pressure relief prior to system	
Location		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.			
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 coalesce.			
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 MHTL vessel. For the purpose of this evaluation a process vessel includes major process equipment with significant volumes (storage vessels, columns, reactors, heat exchangers, etc.); piping, tubing, and pumps are not included. The estimated likelihood of a BLEVE failure in the MHTL system is expected to be very low (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 MHTL components, the following additional scenarios were considered:

- BLEVE failure of a vessel resulting in the BLEVE failure of a second vessel due to shrapnel or pressure impacts
- BLEVE failure of a vessel resulting in the potential failure of an oil filled heat exchanger boundary with subsequent mist generation and ignition.

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.

1.0 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], "Propane may have three different released behaviors (Table 2). It may be released as a jet fire, explosion, and BLEVE or flash fire. By definition, 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, explosion, and flash fire 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 MHTL system 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.

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.

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 diameters. For a cylindrical vessel the equivalent diameter is the diameter of a spherical 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

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 MHTL system. The study was based on larger vessels expecting to generate more fragments; with larger volumes of flashing liquids - equating to higher initial velocities; and ignores the direction bias 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.

1.3 Target Rupture

Sun[5] 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.

2.0 BLEVE Resulting in a Mist Explosion

Explosive mists of pressurized, typically to thousands of psi, industrial fluids (i.e., hydrocarbon based hydraulic, lubricating, heat transfer, and transformer oils) are well documented. In general, for fluid mists to pose an explosive hazard a distinct set of conditions must be met: droplet diameter in the 10 µm - 100 µm range (generally under 50 µm); a cloud concentration of 100 g/m^3 for quiescent conditions, to 500 g/m^3 for turbulent conditions; sufficient fuel flow rate; and an ignition source must be present.

For normal operations (< 100 psi, < 150 °C), a potential spray release of a hydrocarbon heat transfer fluid does not pose a significant hazard due to the inability to adequately atomize the fluid due to its viscosity. General observations of testing performed on *Ignition of hydraulic fluid sprays by open flames and hot surfaces*[1] found that high viscosity fluids are harder to ignite and the minimum hot surface ignition temperatures ranged from 350 ºC to 440 ºC.

Similarly for impacts due to external missiles or overpressure from a BLEVE, a mechanism resulting in the fluid in the shell of the heat exchanger being pressurized or atomized sufficiently would need to occur to pose a concern.

Assuming that 20% of the available fluid in the heat exchanger could be atomized[i] within the specified range, this would equate to about 1.52 liters for a pipe in pipe arrangements or 8 liters for a proto-typical MHTL design of a tube in shell arrangement. The shell and tube volume would equate to about 6500 grams of fluid within the specified droplet diameter. This approximately equates to a concentration of concern of 500 g/m^3 within a 13 m^3 volume. Note: for an energetic event with sufficient magnitude to fail the outer shell of the heat exchanger, the volume encompassed by the released fluid would be expected to be much greater due to the driving forces of pressure and expansion of the bio-fuel slurry (primarily water). In addition, the water within the slurry would act as an additional inhibitor of the combustion.

For the MHTL system, a fire resistant heat transfer fluid, Dynalene 600, has been specified. Dyanlene 600 is a mixed inorganic–organic polymer silicone (polysiloxane) fluid. Dimethyl polysiloxane is the base used in Dynalene 600 and is the most widely used silicon based polymer. Other replacements for hydrocarbon based fluids have been developed and are noted by Factory Mutual as being fire-resistance to non-combustive[ii].

Silicone liquids are difficult to ignite. However, should a fire occur: fires fueled by silicones exhibit low heat release rates and fire severity and result in the formation of a silica crust[2] inhibiting the combustion process; additionally they have low emission of fumes. The low heat release rates make them suitable for various industrial products such as transformer fluids, fire-barrier foam and thermal ablatives[3]. From Hellebuyck, "Among the less-combustible liquids, the silicone liquid had the lowest [heat release rate per unit area] HRRPUA due to the formation of a crust on the surface during combustion."

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[1] Liming Yuan∗ Pittsburgh Research Laboratory, National Institute for Occupational Safety and Health, *Ignition of hydraulic fluid sprays by open flames and hot surfaces*
[2] Hellebuyck D.H., et.al., *Fire Behaviour of Less-Combustible Dielectric Liquids in a Nuclear Facility,* Fire Technology 2015.
[3] Sivathanu, Y., et al. *Characterization of Particulate From Fires Burning Silicone Fluids*

The following design consideration is provided:
Although it is not expected that a BLEVE induced failure of an MHTL heat exchanger would result in the conditions necessary to support combustion, the specification for the use of Dynalene 600 (or equivalent fire resistive fluid) provides additional protection against subsequent impacts should the event occur.

[i] *Explosion Hazards in the Process Industries*, Chapter 3 *Explosions in Clouds of Liquid Droplets in Air (Spray/Mist)*: Forster (1990) argued that accidental generation of large, explosive clouds of sprays/mists of organic liquids of high boiling points is not very likely. The reason is that the mean droplet-droplet distance in the explosive range is of the order of only 10 droplet diameters, which in a turbulent cloud makes fast coalescence of the small droplets to larger ones highly probable. The larger droplets will then "rain out" and the fuel concentration in the cloud will fall below the explosive range. Forster confirmed experimentally that with a high boiling point liquid (octanol) it was indeed very difficult to generate an explosive spray in a 1 m3 explosion chamber unless a highly sophisticated spray nozzle system was adopted.

[ii]Factory Mutual 6930, *Approval Standard for Flammability Classification of Industrial Fluids*, ranks identifies fluid, via the use of a Spray Flammability Parameter, as FM Approved or FM Specification Tested.

FM Approved:	Having a normalized SFP of 5 E-4 or less. These industrial fluids are typically unable to stabilize a spray flame. These fluids represent a low fire hazard and do not require additional automatic sprinkler protection.[ii]
FM Specification Tested:	Having a normalized SFP greater than 5E-04, but less than 1E-03. These industrial fluids are less flammable than mineral oil fluids but may stabilize a spray flame. They can be considered less-flammable. Sprinkler protection may still be needed to control a fire involving these fluids.