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FY16/Q2 Status Report on Initial Dispersion Calculations for Tight Crude Oils Project

Sandia National Laboratories Technical Support for

US DOE/DOT Crude Oil Characterization Research Study

By:
Anay Luketa
Fire Science and Technology Department
Sandia National Laboratories
aluketa@sandia.gov

David Rudeen
GRAM, Inc.
Contractor to Sandia National Laboratories
dkrudee@sandia.gov

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Introduction

The objective of this work is to assess dispersion distances of a vapor mixture of species released from a railcar containing a tight crude oil. Tight crude oils can have higher levels of light ends as compared to conventional crude oils [1], which if released and dispersed could pose a potential hazard with regards to a flash fire, explosion, and/or asphyxiation. A historical accident involving rail transport in Viareggio, Italy illustrates how the spillage of LPG can lead to severe damage as a result of a propagating vapor cloud [2]. One of 14 railcars was punctured after derailment, releasing about 110 m^3 of LPG into a densely populated area (2000 persons/km^2). The resulting vapor cloud propagated and infiltrated nearby buildings and houses which were an average of 10 m in height. Ignition of the cloud occurred approximately 100 to 300 seconds after the start of the spill. A flash fire and explosions resulted, killing 31 people. Evidence suggests that most deaths occurred due to the asphyxiation and thermal hazards from the flash fire. Thus, the motivation for this work is to assess if significant vapors can develop from a railcar carrying a tight crude oil and if this cloud could disperse potentially to nearby populations.

In this work the distance to half the lower flammability limit (LFL) is evaluated. The LFL is defined as the lowest fuel concentration in air that will support combustion. Since there is inherent uncertainty associated with performing simulations, a concentration level of ½ LFL is evaluated.

The initial phase of this effort is to perform exploratory simulations of two oils taken from the Strategic Petroleum Reserve (SPR) database since the oils that will be tested for the SNL combustion tests are not yet procured and characterized. The major portion of this initial effort consists of creating computational meshes and input files, as well as developing realistic scenarios in which vapors can be released.

Currently, two scenarios are considered and are to be assessed through numerical simulation by using Fluent, a computational fluid dynamics (CFD) code. The first scenario involves an accident in which a crude oil pool fire results and the heat flux to a nearby undamaged railcar raises the temperature to a level sufficient to activate the opening of its pressure relief value. The second scenario similarly involves an accident with a resulting pool fire, but instead, the release is through the manway. The most frequent cause of non-accidental releases is through the manway for crude oil [3]. Causes of the unintentional opening of the manway are due to loose bolt/nuts, deteriorated gasket, misaligned gasket, and/or gasket missing. Although non-accidental releases have historically occurred, an accidental release is considered here since a heat source, namely a nearby pool fire, will enhance the rate of vapor generation. To reflect conditions of a release through a pressure relief valve and manway, the two SPR oils evaluated are characterized at 0 psig and 75 psig (520 kPa gauge) as a function of temperature.

The following provides an overview of the approach and results of this initial phase of the project. First, characterization of the fuels is described, then an overview of computational specifications is provided, and finally preliminary results for a release at 0 psig are presented.

Source Term

Properties of Selected Crude Oils

Two oils from the SPR database were chosen, one a Bakken crude denoted Bakken C30+ and the other a non-Bakken crude, denoted BH102 C10+. The BH102 C10+ is included as a limited comparison in scope and not meant to result in a thorough evaluation regarding the simulations. Selected properties of the crude oils used in this analysis, as modeled by UniSim[1], are provided in Table 1, where SG is the crude oil specific gravity or relative density, MW is average molecular weight, BPP is bubble point pressure at 37.8°C (100°F) (initial vapor formation) and GOR is the gas to oil ratio.

Table 1. Selected properties of crude oils used in source term generation.

Property	Bakken_C30+	BH102_C10+
SG	0.7334	0.6007
MW	163.2	128.7
BPP, psia	21.05	12.5
BPP, kPa	145.1	86.2
GOR@14.7 psia, 100°F*, scf/bbl	8.9	0
GOR@101 kPa, 37.8°C*, m^3/m^3	1.6	0

*from "Act. Volume Flow, BPD": vapor/Liquid * 5.6146 scf/bbl

Crude oil Composition

The compositions of the crude oils, provided in Table 2, were determined by processing gas and liquid compositions measured from a specially-designed crude oil separator unit used at the SPR with a Soave Redlich Kwong Equation of State (SRK-EOS) model. The EOS back-calculates the separator input feed oil composition from measured flash gas composition and flash equilibrium conditions (temperature, pressure and volume). Carbon number mole fractions above C10 were determined by unpressurized gas chromatographic analysis of the separator liquid. The SPR Bakken crude used a Sandia in-house EOS code (D2EOS) and blended data from flash separator gas and liquid analysis; the BH102 crude was developed from flash separator gas composition data using the UniSim process model. The C12-C13 hypo components were generated by trial and error so that the EOS calculated the measured BP pressure at a selected temperature.

[1] UniSim Design Suite R440, Process Design/Simulation, Honeywell International Inc., 2015.

Table 2. Composition of Crude oils used in source term generation.

	Bakken C30+		BH102 C10+	
Component	**Mole Fraction**	**Mass Fraction**	**Mole Fraction**	**Mass Fraction**
Nitrogen	0.00025	0.00004	0.00011	0.00002
CO	0	0	0	0
CO2	0.00013	0.00004	0.00072	0.00025
Argon	0.00001	0.00000	0.00001	0.00000
Oxygen	0	0	0	0
H2S	0	0	0.000188	4.99E-05
Methane	0.00083	0.00008	0.00040	0.00005
Ethane	0.00639	0.00119	0.00240	0.00056
Propane	0.02783	0.00759	0.01956	0.00671
i-Butane	0.01138	0.00409	0.01014	0.00458
n-Butane	0.05837	0.02099	0.03596	0.01626
i-Pentane	0.03197	0.01427	0.02811	0.01578
n-Pentane	0.04906	0.02190	0.03465	0.01945
n-Hexane	0.12143	0.06475	0.10858	0.07279
n-Heptane	0.10665	0.06613	0.10900	0.08497
Benzene	0.00343	0.00166	0.00550	0.00334
Toluene	0.00717	0.00409	0.01181	0.00846
E-Benzene	0.00206	0.00135	0.00343	0.00284
p-Xylene	0.01364	0.00896	0.01215	0.01004
n-Octane	0.03051	0.02157	0.16620	0.14769
n-Nonane	0.05144	0.04083	0.07219	0.07203
n-Decane	0.06588	0.05800	0	0
n-C11	0.04958	0.04796	0	0
n-C12	0.03949	0.04162	0.08504	0.11268
n-C13	0.03908	0.04458	0.29384	0.42144
n-C14	0.03163	0.03883	0	0
n-C15	0.02835	0.03726	0	0
n-C16	0.02276	0.03189	0	0
n-C17	0.02023	0.03010	0	0
n-C18	0.01809	0.02849	0	0
n-C19	0.01659	0.02756	0	0
n-C20	0.01361	0.02379	0	0
n-C21	0.01185	0.02175	0	0
n-C22	0.01099	0.02112	0	0
n-C23	0.00924	0.01856	0	0
n-C24	0.00828	0.01735	0	0
n-C25	0.00761	0.01661	0	0
n-C26	0.00679	0.01541	0	0
n-C27	0.00579	0.01364	0	0
n-C28	0.00556	0.01358	0	0
n-C29	0.00503	0.01272	0	0
n-C30+	0.06101	0.15962	0	0
H2O	0	0	0	0
C12+	0.4774	0.7204		

Model to Determine Mass and Composition of Gas Mixture

The UniSim process simulator was used to estimate the mass and composition of gas released from a closed heated tank containing crude oil as a function of temperature at a fixed pressure relief. The venting tank was modeled as a series of liquid-vapor flash equilibrium processes at incrementally increasing flash temperatures as illustrated in Figure 1. In the figure, e_i is the energy input required to heat the system; V_i is the vented vapor phase; L_i is the remaining liquid phase which flows into subsequent flash chamber and T_i is the flash temperature with $T_{i+1} > T_i$. Temperature increments were 50°F (10°C) or less and pressure was held constant at vent pressure through all flash processes. An SRK EOS model within the process simulator calculates the mass and composition of the exiting vapor and liquid phases. The vapor phase data was saved and post processed in Excel in order to normalize component masses to the initial mass of crude oil and to accumulate mass released as a function of temperature. The initial temperature is the bubble point temperature at venting pressure. The final temperature was the minimum of 750°F (399°C) or the temperature at which all liquid is vaporized.

It important to note that these simulations assume equilibrium between the liquid and vapor phases for a constant flow thru system (rates and rate ratios) or, equivalently a closed system (mass and mass ratios) and, therefore, do not provide the actual rate at which vapor is generated.

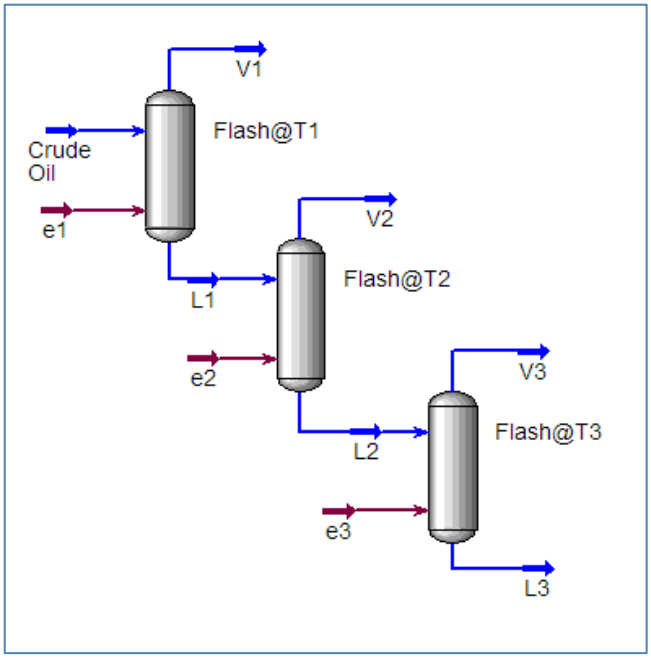

Figure 1. UniSim process simulator schematic of model used to estimate dispersion mass source.

Vapor Generation

The normalized cumulative mass fraction in the vapor phase is determined as a function of temperature for two different pressures, namely, at 0 psig (14 psia) and 75 psig (89.7 psia) using the procedure specified above. The vapor phase mass fractions are normalized by the mass of the feed oil. Figure 2 and Figure 3 show cumulative vapor phase mass fractions for Bakken C30+ and BH102 C10+ as a function of temperature at a pressure of 0 psig, respectively. Figure 4 and Figure 5 show cumulative vapor phase mass fractions for Bakken C30+ and BH102 C10+ as a function of temperature at a pressure of 75 psig, respectively.

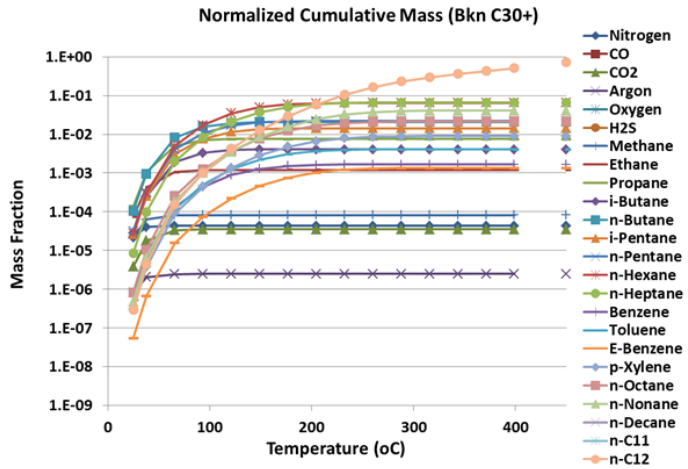

Figure 2: Normalized cumulative mass fraction (Bakken C30+) in the vapor phase as a function of temperature at 0 psig.

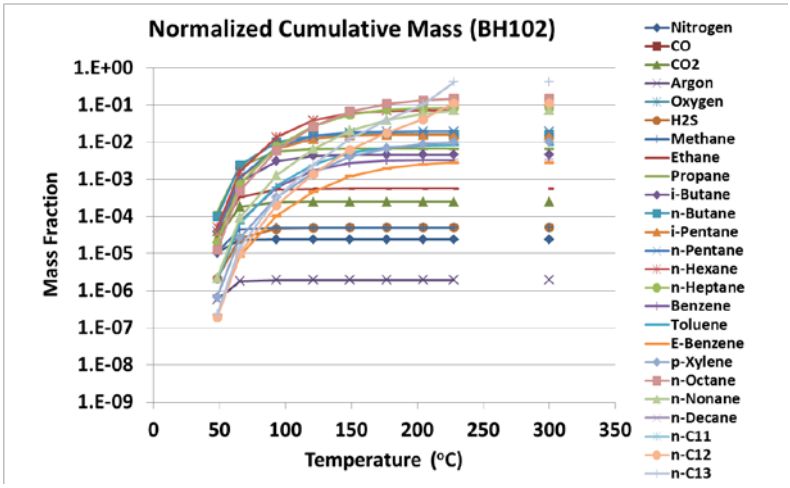

Figure 3: Normalized cumulative mass fraction (BH102 C10+) in the vapor phase as a function of temperature at 0 psig.

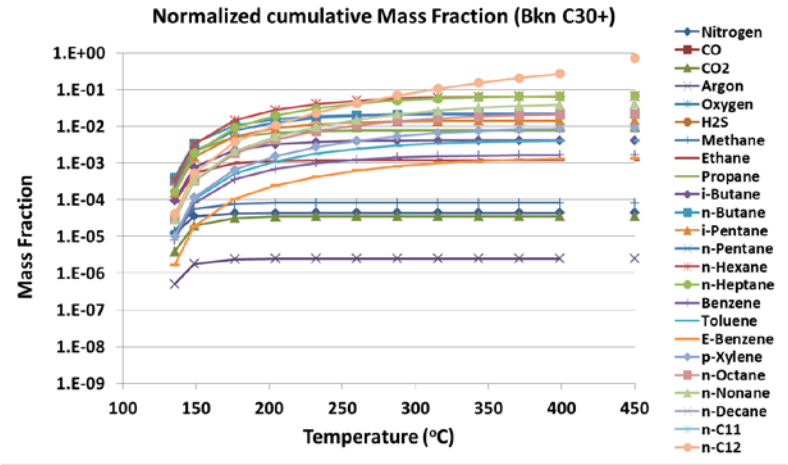

Figure 4: Normalized cumulative mass fraction (Bakken C30+) in the vapor phase as a function of temperature at 75 psig.

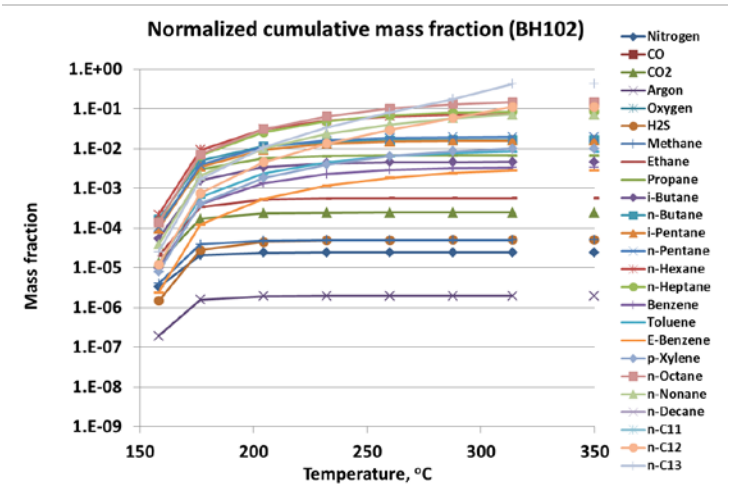

Figure 5: Normalized cumulative mass fraction (BH103 C10+) as a function of temperature at 75 psig.

It is assumed that a pool fire has resulted from an accident and heats the contents of a nearby railcar to a temperature not to exceed about 200°C (392°F), that is, a value below the auto-ignition temperature of the hydrocarbons evaluated. Temperatures higher than this value are not considered because higher temperatures could result in the ignition of escaping volatiles, which would then prevent dispersion of unignited gases.

The evolving hydrocarbons chosen for the dispersion calculations were evaluated at two temperatures at 0 psig, namely, 65°C (149°F) and 204°C (399°F). Temperatures lower than 65°C were not considered because of the low amount of vapors generated below this value. The rationale for choosing 65°C is based on the relationship between release velocity and its effect on inducing turbulent mixing which consequently affects dispersion distances [4]. A lower release velocity of the vapors will induce less mixing than a higher velocity, thus the vapor cloud will travel farther before diluting below the lower flammability limit. Thus, a

temperature of 65°C was chosen since it is the lowest temperature that would provide both appreciable vapors and the lowest release velocity of the evaluated temperature range.

The species used for the calculation and their respective mass fractions, m_i, are provided in Table 3. The mass fractions are normalized based on the total mass of light end species considered. As noted previously, comprehensive evaluation of BH102 C10+ is not considered since it is a non-Bakken crude oil, thus only one case is considered for comparison. For the Bakken C30+, at 65°C only the pressure of 0 psig is evaluated since the vapors generated at 65°C and 75 psig are not appreciable.

To determine the total mass released, an 80% full, 30,000 gallon capacity railcar was considered. The composition mass values based on this railcar capacity are provided in Table 4. The density of the Bakken C30+ oil is 734 kg/m^3 and is comprised of about 3.2% and 24.7% vapors by mass at 65°C and 204°C, respectively, at atmospheric pressure. Thus, the total vapor mass at 65°C and 204°C (399°F) is about 2,100 kg and 20,397 kg with an average molecular weight of 61 and 94, respectively. Thus, the gases are about 2.1 to 3.2 times the density of air at equivalent temperatures and pressures. For the BH102 C10+ at 0 psig and 204°C the total vapor mass is 31,788 kg with an average molecular weight of 108.

Table 3: Cumulative gas mass fractions at 0 psig

	mass fractions			
Oil	***Bakken C30+***			***BH102 C10+***
Temperature	**65°C**	**204°C (399°F)**		**204°C**
Pressure	**0 psig**	**0 psig**	**75 psig**	**0 psig**
Methane	0.0026	0.0003	0.0007	0.0001
Ethane	0.0335	0.0039	0.0095	0.0010
Propane	0.1626	0.0248	0.0560	0.0115
i-Butane	0.0604	0.0134	0.0269	0.0079
n-Butane	0.2628	0.0687	0.1316	0.0279
i-Pentane	0.0979	0.0466	0.0737	0.0271
n-Pentane	0.1293	0.0714	0.1079	0.0334
n-Hexane	0.1575	0.2065	0.2319	0.1244
n-Heptane	0.0634	0.1961	0.1636	0.1423
Benzene	0.0042	0.0053	0.0057	0.0057
Toluene	0.0038	0.0119	0.0094	0.0141
E-Benzene	0.0005	0.0033	0.0020	0.0044
p-Xylene	0.0029	0.0215	0.0129	0.0154
n-Octane	0.0080	0.0547	0.0355	0.2332
n-Nonane	0.0058	0.0802	0.0433	0.1006
n-C_{12} +	0.0049	0.1915	0.0893	0.0718
n-C_{13} +	-	-	-	0.1793

Table 4: Mass of gaseous species at 0 psig from rail car

	mass (kg)			
Oil	***Bkn C30+***			***BH102 C10+***
Temperature	**65°C**	**204°C**		**204°C**
Pressure	**0 psig**	**0 psig**	**75 psig**	**0 psig**
Methane	5	5	5	3
Ethane	70	79	76	31
Propane	341	507	445	367
i-Butane	127	273	214	250
n-Butane	552	1400	1045	888
i-Pentane	206	950	585	862
n-Pentane	272	1456	856	1062
n-Hexane	331	4212	1841	3955
n-Heptane	133	3999	1298	4522
Benzene	9	108	46	182
Toluene	8	243	74	447
E-Benzene	1	68	16	140
p-Xylene	6	439	103	489
n-Octane	17	1115	282	7413
n-Nonane	12	1636	344	3197
$n\text{-}C_{12}+$	10	3906	709	2283
$n\text{-}C_{13}+$	-	-	-	5699

In order to determine the velocity of gases issuing from the manway, the mass flux rate (kg/m^2s) was estimated by using data obtained for a range of crude oils [5]. In ref. [5], the evaporation rate as a function of temperature was obtained for light and heavy crude oils. A light crude oil was chosen from this work to estimate the release velocity and duration for the calculations. The oil type is called Delta West Block 97, USA with the empirically determined evaporation rate represented by the following equation.

$$\%Ev = (6.57 + 0.045T)\ln(t) \qquad (1)$$

%Ev – percent mass evaporated
T – temperature in degrees C
t – time in minutes

The release velocity and duration is then determined by applying a mass balance where the gases are assumed to be generated only at the free surface of the oil inside the railcar. The railcar is approximately 18 m in length and 3 m in diameter. At 80% full, the top surface area is determined by using a width of 2.61 m and length of 18 m, thus 47 m^2. The mixture density and total mass to be released based on the vapor mixture calculations described previously were used to determine the release velocity and release duration. Pertinent quantities to determine the velocity of gases issuing from the manway and the duration

of their release, as well as their values, are provided in Table 5. The source of the vapors from the liquid inside the tank is assumed to be coming from only the top surface of the liquid and the dynamics of boiling is not considered. The LFL of the mixture is calculated using Le Chatelier's method which is an accurate method to determine the LFL of mixtures [6]. The equation for the Le Chatelier's method is,

$$\frac{1}{LFL_{mix}} = \sum_{i=1}^{N} \frac{y_i}{LFL_i}$$

Table 5: Pertinent quantities used to determine source conditions

Oil	***Bkn C30+***			***BH102 C10+***
Temperature	**65°C**	**204°C**		**204°C**
Pressure	**0 psig**	**0 psig**	**75 psig**	**0 psig**
Total mass (kg)	2,100	20,397	7,938	31,788
LFL (%vol)	1.65	1.20	1.32	1.01
mixture density (kg/m^3)	2.2	2.4	2.0	2.8
mass flux* (kg/m^2 s)	0.53	1.04	1.32	0.28
release velocity (m/s)	1.2	2.2	~100	0.5
release duration (min) (s)	1.4 (84)	7 (418)	2.1 (126)	40.2 (2412)

*At top surface of liquid inside rail car, calculated using eq. 1. Note that values have been rounded.

Simulation Specifications

Turbulence model

Fluent provides an array of various turbulence models including the Scale Adaptive Simulation (SAS) method which is utilized in these simulations. This model was chosen because it displays features of large eddy simulation (LES), but with less resolution requirements due to also sharing features of Reynolds Averaged Navier-Stokes (RANS).

The model captures smaller scales in sufficiently unsteady regions of the flow field, but reverts to RANS or URANS in more stable regions. Also, it will turn to a RANS or URANS mode in regions where the resolution is insufficient or the time step is too large. There must be sufficient instability in the flow to switch to the scale resolving mode. In simulations not providing sufficient instability, Fluent provides two different methods to aid in introducing instability by producing stochastic fluctuating velocity components at a boundary. Realistic profiles for velocity, turbulent kinetic energy, and turbulent dissipation are required before applying the methods and can be imported into the SAS-SST simulation by first performing a RANS or Reynolds stress model (RSM) calculation.

Geometry, Mesh, and Boundary Conditions

Pertinent dimensions of the railcar used for the calculations are provided in Table 6.

Table 6: Pertinent railcar dimensions

railcar specifications	***dimension (m)***
length	18
diameter	3.05
height from rail	4.73
manway diameter	0.51
pressure relief diameter	0.1

The domain and mesh specifications are provided in Table 7. Figure 6 and Figure 7 show the exterior and interior view of the mesh. The coarse mesh is only displayed here since it has a sufficiently low density of mesh lines allowing for ease of viewing as compared to the fine mesh. Table 8 provides boundary conditions information regarding types and values.

Table 7: Domain and mesh specifications

Domain	100 m, 60 m, 20 m (x,y,z)
Number of elements	285,477 (coarse mesh) 2,085,336 (fine mesh)

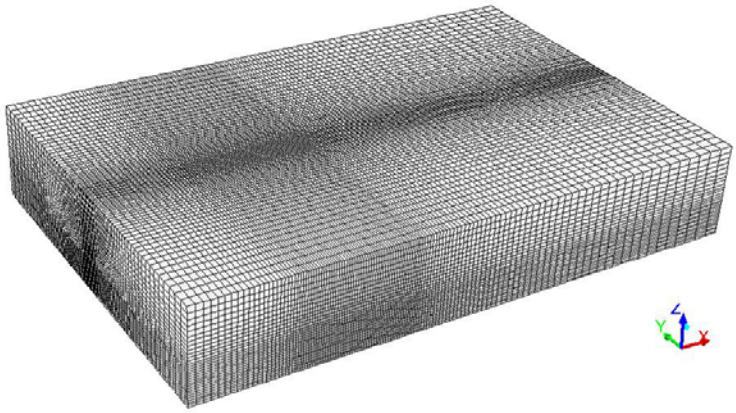

Figure 6: Exterior domain, coarse mesh

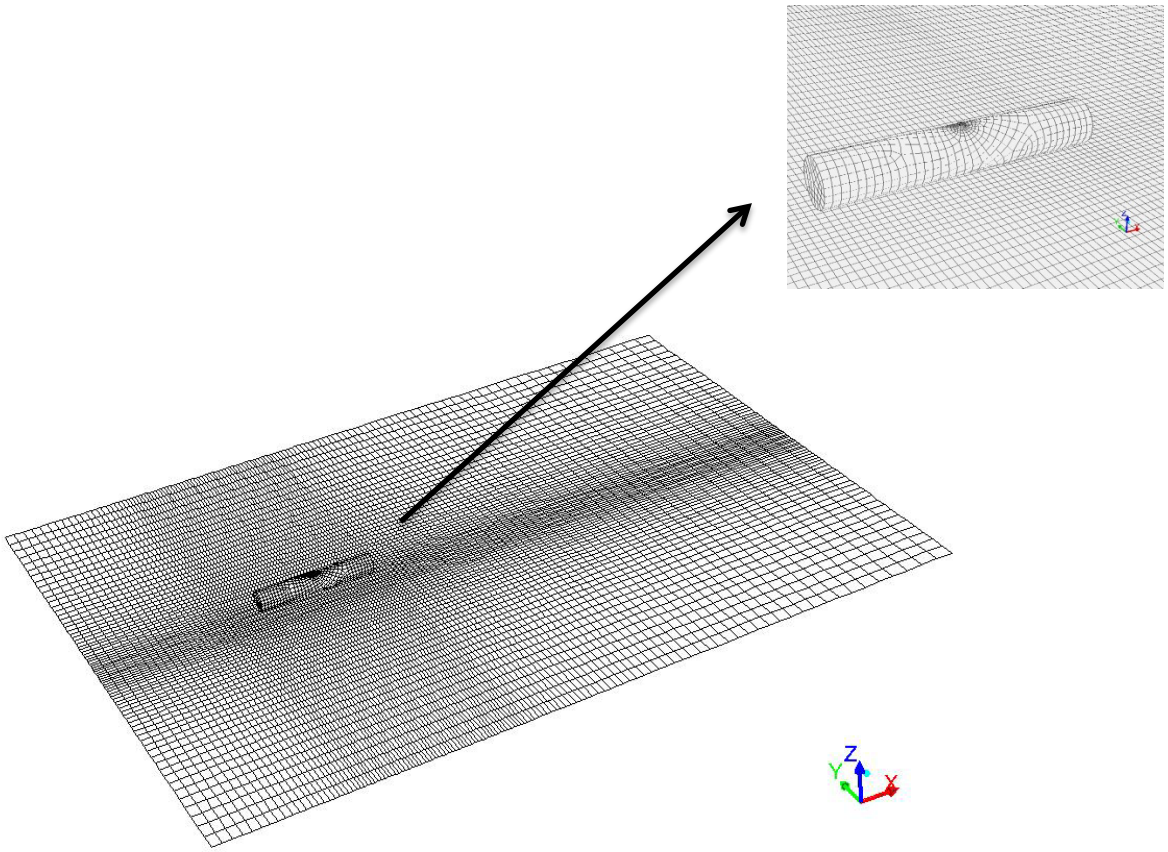

Figure 7: Interior view showing railcar, coarse mesh.

Table 8: Boundary conditions

Surface	**Boundary Type**	**Specification**
wind	velocity-inlet	2 m/s and 9 m/s
sides	symmetry	na
top	symmetry	na
outflow	pressure-outlet	backflow turbulent intensity and length scale, 1%, 1 m
ground	wall	no slip adiabatic
railcar	wall	no slip constant temperature (65^{o}C or 204^{o}C)
fuel source	velocity inlet	see Table 3 for mass fractions and Table 5 for velocities at respective temperatures

The cases are performed with two different wind speeds using slightly different atmospheric conditions, namely, low wind speed with stable conditions and high wind speed with neutral conditions. These were chosen because more stable conditions promote less mixing and result in longer dispersion distances. Stable conditions usually do not prevail at high wind speeds, thus a neutral condition is the closest condition to stable that can be specified.

Preliminary Results

Thus far, the cases for Bakken C30+ at 65^{o}C at 0 psig for two different wind speeds have been performed. Figure 8 shows these preliminary results for a release through a manway. These results are considered preliminary since a grid refinement study has not been performed. The wind direction is from left to right. The figures provide concentration contours at a plane that runs through the center of the railcar. The boundary of the red region indicates the extent of the distance to ½ LFL. The results indicate that the distance to ½ LFL is about 4 m from the end of the railcar. Even though the vapors are heavier than air, sufficient mixing occurs to dilute the cloud before it can sink. Thus, if the cloud were ignited the hazard region would be near the railcar and would only be a significant hazard to persons fairly close to the railcar. These scenarios indicate that the vapor cloud, given their extent, would not propagate into buildings or congested areas where explosion potential increases.

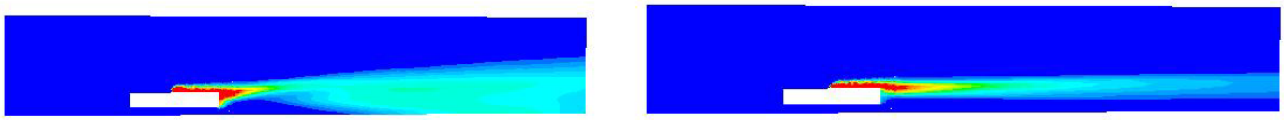

Figure 8: Concentration contours at mid-plane for Bakken C30+ with wind speeds of 2 m/s (left) and 9 m/s (right) for release through manway at 65^{o}C. Red region boundary denotes distance to ½ LFL.

In addition to performing grid refinement, further work will focus on completing the higher temperature and pressure cases listed in Table 3. Additionally, a railcar oriented perpendicular to the wind direction will be investigated. This orientation will result in turbulence induced flow separation, causing a recirculation region on the downwind side of the railcar. There is a potential for vapors to be pulled closer to the ground for this case, causing the vapors to slump or hug the ground rather than to loft or become buoyant.

References

[1] D. Lord, A. Luketa, C. Wocken, S. Schlasner, T. Aulich, R. Allen and D. Rudeen, "Literature Survey of Crude Oil Properties," Sandia National Laboratories, Albuquerque, NM (UUR), March 2015, SAND2015-1823.

[2] M. Pontiggia, G. Landucci, F. Busini, M. Derudi, M. Alba, M. Scaioni, S. Bonvinci, V. Cozzani and R. Rota, "CFD Model Simulation of LPG Dispersion in Urban Areas," *Journal of Hazardous Materials,* vol. 45, pp. 3913-3923, 2011.

[3] Association of American Railroads, "Annual Report of Non-Accident Releases of Hazardous Materials Transported by Rail," Association of American Railrodad Bureau of Explosives, 2013.

[4] R. Sherlock and E. Lesher, "Role of Chimney Design in dispersion of Waste Gases, Air Repair," *Air Repair,* vol. 4, no. 2, pp. 13-23, 1954.

[5] M. Fingas, "Modeling Oil and Petroleum Evaporation," *J. Pet. Sci. Res. (JPSR),* vol. 2, no. 3, pp. 104 - 115, 2013.

[6] F. Zhoa, "Inert gas dilution effects on flammability limits of hydrocarbon mixtures," Doctoral Dissertation, Texax A & M University, December 2011.