A Flammability (Risk) Index for Transportation of Flammable Liquids

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1   *Abstract*

Recent accidents involving trains carrying flammable liquids (crude oil, ethanol, etc.) and consequent release of these flammable liquids have resulted in the formation of large fires. These fires have caused significant property damage and, in some cases, fatalities.

The focus of reducing such accidents has been on implementing train operational controls, improving tank car puncture resistance, and providing thermal protection systems on tank cars to reduce the rate of heat input from an external fire to the liquid in the tank. In addition, one of the current regulatory approaches for reducing the post-accident fire and explosion risk is to require the reduction in the product vapor pressure at the time of loading of the product into tank cars. This is based on the assumption vapor pressure is the sole metric of volatility and flammability.

This paper demonstrates that vapor pressure alone cannot be a metric to evaluate the hazard potential of a flammable liquid. Other vapor properties, including the flammability range concentrations in air and the minimum ignition energy, must be considered. A Flammability Index (FI) is developed and applied to example flammable liquids. FI for a specific Bakken crude oil sample is 1.25 and for ethanol 11.3, making ethanol a more "flammable risk" material than crude oil, at normal temperatures. This result is completely opposite to what one would conclude based purely on vapor pressure (ethanol vapor pressure at 77 ^{o}F is 1.2 psia vs. 8.7 psia for crude oil at the same temperature).

2   *Background*

The U.S. production of crude oil from the Bakken fields in North Dakota, in the Eagle Ford and Permian Basins in Texas have increased significantly in the past few years. Increased use of ethanol as a gasoline additive has also resulted in increased production of ethanol. These production rises have correspondingly increased the rail shipment volumes. Figure 1 illustrates the North American (principally the US) rail shipment volume statistics for both crude oil and

ethanol over the past several years. The dramatic increase in crude oil shipments from 2012 can be seen. The slight decrease in oil shipments in 2014 compared to that in 2013 may be due to the softening of the oil market. Rail transportation of ethanol has peaked at about 300,000 shipments, but has been above 200,000 shipments since 2008.
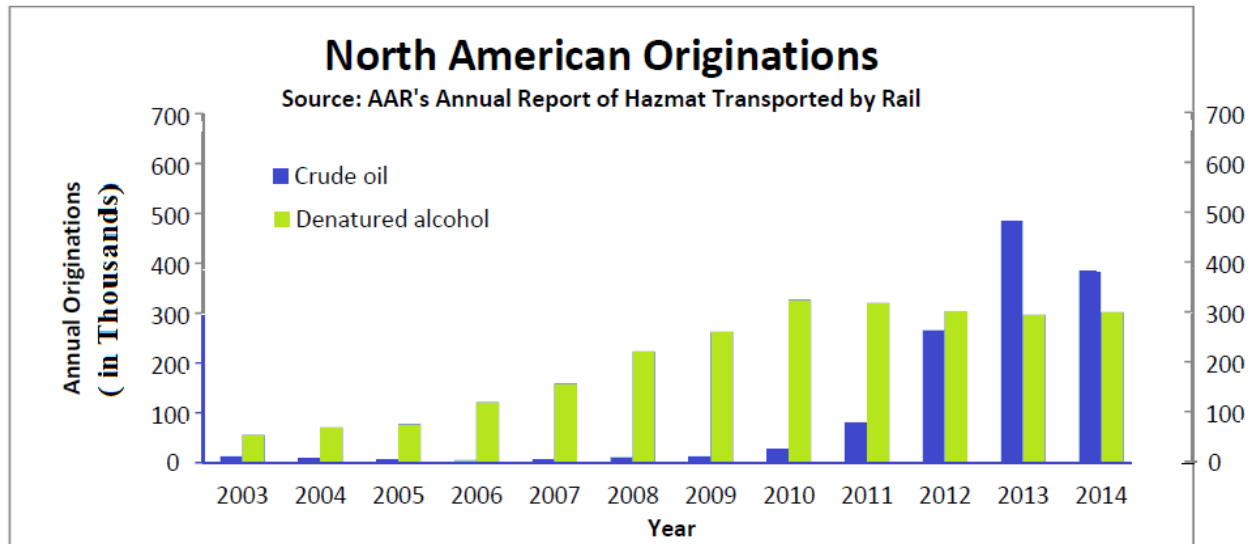

Figure 1: Comparison of historical volumes of shipments of crude oil and ethanol on rail

For shipments on the US transportation system, both crude oil (UN 1267) and ethanol (UN 1170) are classified (by 49 CFR, §172.101) as Class 3 Flammable liquid[1] hazardous materials (HM). For a long time flammable liquids, in general, and oil products in particular have been safely transported on rail. However, the recent significant increase in rail shipments, principally in unit trains[2], have resulted in several accidents leading to the release of products, occurrence of large fires causing fatalities and injuries to the public.

The US Department of Transportation and its operating Administrations (Federal Railroad Administration – FRA, and Pipeline and Hazardous Materials Administration – PHMSA) have taken a number of steps to reduce the occurrence of such accidents and minimize/mitigate the consequences should releases of flammable liquids occur in railroad accidents. These steps have included promulgating new regulations to (i) increase railroad operational safety, (ii) enhance train dynamics, (iii) improve tank car mechanical designs to withstand accident caused forces, (iv) reduce the deleterious effects of a fire on undamaged tank cars, and (v) implement emergency response actions.

Flammable liquids can be transported on rail only in certain specified types of tank cars ("packaging") depending upon the "packaging group (PG)" to which the flammable liquids belong. The packaging groups are PG-I, PG-II and PG-III. Figure 2 shows schematically the

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[1] 49CFR, §173.120 definition of a (Class 3) flammable liquid is "*a liquid having a flash point of not more than 60 °C (140 °F), or any material in a liquid phase with a flash point at or above 37.8 °C (100 °F) that is intentionally heated and offered for transportation or transported at or above its flash point in a bulk packaging…*"

[2] A unit train consists of tank cars all carrying the same material (ex., crude oil or ethanol) and could consist of more than 100 tank cars in a train.

definitions of the three packaging groups for shipment of flammable liquids in tank cars. PG-I material has to be transported in tank cars with additional safety features.
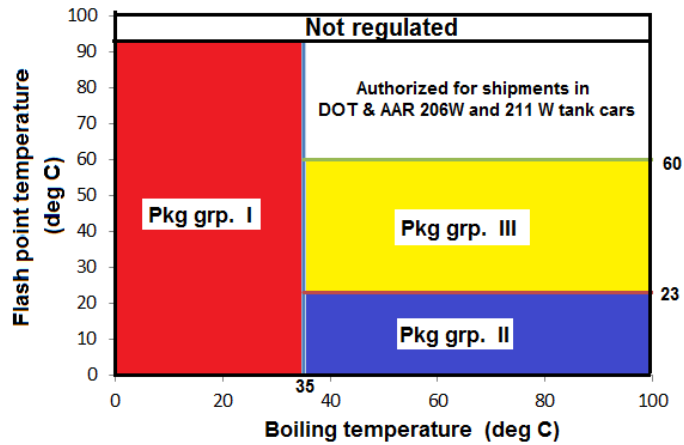

Figure 2: Definitions of packaging groups based on boiling point and flash point

As can be seen from Figure 2, the PG group is based on the (initial) boiling point of the liquid at atmospheric pressure and the "flash point" temperature of the liquid. While the Federal Regulations do not provide any rationale for the above classification of the flammable liquids it can be surmised that the classification is based on the assumption that the vapor pressure of the liquid (with flash point as the surrogate measure of its vapor pressure at ambient temperature) is a metric of its flammability. However, flammability of a vapor depends not only on the vapor pressure but also on other ignition properties of the vapor such as the lower and upper flammability concentration range in air and the strength of an ignition source. Many of the rail accidents in which large fires have occurred seem to indicate that vapor pressure alone cannot represent the whole story for the types of hazards that have resulted. In the following section some of the recent accidents involving crude oil and ethanol releases are reviewed.

3   *Historical Rail Accidents*

Table 1 shows the rail accidents in the past 10 years that have resulted in releases of crude oil or ethanol. Some of these accidents have resulted in large fires and near-field harmful consequences to the public.

Figure 3 and Figure 4 show, respectively, the fireball type of burning of crude oil and ethanol (alcohol) releases from tank cars in rail accidents. In most cases the releases were due to sudden rupture of the tank car wall and the consequent release of superheated and pressurized gas and liquid into the environment where there was already a pool fire in the vicinity. Figure 5 shows examples of the tank car wall ruptures in an accident involving the release of ethanol. Figure 6 shows similar crude oil tank car wall damages. It is clear that in both crude oil and ethanol releases the effects are very similar for tank car damages and the type of fires that resulted (type, shape and intensity) from the releases.

Table 1: Train derailments (in 2006 to 2015) involving crude oil and denatured alcohol releases from tank cars

Train accident location	Month & Year	Number of tank cars derailed	Tank car contents	Train make-up
Heimdel, ND	May 2015	6	Crude oil	Unit train
Galena, IL	Mar 2015	21	Crude oil	Unit train
Mt. Carbon, WVA	Feb 2015	27	Crude oil	Unit train
LaSalle, CO	May 2014	5	Crude oil	Unit train
Lynchburg. VA	May 2014	17	Crude oil	Unit train
Vandergrift, PA	Feb 2014	21	Crude oil, LPG	Large block of HM cars
New Augusta, MS	Jan 2014	11	Crude oil	Unit train
Plaster Rock, NB	Jan 2014	9	Crude oil, LPG	Large block of HM cars
Casselton, ND	Dec 2013	20	Crude oil	Unit train
Aliceville, AL	Nov 2013	26	Crude oil	Unit train
Lac-Megantic, Qubec	Jul 2013	63	Crude oil	Unit train
Plevna, MT	Aug 2012	17	Denatured alcohol	Large block of HM cars
Columbus, OH	Jul 2012	3	Denatured alcohol	Large block of HM cars
Tiskilwa, IL	Oct 2011	10	Denatured alcohol	Large block of HM cars
Arcadia, OH	Feb 2011	31	Denatured alcohol	Unit train
Rockford, IL (Cherry Valley)	Jun 2009	19	Denatured alcohol	Unit train
Luther, OK	Aug 2008	8	Crude oil	Large block of HM cars
Painesville, OH	Oct 2007	7	Denatured alcohol	Large block of HM cars
New Brighton, PA	Oct 2006	23	Denatured alcohol	Unit train

Casselton, ND accident, 2013   Galena, IL accident, 2015
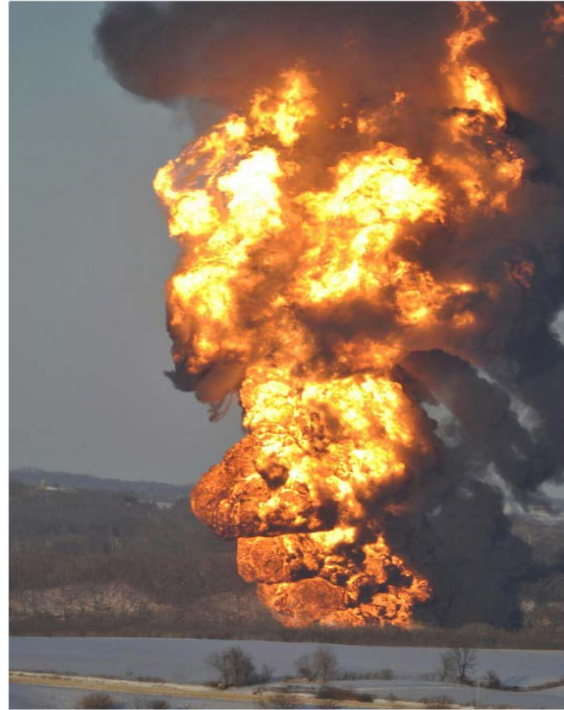
Figure 3: Fireball type fires resulting from crude oil releases from rail tank cars

Arcadia, OH accident, 2011   Plevna, MT accident, 2012

Figure 4: Fireball type fires resulting from ethanol releases from rail tank cars

Fish-mouth tear in a tank car wall.   Part of the tank car "tub" rocketed.

Figure 5:   Tank car wall damage and tear in the Arcadia, OH accident; Ethanol release

Fish-mouth tear in a tank car wall.   Circumferential tear and tub separation.

Figure 6:   Tank car wall damage and tear in the Aliceville, AL accident; Crude Oil release

In response to recent rail accidents involving crude oil releases and fires (discussed above) the Pipeline and Hazardous Materials Safety Administration (PHMSA) and the State of North Dakota have promulgated certain regulations. One of the requirements is to reduce the vapor pressure of crude oil before being loaded on to tank cars. While the reduction in vapor pressure does reduce the "volatility" of the liquid, vapor pressure alone does not affect the ignition potential of any flammable liquid releases, and fire/explosion hazards such releases may cause.

There are a number of chemical property parameters and circumstances of release which affect the type and magnitude of the hazard when a flammable liquid is released from a tank car. These parameters include, (i) the vapor pressure of the liquid at a specified (say, 100 ^{o}F) temperature, (ii) the range of flammability concentrations of the vapor when mixed with air, (iii) the thermodynamic properties including the relationship between liquid temperature and the equilibrium pressure of the vapor, (iii) the normal boiling point, (iv) the super heat limit temperature, etc.

The release scenarios and the associated types of hazards that may arise in an accident involving a tank car carrying a flammable liquid include:

1. Condition of vapor in the ullage volume of tank cars with different flammable liquids loaded at atmospheric pressure through open manway. Is the vapor flammable?

2. Puncture of tank car in the ullage space, release of vapors and ignition by very close pilot igniter, all at ambient temperature.

3. Tank car puncture below liquid line and release of liquid at ambient temperature on to ground – formation of pool and evaporation. Vapor generation, its dispersion and ignition. Immediate ignition if the ignition source is very close by.

4. Exposure of a non-thermally protected tank car to a fire, thermal tear at a pressure higher than the start-to-discharge-pressure (STDP) of the pressure relief valve. Instantaneous release of vapor (flashing) and the entrained liquid. Formation of a fireball and possible explosion.

Investigations of recent crude oil and ethanol release accidents indicate that most tank cars that show thermal tears have steel wall thicknesses thinned to about 75% of the original thickness. Also, it is estimated that at the time of the thermal tear, the steel yield strength would have decreased to about 50% of its ambient temperature value[3]. Based on these findings the pressure in the tank car (just before the thermal tear) can be estimated by knowing the design burst pressure of the tank car. This result is used to estimate the liquid temperature in the tank car just prior to the thermal tear. The fraction of liquid mass that flash vaporizes when the tank car wall suddenly ruptures can also be calculated.

This suddenly released mass of vapor burns in the form of a fireball. The fireball effects will be exacerbated if liquid is entrained into the vapor. Liquid releases are entirely possible due to the sudden vaporization throughout the volume of the superheated liquid. The rising vapor bubbles will essentially push a lot of liquid out of the tear. It is uncertain what fraction of the post flash mass of the liquid in the tank car will be released and the form (i.e., the droplet sizes) in which the liquid is released. If the liquid is released as fine droplets (in the 10 μm to 30 μm range) there exists a potential for the formation of very rapid spray combustion resulting the production of a blast wave [Bowen & Cameron, 1999]. Such blast wave creating combustion has not been observed in rail accidents to date with either crude oil or ethanol releases; however (as seen in Figures 3 and 4) fireball combustion is very likely.

This paper does not model the (important) phenomena associated with the sudden release of a superheated liquid from a tank car with which to estimate the magnitude of the fire or blast related consequences. However, the paper discusses a more relevant criterion for classifying flammable liquids than purely on the flash point (or vapor pressure).

4 *Objective of the Model*

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[3] The transition temperature of steel where its yield strength begins to decrease is 427 $^{\circ}$C (800 $^{\circ}$F). At about 550 $^{\circ}$C (1020 $^{\circ}$F) the steel strength is about 50% of its ambient temperature value.

The objective of the work presented in this paper is to develop a methodology for quantitatively rank ordering the hazard potential and the flammability risk of a liquid hydrocarbon fuel released (from storage) at near ambient pressure. To achieve this objective a model is developed which:

1 Considers vapor pressure and other flammability characteristics of the vapor generated by the flammable liquid.

2 Develops a procedure for calculating the "Flammability Ranking Index" for each liquid fuel.

3 Compares the hazard potential of crude oil and ethanol using this index.

This rank ordering will provide a rational risk basis by which to assign a flammable liquid product to the proper packaging group, based on more than one property parameter. The model is not intended to classify flammable liquids on a hazard impact scale nor intended to be applicable to releases of superheated and pressurized liquids.

5 *Details of the Model*

The model below takes into account the contribution of the vapor pressure, ignitability and ignition energy.

5.1 *Vapor pressure*

The vapor in thermodynamic equilibrium with a liquid inside a closed container will exert a pressure termed "the vapor pressure." For pure liquids, such as water or anhydrous ethanol, there is unique relationship between the temperature and vapor pressure. For a single component liquid whose atmospheric boiling point temperature is higher than that of normal atmospheric temperature (say, from 278 to 320 K or 40 to 115 ^{o}F), the vapor pressure is lower than the atmospheric pressure.

There is generally no unique vapor pressure – liquid temperature relationship for multicomponent liquids, such as crude oil. The pressure exerted by the vapor in equilibrium with a multicomponent mixture liquid (at any specified liquid temperature) depends upon the molar concentration of the various pure components in the liquid and the individual pure liquid vapor pressures. Table 2 shows the vapor pressure, at a temperature of 298 K (77 ^{o}F) for crude oil with a particular mixture of individual hydrocarbon components[4]. Table 2 also shows the details of calculation of the overall crude oil vapor pressure, at the specified temperature and specified molecular component concentrations in the liquid. Also shown in Table 2 is the vapor pressure for ethanol at the same temperature.
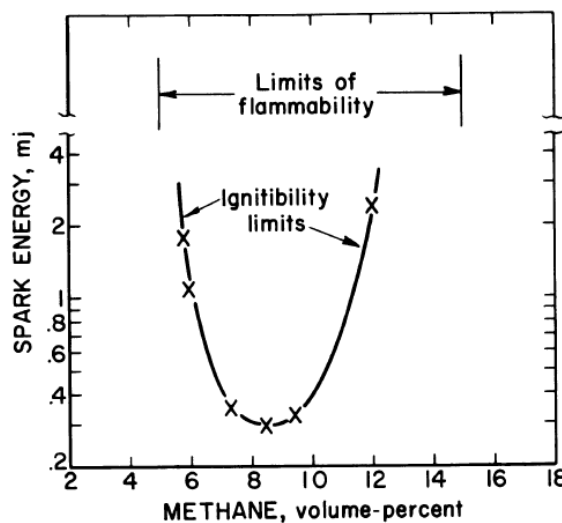
5.2 *Vapor Ignition*

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[4] *The concentration values of C2 to C10 components in a sample of Bakken crude oil (sample # MDND 44-001) measured by Intertek, Inc., in 2014 are used in the calculations indicated in this paper. Concentrations of components higher than C10 are calculated by equally distributing to each component the remainder of 100% less C2 to C10 concentrations.*

When a flammable vapor is mixed with air it can be ignited only if the vapor concentration in air is within a range called the flammability range. There is an upper limit concentration of vapor above which the vapor-air mixture is NOT ignitable ("Upper Flammability Limit – UFL"). Similarly, when the vapor mixture is dilute, a lower limit concentration exists below which the vapor-air mixture is NOT ignitable ("Lower Flammability Limit – LFL"). In a real vapor cloud dispersing in the atmosphere these limits may get extended because the mixture is not uniform in concentration (due to turbulence); when the average concentration is below the lower flammable limit (LFL) there may exist pockets of gas that are in the flammable range and so may, in fact, be ignitable. The same is true on the upper flammable limit (UFL) concentration. The LFL and UFL values for a number of pure paraffin vapors and ethanol are also indicated in Table 2.

A liquid fuel, such as crude oil, is a mixture of different saturated paraffins (ex., ethane, propane, butane, pentane, hexane, etc.) and other constituents in different molar proportions. The evaporation of such a mixture liquid fuel results in the formation of a vapor with different molar proportions of the constituent hydrocarbons, depending upon the temperature of vaporization and the initial liquid composition. Vapors of constituent paraffins will have different sets of LFL and UFL values. The LFL and UFL of the mixture of vapors are calculated by using Le Chatelier's method. The combined LFL (or UFL) is the harmonic mean of the LFLs (or UFLs) of the different paraffin vapor components, weighted by their respective molar concentrations (or partial vapor pressures) in the vapor mixture, emanating from liquid evaporation.

The necessary condition for the burning of a vapor cloud is that it has a vapor-to-air concentration value within the UFL to LFL range. However, this is not a sufficient condition. The ignition can only be effected when the ignitor has sufficient energy, termed the "*minimum ignition energy.*" This minimum ignition energy is relatively small but does vary with the molecular structure of the vapor species, temperature and pressure. There exists a vapor concentration at which the energy to ignite is a minimum.

Figure 7 below shows the energy required to ignite a methane-vapor-air mixture as a function of the vapor concentration. This data can be interpreted as the probability of ignition being inversely proportional to the ordinate (ignition energy) for a given ignition source strength.

Figure 7:   Ignition energy vs. vapor concentration for methane in air

Based on the above argument Figure 8, shown below, is developed to represent the ignition probability density function ("pdf") and its variation with the vapor concentration in air for a specified energy of the ignitor. It is noted that the area under the curve in Figure 8 is unity, representing the total probability of ignition, given that the energy of the ignitor is above the minimum ignition energy. It is noted that the pdf is high in the concentration range between LFL and UFL. The features of this distribution and the relationship between the parameters are indicated in Appendix A.

Figure 8:   Schematic representation of the variation of probability density of flammable vapor ignition with vapor concentration in air

5.**3**   *Analysis*

The pressure of the vapor in equilibrium with the liquid (at the specified liquid temperature) is P_V. For multicomponent liquids, such as the crude oil, this is calculated using the methodology describe in a recent White Paper (Raj, 2014). The results for a specific sample of Bakken crude oil are presented in Table 2.

For the case where the absolute vapor pressure is less than the atmospheric pressure, the molar concentration C_v (or the volume fraction concentration) of the vapor in air is the same as the ratio of the vapor pressure (P_v) to the atmospheric pressure (P_{Atm}). That is,

$$C_V = p_V = \frac{P_V}{P_{Atm}} \quad \text{for} \quad p_V \leq 1 \tag{1}$$

Flammability Index (FI): A "Flammability Index" for a flammable liquid is postulated to be directly proportional to the ignition probability density value at the vapor concentration in air

(immediately above the liquid) and inversely proportional to the minimum ignition energy. Using this thesis, a Flammability Index is defined as follows:

$$FI = \frac{\text{Ignition pdf at the vapor pressure } (p_v)}{\text{Minimum ignition energy for igniting the vapor (in mJ)}} \quad \quad (2)$$

The above definition of the flammability index will indicate that the larger the value of FI the higher is the risk of ignition of the flammable liquid.

6   *Application (of the FI model) to Ethanol and Crude Oil*

6.1   *Calculated Results*

The calculated vapor pressure for a particular sample of Bakken Crude Oil is 60 kN/m^2 (8.7 psia) at a liquid temperature of 298 K (77 ^{o}F) – See Table 2. The calculated vapor pressure at the same temperature for ethanol is 8 kN/m^2 (1.2 psia). This means that ethanol has a much lower vapor pressure at the specified temperature than the sample Bakken crude oil. The minimum ignition energies, respectively, for crude oil vapors and ethanol vapors are 0.24 mJ and 0.64 mJ. That is, it takes a more energetic spark to ignite ethanol vapors than is required to ignite crude oil vapors. Based on these two parameters alone one can conclude (erroneously) that ethanol has less ignition potential than crude oil – an incorrect conclusion.

Table 3 shows the calculations of the various terms that are used in the calculation of the Flammability Index (FI), defined in equation 2. It is seen that the Flammability Index is 1.25 for Crude Oil and 11.31 for Ethanol.

Table 2: Calculation of Vapor Pressures, LFL & UFL for Crude Oil & Ethanol
(Crude oil: Intertek sample # MDND 44-001)

Carbon number			2	3	4	4	5	5	6	7	8	9	10	11	12	13	14	15	TOTAL	Ethanol
Property	Symbol	Units	Ethane	Propane	n-Butane	Iso-Butane	n-Pentane	Iso-Pentane	n-Hexane	n-Heptane	n-Octane	n-nonane	n-decane	$C_{11}H_{24}$	$C_{12}H_{26}$	$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	Crude Oil	
Molecular formula			C_2H_6	C_3H_8	C_4H_{10}	C_4H_{10}	C_5H_{12}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$	$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	Oil	C_2H_6O
Molecular Weight	μ	kg/kmol	30.07	44.10	58.12	58.12	72.04	72.04	84.98	98.71	112.30	126.52	141.58	170.00	184.00	198.00	198	212		46.07
Freezing Temperature	T_F	K	89.9	85.5	134.8	113.6	143.4	113.3	177.8	182.6	216.4	219.7	243.5							159.1
Atmospheric boiling temperature	T_b	K	184.6	231.1	272.7	261.4	309.2	301.1	341.9	371.6	398.8	424.0	447.3	469.1	489.5					352
Liquid density at boiling point (or at 293K if boiling pt is above 293K)	ρ_L	kg/m^3	548.0	582.0	579.0	557.0	626.0	620.0	659.0	684.0	703.0	718.0	730.0							789
Critical Temperature	T_c	K	305.3	369.9	425.1	407.8	469.7	460.4	507.5	540.3	568.8	594.6	617.7	638.8	658.2					514
Critical Pressure	P_c	bar	48.7	42.5	38.0	36.3	33.6	33.8	30.2	27.4	24.9	22.9	21.2	19.7	18.2					63.0
Vapor Pressure at 20 °C	P_{20}	bar	37.6	8.34	2.07	3.00	0.56	0.76	0.16	0.047	0.014	0.004	0.001							0.060
Vapor pressure equation coefficients	A	ND	-6.34070	-6.72219	-6.88709	-6.95579	-7.28936	-7.12727	-7.46765	-7.67468	-7.91211	-8.24480	-8.56523	73.501	77.628					-8.51838
	B	ND	1.01630	1.33236	1.15157	1.50090	1.53679	1.38996	1.44211	1.37068	1.38007	1.58850	1.97756	9305.8	10012.5					0.34163
$P_{vp}(T)=P_c \exp\left[\frac{Ax+Bx^{1.5}+Cx^3+Dx^6}{(1-x)}\right]$ where $x=\left(1-\frac{T}{T_c}\right)$	C	ND	-1.19160	-2.13868	-1.99873	-2.52717	-3.08367	-2.54302	-3.28222	-3.53620	-3.80435	-4.38155	-5.81971	-8.729	-9.236					-5.73683
	D	ND	-2.03539	-1.38551	-3.13003	-1.49776	-1.02456	-2.45657	-2.50941	-3.20243	-4.50132	-4.04412	-0.29982	8,813.0	10030					8.32581
Minimum temperature for use of vap pr eqn	T_{min}	K	133.0	145.0	170.0	165.0	195.0	220.0	220.0	240.0	260.0	343.0	368.0	350	360					293
Temperature at which vapor pressure is needed	T	K	298	298	298	298	298	298	298	298	298	298	298	298	298					298
Reduced temperature deviation	X	ND	0.02397	0.19436	0.29904	0.26927	0.36548	0.35267	0.41281	0.44845	0.47609	0.49882	0.51757	0.53350	0.54725					0.4202335
Vapor pressure	P	bar	41.853975	9.4895	2.429372	3.480218	0.676951	0.911757	0.200881	0.060278	0.018437	0.005698	1.849E-03	6.164E-04	2.055E-04	6.849E-05	2.283E-05	7.609E-06		0.0799801
		N/m^2	4,185,398	948,950	242,937	348,022	67,695	91,176	20,088	6,028	1,844	569.8	184.9	61.6	20.5	6.8	2.3	0.8		7,998.0
Molar concentration of vapor in air mixture at 1 atmospheric pressure	Y	%	100.0	100.0	100.0	100.0	66.8	90.0	19.8	5.9	1.8	0.6	0.2	0.1	0.0	0.0	0.0	0.0		7.9
Heat of Vaporization of liquid at atmospheric saturated condition	λ	kJ/kg	489.4	425.6	385.7	365.1	366.8	357.5	371.5	370.2	370.6	367.0	360.5							837.0
LowerFlammable limit in air (molar)	LFL	%	3.0	2.1	1.60	1.80	1.40	1.32	1.10	1.05	1.30	0.83	0.77	0.68	0.60					3.3
Upper Flammable limit in air (molar)	UFL	%	12.4	9.6	8.40	9.60	7.80	9.16	7.50	6.70	7.60		5.35							19.0
Minimum Ignition energy	IE	mJ		0.25	0.25	0.25	0.18	0.18	0.24											0.64
Mole concentration in liquid	$X_{m,i}$	%	0.383	2.308	2.551	2.551	2.917	2.917	8.089	9.254	9.193	7.341	2.098	11.750	10.782	9.962	9.258	8.646	100.000	
Vapor Pressure exerted by each component	p_i	N/m^2	16,049.8	21,899.4	6,197.8	8,878.7	1,974.5	2,659.4	1,625.0	557.8	169.5	41.8	3.9	7.2	2.2	0.7			60,067.7	7,998.0
		psia																	8.7	1.2

p_i/LFL			5349.93	10428	3873.62	4932.61	1410.34	2014.66	1477.28	531.234	130.374				LFL of vapor mixture in equilibrium with liquid	1.99	%
	p_i/UFL		1294.34	2281.2	737.832	924.864	253.139	290.322	216.668	83.2532	22.3008				UFL of vapor mixture in equilibrium with liquid	9.83	%

Table 3: Calculation of the Flammability Index
For Crude Oil & Ethanol

Commodity	Min ignition ennergy	Vapor Pressure	Vapor molar concen. in air	Lower Flammability Limit	Upper Flammability Limit	a	c*	Y_{max}	$(c_V-c^*)/a$	c_V/C_{LFL}	c_V/C_{UFL}	pdf	Flammability Index
	mJ	psia	Mole fraction	Fraction	Fraction	Fraction	Fraction	1/fraction				1/fraction	
	(IE)	(P_V)	(C_V)	(C_{LFL})	(C_{UFL})								(FI)
Crude oil	0.24	8.7	0.6	0.0199	0.0983	0.0392	0.0591	13.3	13.6	29.7	6.0	0.3	1.25
Ethanol	0.64	1.2	0.1	0.0300	0.1900	0.0800	0.1100	7.8	0.4	2.7	0.4	7.2	11.31

Notes: (1)   Ignition pdf is that shown in Figure 8.
    (2)   The value of "q" is 0.05 in Figure 8.
    (3)   Liquid spill (at atmospheric) temperature = 298 K (77 °F)

6.2   *Discussion on the Results*

The vapor pressure of ethanol at 298 K (77 °F) is 8 kN/m² (1.2 psia) and that of a sample Bakken crude oil is 60 kN/m² (8.7 psia). Based on this parameter alone, one would conclude that ethanol is almost 7 times better (or less hazardous) than crude oil as far as the ignition potential for their vapors are concerned. Even if the minimum ignition energy alone is considered as a parameter it is seen that ethanol vapor is more difficult to ignite (0.64 mJ) compared to vapors of crude oil (0.24 mJ). One may, therefore, conclude that ethanol vapors are less prone to ignition than crude oil vapors. However, this conclusion would be incorrect.

Vapor ignition does not depend only on the vapor pressure (or its equivalent the concentration of vapor in the vapor air mixture) but also on the flammability range of the vapors in air. This is a very important parameter that has to be considered in any "Hazard Index" consideration.
All three parameters, namely, (i) the vapor pressure (or the equivalent vapor concentration in air), (ii) the vapor flammability concentration range in air, and (iii) the minimum ignition energy must be considered in defining the potential flammability hazard arising from the release of a flammable liquid at any temperature. This has been achieved in this Paper.

The Flammability Index values for ethanol and Bakken sample crude oil show (see results in Table 2) that ethanol has a Flammability Index that is about 9 times that of crude oil! This result is not only contrary to the erroneous conclusion from vapor pressure alone (ethanol is 8.7/1.2 = 7.5 safer than crude oil).

7   Conclusions

The conclusions from the model developed and the results presented in this study are:

1   Vapor pressure of a flammable liquid alone is not sufficient to classify a flammable liquid into packaging groups for rail transportation different strength packages.

2   Vapor flammability range in air and the minimum ignition energy for igniting the vapor must be considered, in addition to the vapor pressure, in determining the relative magnitude of flammability hazards between two different flammable liquids.

3   A Flammability Index has been defined and developed to perform the relative flammability hazards of vapors from flammable liquids.

4   The result of application of the methodology (and the determination of the Flammability Index) for ethanol and a sample crude oil from Bakken indicates that ethanol poses about 9 times higher magnitude flammability hazard compared to that from crude oil vapors at normal ambient temperatures.

5   This paper did not consider other modes of flammable liquid releases such as release due to the sudden failure of the tank wall from thermal tear. That is, the relative hazard potentials from two flammable liquids released from superheated conditions and high pressure causing rapidly flashing superheated liquid and liquid entrained vapor mass release from a tank car are not modeled.

References

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➢   Raj, P.K., "Calculation of the Vapor Pressures exerted by Crude Oil," White Paper, Hazmat Division, FRA Office of Safety, Federal Railroad Administration, Washington, DC, July 2014.

➢   Zabetakis, M.G., "Flammability Characteristics of Combustible Gases and Vapors," Bulletin # 627, Bureau of Mines, US Department of the Interior, Washington, DC, 1965.

<center>**Appendix A**</center>

<center>**Calculations related to the Ignition Probability Density Function**</center>

The schematic representation of the ignition probability density function (pdf) vs. the vapor concentration (or partial vapor pressure) in air is shown below. The curve, within the UFL – LFL region is assumed to be a parabola.
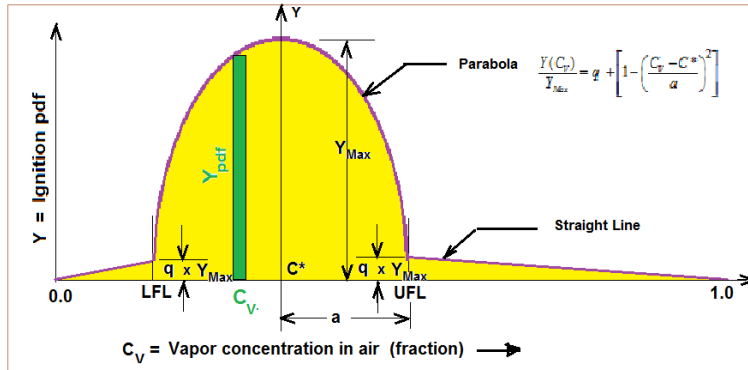
The following parameters are defined.

$$C* = \frac{(C_{UFL} + C_{LFL})}{2} \quad \text{(A-1)} ; \qquad a = \frac{(C_{UFL} - C_{LFL})}{2} \qquad \text{(A-2)}$$

The pdf curve is defined by the following distributions:

$$\frac{Y(C_V)}{Y_{Max}} = q \; \frac{C_V}{C_{LFL}} \qquad \text{for} \qquad \frac{C_V}{C_{LFL}} \le 1 \qquad\qquad \text{(A-3)}$$

$$\frac{Y(C_V)}{Y_{Max}} = q \; + \left[1 - \left(\frac{C_V - C*}{a} \right)^2 \right] \quad \text{for} \quad abs\left(\frac{C_V - C*}{a} \right) \le 1 \qquad \text{(A-4)}$$

$$\frac{Y(C_V)}{Y_{Max}} = q \; \frac{1 - C_V}{1 - C_{UFL}} \qquad \text{for} \qquad \frac{C_V}{C_{UFL}} \ge 1 \qquad\qquad \text{(A-5)}$$

Where "q Y_{Max}" represents the pdf at the LFL and UFL concentrations and C_V is any vapor concentration in air. The value of Y_{Max} is determined using the identity,

$$\int_{C_V = 0}^{C_V = 1} Y(C_V) \; dC_V = \; \text{Total Probability of ignition} \; = \; 1 \qquad\qquad \text{(A-6)}$$

Using equations A-1 through A-6 the value of Y_{Max} is calculated to be

$$Y_{Max} = \frac{1}{\left[\dfrac{q}{2}(1 + C_{LFL} - C_{UFL}) + \dfrac{2}{3}(C_{UFL} - C_{LFL}) \right]} \qquad\qquad \text{(A-7)}$$