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A flammability (risk) index for use in transportation of flammable liquids

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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 °F is 1.2 psia vs. 8.7 psia for crude oil at the same temperature).

1. 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. Fig. 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.

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

[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.

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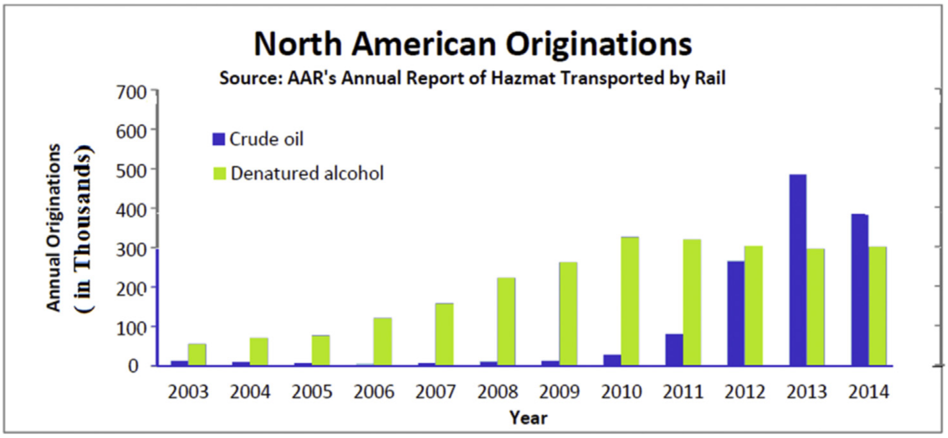

Fig. 1. Comparison of historical volumes of shipments of crude oil and ethanol on rail.

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. Fig. 2 shows schematically the 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.

As can be seen from Fig. 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.

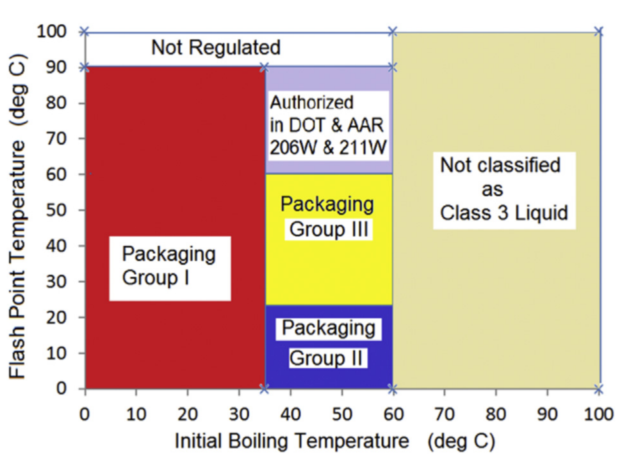

Fig. 2. Definitions of packaging groups based on boiling point and flash point.

2. 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.

Figs. 3 and 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. Fig. 5 shows examples of the tank car wall ruptures in an accident involving the release of ethanol. Fig. 6 shows similar crude oil tank car wall damages. The volume of ethanol and crude oil carried in each respective tank car was about 114 m^3 (~30,000 gallons). Also, the tank cars were DOT 111 specification (non insulated) cars. That is, the tank cars carrying crude and ethanol were made of the same steel, had the same wall thickness, similar in construction and were of the same structural strength and dimensions. 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.

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 °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

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