<u>Flammability of Bakken Crude Oil: Dangerous Rail Cargo Even When Empty</u>

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Suppose for the moment a noteworthy author published a paper dealing with the chemical properties of a flammable substance (like ethanol) made the following statements:

1) The flammability as measured by the LFL (Lower Flammable Limit) and flash point (FP) of ethanol vary with the amount of ethanol that has evaporated.
2) The LFL and FP of ethanol are not constant values and may vary with time even at constant temperature and pressure.
3) A container containing 2 ounces of ethanol is more flammable than one containing 12 ounces.

Even a novice scientist would disagree with the accuracy of the statements (1) and (2) because they contradict the fundamental principles of the properties of a substance, i.e., the LFL and FP of substance are intensive properties (like boiling point or density) and do not vary with the amount of material as the extensive properties (like mass or volume) vary and therefore must remain constant regardless of the amount of material present or the amount of time that has past. Statement (3) may require a bit more thought. We will get to this later.

The properties of LFL and FP are constant for a pure substance (provided certain criteria like LFL at a specific temperature and flash point type - closed or open cup are observed). But the key word is “pure” substance. Crude oil, however, is not a pure substance but a mixture of a variety of liquid petroleum fractions and dissolved volatile gases, each of which has their own characteristic LFL and FP values.

Therefore, from the moment the crude oil is loaded from the well head onto tanker cars or into a pipeline, the more volatile fractions start to degas from the bulk liquid changing the properties of the delivered crude oil depending on the amounts lost through evaporation.

Oil production is now at an all-time high in America and a significant proportion delivered by rail – over 100 tanker cars each trip carrying over two million gallons of crude oil travelling distances of over one thousand miles. These many rail shipments inevitably have led to derailments resulting in fiery explosions, destruction of many towns, and spills to the environment.

Crude oil is comprised of a blend of various types of hydrocarbons: lighter components of lower molecular weights, C1 to C10, which volatilize readily within hours, a middle fraction of medium molecular weights, C11 to C22, which volatilize over days, and the heavy components, which are separated into petroleum fractions at the refinery.

Bakken Crude is the name of the crude oil from the oil producing rock formation in North Dakota, Montana, and the adjoining Canadian provinces, which has become the second largest oil producer in the US, only behind Texas.

Bakken Crude is a light-weight petroleum crude, containing a higher percentage of the lighter end petroleum components – including flammable gases like methane, ethane, propane, and butane (called “condensates”). The main differentiating characteristic of Bakken crude is its vapor pressure – the ability of a liquid to vaporize at a specific temperature. These flammable gases that are in solution at loading but as the ambient temperature increases, the gases held in solution evaporate into the vapor space inside the tank cars. It is this mass of flammable vapor in the tank car that becomes a fire ball in the event of a train derailment. Tank cars do contain the useful safety feature: relief valves (set for both maximum temperature and pressure limits) which vent excess gas from the vapor space.

Vapor pressure measurements of tank cars transporting Bakken crude oil at loading are typically higher than average crudes (11.8 psi vs. 7.0 psi) which is attributed to the higher percentages of volatile condensates which average 3% in Bakken crude versus 1% in other average light crudes. These values are still within the North Dakota state limit of 13.7 psi for transport in rail cars.

Not only are the tank cars filled to capacity with the Bakken crude oil considered dangerous loads, but even empty cars present a hazard. According to an API publication ("Classification and Loading of Crude Oil into Rail Tank Cars", September, 2004), the likely volume of crude oil "heel" remaining in an "empty" car is approximately 7%, or about 2100 gal for a 30,000 gal tank car after unloading.

Therefore, a 30,000 gal tank car filled to capacity is 4,010 cubic feet (cf) but when empty contains 2100 gal or 280 cf of heel and 3700 cf of space. Assuming an average density of 8 lb/gal for crude and a 3% content for the condensates (as propane),

Weight (propane) = (8 lb/gal) (2100 gal) (.03) = 504 lb condensates total

Using a simplified ideal gas law to estimate the quantity of condensates that could occupy the 3700 cf of space in the vapor headspace (provided the gas pressure remained below 13.7 psi),

$$\text{Weight (gas)} = \frac{(0.93\ \text{atm})\ (3700\ /.035\ \text{L})\ (56\ \text{g/mole})}{(454\ \text{gm/lb})(.082)(298^{o}\text{K})} = 504.8\ \text{lb in vapor}$$

Assumptions: condensate average molecular weight (propane) = 56; pressure = 13.7 psi or .93 atm; convert 3700 cf to 105,714L; 0.082 = universal gas constant.

Therefore, most of the condensates dissolved in the crude oil could degas and occupy the 3700 cf of available space in the tank car.

Performing the same calculation for a full tank car of 30,000 gal with an assumed vapor headspace of 5-10% volume,

Total volume (30,000 gal) =	4010 cf
Volume of 10% headspace =	401 cf
Volume of crude (27,000 gal) =	3609 cf

Weight (propane) = (8 lb/gal) (27000 gal) (.03) = 6480 lb condensates total

Only a fraction of the 6480 lb of condensates evaporate. Whatever quantity degasses from the liquid, it is limited to a pressure of 13.7 psi in the space of 401 cf because any excess pressure above that is vented through the pressure relief valve set at 13.7 psi (0.93 atm) to the outside, reducing the condensate gases to the following:

$$\text{Weight (gas)} = \frac{(0.93\text{ atm})\,(401\,/.035\text{ L})\,(56\text{ g/mole})}{(454\text{ gm/lb})(.082)(298^{o}\text{K})} = 53.7\text{ lb vapor}$$

Therefore, an "empty" tank car has sufficient flammable content in the vapor space to cause a fire and/or explosion if derailed and ignited by sparks – in fact, more vapor than a full tank car at the moment of tank rupture and release of gases. Of course, a full tank also releases its headspace of gases and immediately after release of the full tank's liquid contents, the remaining dissolved condensates flash off and ignite as well.

Therefore, the full tank car has in addition more combustible liquid fuel and dissolved condensate gases to feed a fire but it is not the liquid that ignites but the vapors that initially catch fire and as the vapors are consumed, more liquid evaporates to establish equilibrium, and the fire continues to burn.

Therefore, unlike pure substances (like ethanol), which have distinct and invariant LFL and FP that do not change with time or quantity of material, Bakken crude oil is a mixture of various hydrocarbons with a wide range of LFLs and FPs. After the crude oil is loaded into tank cars, the more volatile condensates evaporate over time changing the flammability characteristics of the crude oil remaining in the tank car. Yet, at the end of the journey, the Bakken crude oil will still have a significant level of dissolved condensate vapors remaining in the bulk liquid. These are the properties that make Bakken crude riskier to transport and handle but desirable to the petroleum industry because it is richer in the lighter products like gasoline and diesel requiring a minimal refining process and has a higher market value.

In the final analysis, the wide variance of LFL and FP values in Bakken crude oil (variances taken from the same well head and variances both at loading and over the duration of the journey) have created significant quantitative analysis and data interpretation challenges. Attempts are being made by DOT and other regulatory agencies to promulgate suitable test protocols to better define the flammability characteristics of these illusive mixtures.

Defining an accurate DOT Packing Group (based on FP and LFL) which measures the danger level of the transported material in a predictable manner is almost impossible because these flammability characteristics are different from tank car to tank car for the same shipment and then are changing during transit depending on the degree of off-gassing. The potential danger of these shipments remain a concern to the public and governmental agencies, who are attempting to improve the design and construction of the outdated DOT-111 rail cars, impose stricter regulations limiting tanker loads, reducing rail speeds, and other controls as well as improving railway operating practices in an attempt to minimize the probability and severity of derailments and fires caused by these speeding, deceptive “Molotov cocktails”- among which even an empty one can pack a lethal blow to a village or town .