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Extended vapor cloud analysis methodology—Part 2

The Buncefield explosion in the UK was the worst post-World War 2 fire/explosion incident. The fire, which shut down Heathrow and Gatwick airports in the UK, resulted in a regulatory tidal wave for aboveground petroleum storage tanks. Based on HSE vapor cloud explosion studies on petroleum storage tanks by the Fire and Blast Information Group (FABIG), new models have been proposed to understand and quantify whether vapor cloud explosions (VCEs) can occur.

Part 1, featured in the December 2018 issue of *Hydrocarbon Processing*, examined vapor cloud analysis (VCA) methodology and key input parameters. The following is a simplified approximate method, developed by the authors, to extend the VCA methodology to any crude oil.

Calculating the radius of ignition for overfill events. The industry lacks a simple and effective method for calculating the radius of ignition (R_{ign}) and minimum distance to evacuate personnel (R_{esc}) in the event of an overfill. Therefore, the authors' goal was to develop a method to calculate the radius of ignition for a wide variety of overfill events and parameters.

TABLE 4. Crude component fractions

Component	Vol%
C_3	0.34
Butane	4.37
Pentane	5.08
Hexane	7.05
Heptane	7.3
Octane	5.67
Nonane	4.06
Decane	2.64
Benzene	0.26
Toluene	0.92
Ethylbenzene	0.18
Xylenes	1.24
Unaccounted	60.9
Total	**100**

These parameters include the ambient temperature (T_{amb}), the fuel temperature (T_{fuel}), the height of the tank (H), the diameter of the tank (D), the mass flowrate of the overfill event ($\dot{M}$), the time length of the overfill event (t) and, most uniquely, the type of fuel being overfilled. The following calculations make some critical assumptions, including: no wind, a disk-shaped vapor cloud, and a lower explosive limit based upon hexane. Crude oil data is provided by Canada's National Energy Board (NEB) statistics. This source was selected because it supplies the volume fraction of many of the vapor-contributing components within crude oil.

Establish overflow event parameters. The following example is a crude data set supplied by Canadian NEB statistics:

- Crude name: Mixed Sweet Blend (MSW)
- Date: August 6, 2017 (Batch #MSW-814)
- API gravity: 42.3
- Location: Edmonton, Alberta.

The parameters include:

D = 75 m
H = 25 m
$\dot{M}_{fuel}$ = 800 kg/s
T_{amb} = 20°C
T_{fuel} = 14°C
t = 1,400 sec.

Convert volume or mass fraction to molar fraction. Data from the Canadian NEB statistics is given in a volume fraction. This is the most common method of displaying crude component fractions (TABLE 4).

The lighter components will be the majority of what evaporates into the air when crude is being overfilled. This action occurs because the lighter components have a higher vapor pressure than heavier components. We assume that ideal gas law on the vapor phase and the liquid phase behaves as an ideal mixture. We then convert the volume fraction data in TABLE 4 into a molar fraction by using known molar density data.

The following molar densities (mol/l) are provided from literature[1] and assume standard temperature and pressure conditions:

- C_3: 0.04228
- Butane: 0.04294

- Pentane: 8.6731
- Hexane: 7.6514
- Heptane: 6.8244
- Octane: 6.1481
- Nonane: 5.5985
- Decane: 5.1336
- Benzene: 11.252
- Toluene: 9.4086
- Ethylbenzene: 8.46774
- Xylenes: 7.620966
- Unaccounted components: 5.

Regarding "unaccounted components" for crude oil, the entire molar composition is usually unknown. Therefore, it is necessary to group unknown components together into an "unaccounted component" group. A value is selected with properties like the heavy alkanes. The molar density for unaccounted components will vary for every crude oil, but the value of 5 optimizes the results for a wide variety of crude oils for the vapor pressure trend, as shown in FIG. 3.

Hexane example of 1 l of sample:

$$mol_{hexane} = (100\ l)(7.05\ vol\ \%)\left(7.7514\ \frac{mol}{l}\right) = 53.942\ mol$$

$$mol_{total} = \Sigma\ mol_i$$

$$mol_{total} = 546.17\ mol$$

$$mol_i\ \% = \frac{mol_i}{mol_{total}} = \frac{53.942}{546.17} = 9.9\ mol_{hexane}\ \%$$

In application, the method above must be applied to each component. This process yields the values shown in TABLE 5 for molar composition of the crude sample.

Pure component vapor pressure calculation. To find the total vapor pressure of the crude oil, one must calculate the pure vapor pressure at ambient temperature (T_{amb} = 20°C). The P(vap) of pure substances is achieved by the following equation and information from literature:[1]

$$\ln(P_{vap\ pure}) = C1 + (C2/T) + C3 \times \ln(T) + C4 \times T^{C5},$$
$$P_{vap\ pure} = [Pa]$$

The results at T_{amb} = 20°C are shown in TABLE 6.

In application, one can ignore the vapor pressure contributions of components with more carbons than C_8 (octane). These heavier components can be ignored, since their vapor pressures are very low relative to the light components of crude oil, such as propane and butane. Unknown heavy components contribute negligible vapor pressure, thus simplifying the model without losing much accuracy.

With pure vapor pressure data and molar composition of a crude oil, we can calculate an idealized total vapor pressure through Raoult's law:

$$P_{vap\ total} = \Sigma P_{i\ vap}$$

$$P_{i\ vap} = P_i^* \times x_i.$$

The MSW-814 crude oil sample yields a $P_{vap\ total}$ = 6,816 Pa. The total vapor pressure of the components is crucial for calculating the R_ign and R_esc.

Vapor pressure and Cθ correlation. To calculate the R_{ign} and R_{esc}, one needs a concentration of vapor at the base of the storage tank. The concentration at the foot of the tank can be determined by using a linear regression for the $\ln(P_{vap\ total})$ vs. Cθ

TABLE 5. Molar composition of crude sample MSW-814

Paraffins	
C_3	0.002632
C_4	0.034357
C_5	8.066969
C_6	9.876483
C_7	9.121361
C_8	6.38258
C_9	4.161693
C_{10}	2.481408
Aromatics	
C_6	0.535643
C_7	1.584839
C_8	0.279069
Xylenes	1.730231
Heavy components	
55.74273533	

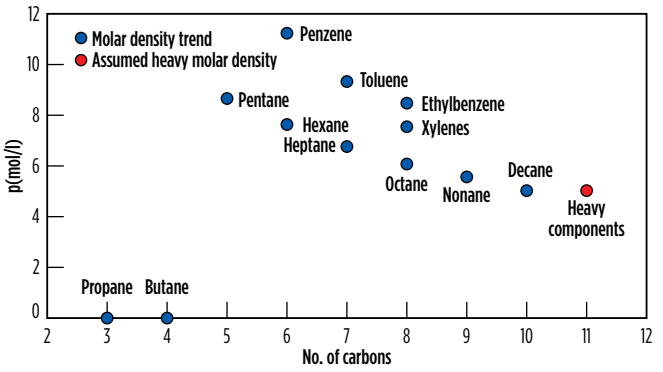

FIG. 3. Carbon number vs. molar density of hydrocarbons.

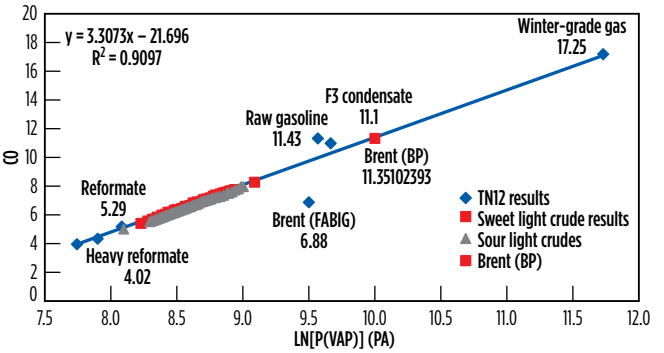

FIG. 4. FABIG TN12 linear regression and crude results.

from the FABIG TN12 documents (TABLES 7 and 8). The trend relates the natural logarithm of the total vapor pressure to the concentration at the foot of the tank as follows:

$$C\theta = 3.3073 \times \ln(P_{vap\ total}) - 21.696$$

This trend is determined by a least squares regression fit of the data supplied by the FABIG TN12 document. The trend yields a strong fit with an $R^2 = 0.9097$ (FIG. 4). The difference in the two values for Brent crude is explained by the different molar fractions of each sample, as shown in TABLE 9, when using the total vapor pressure from components:

$$C\theta = 3.3073 \times \ln(6816\ Pa) - 21.696 = 7.4976\ kg/m^3$$

Correction factor. The value for Cθ must then be multiplied by a correction factor (F). The value of this correction factor has an average of 0.07834679 ($\bar{x} = 0.07834679$) and a standard deviation of 0.336811 ($\sigma_{\bar{x}} = 0.336811$). These values are appropriate only under the following conditions:

- T_{amb}: –20°C to 30°C
- T_{fuel}: –20°C to 30°C
- M_{air}/M_{fuel}: 0.3 to 3.

The FABIG TN states, "over these ranges, the corrections factor (F) has an average accuracy of ±2% with large deviations of up to 15%."

$$F = \alpha\left(\frac{M_{air}}{M_{fuel}}\right)^{\beta} exp\left(\gamma\left(T_{air} - 10\right)\right) exp\left(\delta\left(T_{fuel} - 10\right)\right)$$

$$C_{foot} = C\theta \times F$$

For the example scenario: T_{amb} = 20°C, T_{fuel} = 14°C, *Greek variables* = $\bar{x}$ F = 1.3237.

Remaining steps in calculating the radius of ignition and escape. For the equation:

$$\therefore C_{foot} = C\theta \times F = 7.4976 \times 1.323759 = 9.9251\ kg/m^3$$

This is the concentration value needed to continue the process of calculating the R_{ign} and R_{esc}.

TABLE 6. The results at T_{amb} = 20°C

T(K)		C_1	C_2	C_3	C_4	C_5	Pvap (Pa)
Paraffins	C_3	59.078	–3,492.6	–6.0669	1.09E–05	2	834184.2
	C_4	66.343	–4,363.2	–7.046	9.45E–06	2	206981.9
	C_5	78.741	–5,420.3	–8.8253	9.62E–06	2	56278.83
	C_6	104.65	–6,995.5	–12.702	1.24E–05	2	16121.63
	C_7	87.829	–6,996.4	–9.8802	7.21E–06	2	4666.773
	C_8	96.084	–7,900.2	–11.003	7.18E–06	2	1391.773
	C_9	109.35	–9,030.4	–12.882	7.85E–06	2	416.4769
	C_{10}	112.73	–9,749.6	–13.245	7.13E–06	2	125.5671
Aromatics	C_6	83.107	–6,486.2	–9.2194	6.98E–06	2	9913.166
	C_7	76.945	–6,729.8	–8.179	5.3E–06	2	2902.748
	C_8	89.063	–7,733.7	–9.917	5.99E–06	2	945.5245
	C_9	91.379	–8,276.8	–10.176	5.62E–06	2	334.2583
Naphthenes	C_5	66.341	–5,198.5	–6.8103	6.19E–06	2	34429.28
	C_6	51.087	–5,226.4	–4.2278	9.76E–18	6	10311.3

TABLE 7. Molar compositions from FABIG TN12 samples

	Paraffins							Aromatics				Naphthenes	
	C_3	C_4	C_5	C_6	C_7	C_8	C_{10}	C_6	C_7	C_8	C_9	C_5	C_6
Winter-grade gasoline	9.6	17.2	16				57.2						
Naphtha		2	56	21	7			4				5	5
Raw gasoline		1	9	21				35	13	7	14		
Reformate				4	20	19		5	24	23	5		
Heavy reformate				4	5	3		1	31	34	22		
F3 condensate		4.7	6.5	4.1	6.5		69.3	4.7	1.4			2.8	
Brent	0.81	1.75	2.65	2.27	2.84		84.4	3.78				1.5	

$$M_{air} = 90\left(\frac{D}{25m}\right)^{0.75}\left(\frac{H}{10m}\right)^{0.45}\left(\frac{M_{fuel}}{\frac{115\ kg}{S}}\right)^{0.25}$$

$$\therefore M_{air} = 503.2\ kg/sec$$

It is now necessary to consider the mass of fuel vaporized and splashed. Vaporized fuel is based on the concentration on the foot of the tank and M_{air}:

$$M_{vap} = M_{air} \times \left(\frac{C_{foot}}{100 - C_{foot}}\right)$$

$$\therefore M_{vap} = 55.45\ kg/sec$$

Only components that are equal to, or lighter than, octane will contribute to M_{splash}. To calculate this component fraction, add the component fractions that are below C_8:

$$M_{splash} = 0.02 \times M_{fuel} \times x_{\leq C_8}$$

$$\therefore M_{splash} = 574.14\ kg/sec$$

Now that we have calculated the mass contributions by air, vaporized fuel and fine droplet splash, one can calculate the total mass of the vapor cloud:

$$M_{cloud} = 2(M_{splash} + M_{vap} + M_{air})$$

$$M_{cloud} = 2265.6\ \text{kg/s}.$$

The density of air at the ambient conditions, ρ_{air} = 1.3015 kg/m^3, is then used to determine the volume of the vapor cloud:

$$V_{cloud} = \frac{M_{cloud}}{\rho_{air}} = 1740.8\ m^3$$

Using the mass of explosive components and volume of the cloud, one can calculate the concentration of explosive vapor in the cloud:

$$C_{cloud} = \frac{M_{splash} + M_{vap}}{V_{cloud}} = 0.3617\ kg/m^3$$

All values used to calculate R_{ign} and R_{esc} are calculated:

$$R_{ign} = \left(\frac{1}{\pi} \times V_{cloud} \times t\right)^{1/2}$$

$$R_{esc} = \left(\frac{1}{2\pi} \times V_{cloud} \times t\right)^{1/2}$$

$$R_{ign} = 880.8\ m$$

$$R_{esc} = 622.8\ m$$

TABLE 8. Cθ and correction factors for FABIG TN12 samples

	C^{θ}_{fuel}	α	β	γ	δ
Hexane	14.24	0.946	−0.225	0.0133	0.0212
Acetone	12.21	0.941	−0.262	0.0128	0.0192
Ethyl acetate	9.89	0.957	−0.181	0.0177	0.0242
Benzene	9.29	0.959	−0.176	0.0182	0.0222
Methyl ethyl ketone	8.71	0.955	−0.182	0.0163	0.0255
Toluene	4.7	0.981	−0.061	0.025	0.03
Methanol	4.53	0.95	−0.215	0.0167	0.0287
Ethanol	3.63	0.967	−0.133	0.0212	0.0345
Naphtha	20.3	0.928	−0.312	0.0093	0.0142
Winter-grade gasoline	17.25	0.888	−0.454	0.0074	0.0131
Raw gasoline	11.43	0.936	−0.264	0.0137	0.0179
F3 condensate	11.1	0.881	−0.476	0.0085	0.0132
Brent	6.88	0.876	−0.511	0.0088	0.0136
Reformate	5.29	0.967	−0.114	0.021	0.0295
Heavy reformate	4.02	0.97	−0.095	0.0234	0.0302

TABLE 9. The difference in the two values for Brent crude is explained by the different molar fractions of each sample

	Paraffins							
	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Brent (FABIG TN12)	0.81	1.75	2.65	2.27	2.84	0	0	84.4
Brent (BP)	1.433409	3.41828	3.692294	3.26147027	0	0	0	0

Composition chart FABIG TN12 and BP

The overall process requires first defining the components within the fuel system and the other parameters, and then determining the vapor pressure due to the contributing components. This vapor pressure is used with the linear regression from the FABIG TN12 data to obtain the Cθ value. Cθ is then corrected by the correction factor (F) to obtain C_{foot}. Calculate the M_{air}, M_{splash} and M_{vap} to get M_{cloud}. Use the M_{cloud} to obtain the V_{cloud}. Then determine the C_{cloud}, R_{ign} and R_{esc} from V_{cloud}.

Eliminating the potential for a VCE. It is surprising that the authors found no references as to how to positively eliminate the large vapor cloud from forming. In the past, many tanks were constructed with an "overflow pipe" that directed an overflow to the ground. While this has typically been done for reasons unrelated to vapor cloud formation, it was applied to smaller tanks. This idea has not been used on large tanks above 50 m. The problem with applying this idea to tanks constructed to a standard is that the standards do not anticipate a design aimed at mitigating potential overfill vapor cloud events.

UK Health and Safety Executive (UK HSE) research has resulted in two documents that provide a method for determining the size of a potential vapor cloud that might develop from a petroleum tank overfill. Research Report (RR) 908 was the first document to be published, followed by the FABIG TN12 document. In RR908, the VCA method was applied through examples of overfills involving gasoline and ethanol. FABIG TN12 extended the method to a list of 15 fluids, but only one of the fluids was crude oil. That fluid was Brent crude oil, and, in an example given in the document, a vapor cloud with an ignition radius of 612 m was computed.

The authors expect that these principles could be used to estimate emissions caused by heavy multicomponent hydrocarbon mixtures, such as "fuel oil 6," for tanks and piping. The emissions estimation tools are effective for a wide variety of light-end fuels, such as gasoline or diesel, but may be significantly inaccurate when dealing with heavy fuels. This has led to some facilities being fined by the US EPA for misreporting emissions. The ultimate goal of this method is to better manage these flammable emissions, protecting personnel and the environment alike. HP

LITERATURE CITED

[1] Green, D. W. and R. H. Perry, *Perry's Chemical Engineers' Handbook,* McGraw-Hill, New York, New York, 2017.

PHILIP MYERS is the Founder of PEMY Consulting, LLC. He has worked with the American Petroleum Institute to develop large-diameter tank fire studies, and with other groups to develop the "Last Fire" initiative—sponsored by ExxonMobil, Chevron and BP.

BROCK TROTTER has coauthored publications for Endress+Hauser and Emerson regarding tank level equipment and overfill prevention. He has also performed engineering analysis for an expert witness regarding petroleum overfill and has authored a paper regarding API 2350, "Overfill protection for storage tanks in petroleum facilities."