Estimating Evaporative Losses from Crude Oil Spills

by Traci Johnson, P.E.

Of the 4.9 million barrels of crude oil released to the Gulf of Mexico as a result of the *Deepwater Horizon* drilling rig failure, the U.S. Geological Survey (USGS) estimates that 25% of the oil quickly evaporated or dissolved into the water column! These evaporated "light ends," as they are called in the petroleum industry, typically consist of low molecular weight hydrocarbons, known as volatile organic compounds (VOCs). Many VOCs found in crude oil, such as benzene, toluene, and xylene, are known human toxicants and exposure to them can result in a wide variety of adverse health effects, from irritated eyes and respiratory pathways to cancer and birth defects.

Tens of thousands of workers were involved in the cleanup response in the months following the *Deepwater Horizon* rig explosion. These workers, as well as shore cleanup crews and coastal residents along the Gulf Coast, may have been exposed to hazardous compounds. Strong winds effectively disbursed the VOCs, and even residents of New Orleans approximately 130 miles from the rig complained of foul odors. In March 2011, the National Institute of Environmental Health Sciences commenced its $17.8 million Gulf Long-term Follow-up Study (GuLF Study). The largest study of its kind, it will focus on spill workers' exposure to crude oil and track their illnesses for at least five years. To complement this and other health risk studies, it is imperative to correlate illness type and severity with exposure concentrations.

To determine the concentration of crude oil VOCs in air, a sample can be collected and directly analyzed for compounds of concern. If a sample is not available immediately following an oil spill (i.e., when the majority of volatilization occurs), or if one is interested in predicting concentrations from a future spill for planning purposes, air dispersion modeling using any number of commercially available software products can be performed to estimate such concentrations. However, a requirement of these models is an emission rate—that is, the mass of VOCs that are generated over time from a source (e.g., an oil spill).

Like any other volatile liquid, when crude oil is spilled, it will spread out, vaporize, and result in air emissions. However, what makes crude oil such a tricky liquid to model is the fact that it is composed of several components, each with its own unique set of physical and chemical characteristics. When a spill occurs, the components with the highest vapor pressures will evaporate most rapidly.[2] Some predict that in a few days, light crudes can evaporate as much as 75% of the starting oil mass and medium crudes up to 40%.[3] As a result, the vapor pressure of the remaining spilled mixture can decrease significantly with time.

In fall 2010, a group of fellow University of New Orleans graduate students and I enrolled in an Oil Spill Management class led by Dr. Bhaskar Kura. We were asked to spend the semester evaluating some aspect of the *Deepwater Horizon* release or its impact to humans and the environment. I chose to examine available methods for the estimation of air emissions attributable to crude oil spills. In my research, I came across the work of Drs. Warren Stiver and Dennis Mackay of the Chemical Engineering Department at the University of Toronto. Stiver and Mackay developed a simple model in the 1980s for predicting emissions from a crude oil spill, without the use of high-tech gadgetry or computer models, just experimental data that could be easily obtained in any modest laboratory. To demonstrate just how simple their method is, I set out to reproduce their wind tunnel experiment on the front porch of my home in the Lakeview neighborhood of New Orleans.

Estimating Emissions of Spilled Liquids

In 1999, the U.S. Environmental Protection Agency (EPA) published a procedure for estimating evaporative losses resulting from liquid spills.[4] The methodology depended upon a number of factors, including:

- volatility of the spilled material;
- size of the spill;
- temperature of the surrounding area;
- wind speed; and
- length of time that the liquid from the spill is allowed to evaporate.

The vaporization model adopted by EPA is a somewhat simplistic equation that relies on a limited number of parameters:

$$QR = \frac{\overline{(0.284 \upsilon^{0.78} \, MW^{2/3} \, AVP)}}{82.05T}$$

where,

QR = evaporation rate (lb/min)
υ = wind speed (m/sec)
MW = molecular weight of liquid
A = surface area of liquid pool (ft²)
VP = vapor pressure of liquid (mmHg)
T = temperature (K)

The model is primarily intended to be treated as a screening tool to obtain an approximate evaporation rate to help identify high-priority hazards to neighboring communities in the event of a spill.[5] Further, the model assumes that the vapor pressure of the spilled material does not vary with time,
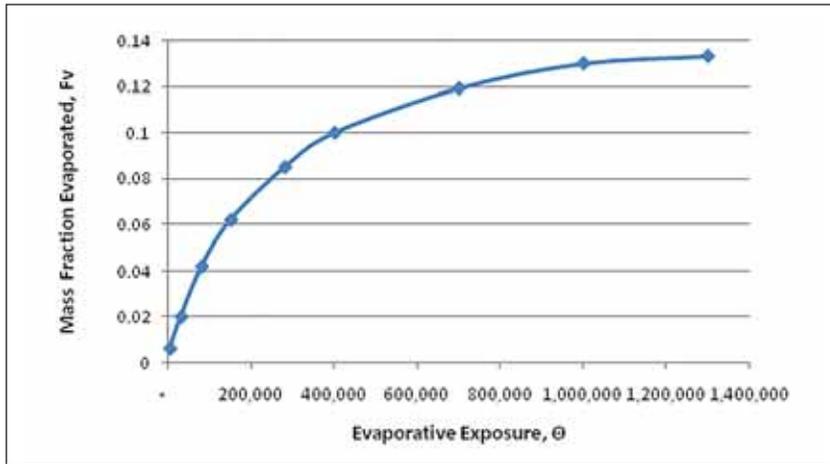
Figure 1. Typical plot of volume fraction evaporated vs. evaporative exposure for crude oil.

t = elapsed time since the spill (sec)
V_o = volume of the spill (m^3)
d_o = depth of the spill (m)

The evaporative exposure is a function of exposure time, the spill area and volume (or thickness), and the mass transfer coefficient (which is dependent upon the wind speed). In summary, the key characterization of a specific crude oil's evaporative behavior is a plot of F_V versus Θ at different temperatures.[7] Stiver and Mackay obtained these curves for various crude oils from wind tunnel and gas stripping experiments. By calculating the evaporative exposure and referring to a plot of F_V versus Θ for a particular crude oil at a specific temperature, the volume fraction evaporated may be estimated with relative ease, as shown in Figure 1.

as is the case of spills involving one single chemical component. Given that crude oil is a mixture of components with varying vapor pressures, using the aforementioned EPA methodology to estimate emissions from a crude oil spill can lead to significant overestimating, particularly for large elapsed times.

In 1984, Stiver and Mackay[6] presented a method for estimating evaporative losses from crude oil spills, which accounts for the fact that the oil's vapor pressure decreases over time as the lighter fractions evaporate more quickly than the heavier fractions. The model assumes that[3]:

• the oil is composed of a number of hydrocarbon groups;
• the evaporative loss of a given hydrocarbon component follows a logarithmic fashion, or a first-order kinetics; and
• the evaporation rate is a function of the following key parameters: spill area, wind speed, vapor pressure, slick thickness, and temperature.

The Stiver and Mackay method requires experimental data specific to the oil spilled. Their method consists of specifying the volume fraction of oil evaporated as a function of a variable that they refer to as evaporative exposure. The evaporative exposure is defined as:

$$\Theta = kat/V_o$$
$$= kt/d_o$$

where,

Θ = evaporative exposure (dimensionless)
k = mass transfer coefficient (m/sec)
a = area of the oil surface (m^2)

Stiver and Mackay performed their tray evaporation procedure using a rectangular-shaped, variable speed wind tunnel. A pitot tube equipped with a manometer was used to determine wind speed. Samples of crude oil were placed in a tray located on top of a balance such that the mass of remaining liquid could be determined at any point during the experiment. To determine the mass transfer coefficient for the wind tunnel for a particular wind speed, Stiver and Mackay measured the evaporating molar flux of a sample of toluene inside the tunnel and used the following equation:

$$k = RTN/aP$$

where,

k = mass transfer coefficient under prevailing weather conditions (m/sec)
a = surface area of liquid pool (m^2)
P = spilled liquid's vapor pressure (Pa or atm)
R = universal gas constant (8.314 Pa-m^3/K-mol)
T = ambient temperature (K)
N = molar flux (mol/sec)

Next, a small sample of crude oil was weighed and placed onto a tray in the wind tunnel for a period of time. The final mass of the sample was recorded and the density of the remaining oil was determined using a pycnometer.

Stiver and Mackay performed the above described experimental procedure several times for various

crude oils and various wind speeds, each trial run lasting from 6 hours to 2 weeks. For each iteration, the evaporative exposure (Θ) and volume fraction evaporated (F_v) were calculated. The volume fraction evaporated can be calculated using the mass fraction evaporated (F_m) and the initial and final densities of the oil sample:

$$1\text{-}F_v = (1\text{-}F_m)(\rho_o/\rho_f)$$

where,

F_v = volume fraction evaporated
F_m = mass fraction evaporated
ρ_o = initial oil density (kg/m³)
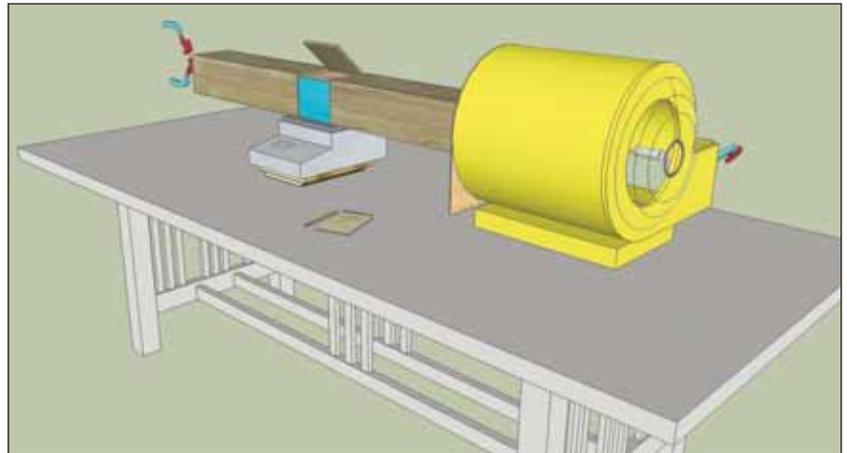ρ_f = final oil density (kg/m³)

For each type of crude oil studied, the volume fraction evaporated was then plotted against the various calculated evaporative exposures (F_v vs. Θ), similar to Figure 1.

Modified Experiment

A wind tunnel similar to that of Stiver and Macay was constructed (see Figures 2 and 3). The tunnel consisted of 6-inch pine wood panels secured around a mass balance. Above the balance was a hinged access door, which allowed the user to top load liquid samples into a dish located on the balance. Wind speed through the tunnel and the ambient temperature were determined using a hand held David WindScribe monitor. Given that the author did not have the ability to control the temperature of the experimental setting, temperature fluctuation was expected.

Wind speeds of 4–9 m/sec were determined to be achievable and desirable for this experiment. A box fan, equipped with cardboard side panels, was used to achieve a wind speed of 4.0 m/sec. For wind speeds 6.5 m/sec and 9.0 m/sec, the box fan was replaced with a 10-inch, 0.5-hp Emerson carpet blower. Cardboard was used to cover the exposed inlet side of the blower surrounding the wind tunnel outlet. The mass transfer coefficient of the wind tunnel at each speed was determined by measuring the evaporative molar flux of ethanol using the procedure previously described and used by Stiver and Mackay.

For this study, Castilla crude oil, a heavy crude oil

Figure 2. (Top) Wind tunnel in box fan configuration (Illustration by John Haynes).

Figure 3. (Bottom) Wind tunnel in carpet blower configuration (Illustration by John Haynes).

collected off the coast of Columbia, was used. Before beginning the wind tunnel experiments, the initial density of the Castilla crude was determined by dividing a known mass of crude oil by its measured volume.

For each iteration of the experiment, a sample of Castilla crude oil was poured into a plastic petri dish to a depth of 7–10 mm. The depth of the sample and its mass was recorded. The dish was then placed in the wind tunnel on top of the mass balance, where it remained for at least one hour and up to one week. After the appropriate period of time elapsed, the final depth and mass of the sample were recorded. The final density of the crude was also calculated using the same procedure described above. The volume fraction evaporated (F_v) was also calculated.

Results

Figure 4 is a plot of the volume fraction of evaporated crude (F_v) versus the calculated evaporative Exposure (Θ). Note that the shape of the curve generally follows the shape of the example Stiver
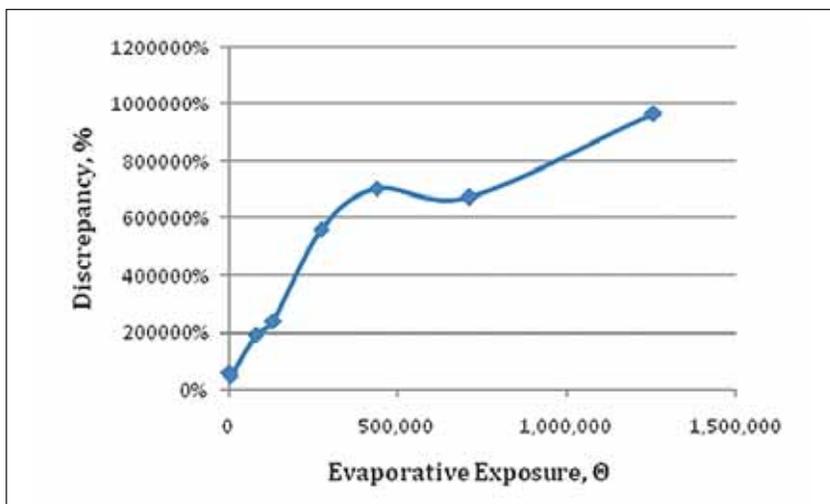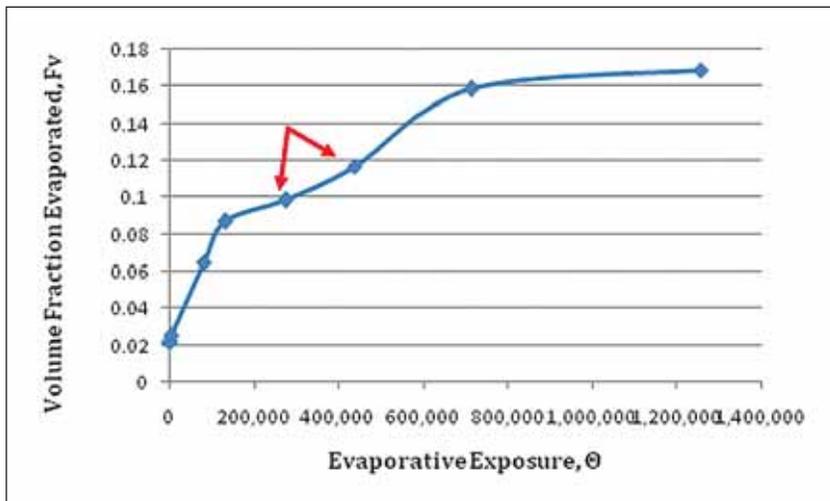
Figure 4. (Top) Plot of volume fraction evaporated vs. evaporative exposure for Castilla crude.

Figure 5. (Bottom) Discrepancy between experimental and EPA model predicted losses for Castilla crude vs. evaporative exposure.

From the dip in the Figure 4 curve, it is evident that Stiver and Mackay's model is temperature-dependent. However, given the shape of the curve is generally consistent with Figure 1, despite the wide range of ambient temperatures seen during this experiment (40–75 °F), it appears that the model is not hypersensitive to temperature fluctuation.

The experimental crude oil evaporative losses were also compared to results predicted by the previously mentioned EPA model for estimating evaporative emissions. The discrepancy in results increases drastically with increasing evaporative exposure, as shown in Figure 5. As a point of reference, the evaporative losses of ethanol measured in the development of the wind tunnel mass transfer coefficients were compared to values predicted by the EPA model for ethanol. The EPA model predicted values 45–90% higher than those actually measured, an acceptable range of overestimation considering the model is used for emergency planning. However, it is abundantly clear that simplistic models for single component spills are not appropriate for heterogeneous mixtures such as crude oil.

Future Work

The primary usefulness of this body of work is a graphical tool that can be used to estimate actual evaporative losses of Castilla crude oil. Similar curves can be generated for several other crude oils, including the Louisiana sweet crude, which was released by *Deepwater Horizon*, to develop a database to be used in quickly estimating emissions of crude oil spills in the environment. Ideally, each curve would be developed for a specific temperature (or season). Additionally, emission estimates from these models can be used to predict health risk impacts from spill events to emergency responders, cleanup workers, and neighboring communities. **em**

and Mackay curve in Figure 1, except for the two data points identified by red arrows. For these two evaporative exposures (275,670 and 437,829), their associated volume fraction evaporated (0.10 and 0.12, respectively) were less than expected. A closer look at the experimental data revealed that these two runs were conducted when the ambient temperature had drastically decreased to as low as 40 °F. The remaining runs were conducted when ambient temperatures were in range of 60 °F to 75 °F. Such is the nature of the fall season in New Orleans.

References

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