Flash Atomization of HF and MHF

George Harpole, Ph.D., 1/22/2017

Introduction

Liquid flowing out of a pressurized tank will flash atomize if the liquid superheat (temperature difference above the boiling point) is large enough. Fthenakis claimed, "The critical superheat typically ranges from 5 to 15 K [9 to 27°F] for many fluids of interest."[1] Flash atomization is the shattering of liquid jets into very small (often submicron) aerosol droplets due to the rapid vapor bubble growth of boiling. By contrast, subcooled (below the boiling point) liquid jets will still atomize when exiting an orifice, but then to droplets that are orders of magnitude larger, hundreds of microns in diameter.

Two significant consequences of the much smaller droplets with flash atomization are – 1) faster subsequent vaporization, and 2) liquid moving inseparably with the gas. For a given volume of liquid, its total surface area is inversely proportional to droplet diameter. Moreover, the droplet heat and mass transfer coefficients (transfer per unit surface area) are also inversely proportional to diameter. Therefore, evaporation rates are inversely proportional to the square of droplet diameter. Ten times smaller droplets evaporate one hundred times faster. The small aerosol droplets evaporate essentially instantaneously to local equilibrium conditions.

Barriers and Liquid Separation

Small aerosol droplets have very little inertia, so can turn fast, tight corners together with the gas carrying them. Conversely, large droplets cannot readily turn tight corners in a gas flow. Physical barriers and liquid separators can cause large droplets to impinge on walls as the gas turns around the wall. However, barriers and liquid separators cannot trap droplets smaller than about 10 μm in diameter. Even large droplets, impinging on walls, are not necessarily trapped unless there are drainage features, and the drain feature is not flooded (overwhelmed by large liquid flow), and the liquid is not swept back into the gas flow by the shear of high velocity gas. The effectiveness of a barrier is not a constant, but is dependent on droplet size, liquid flow rate, gas velocities, and for that matter, whether the leak is within the barrier system.

Rainout Models

In the 1990s, Mobil researchers published papers predicting "rainout" or "percent HF capture" or "Airborne Reduction Factor (ARF)" for HF (hydrogen fluoride) and MHF (modified hydrogen fluoride, which is HF with an additive) jets leaking from pressurized tanks.[2,3] In this work, the progressive evaporation of HF was computed by heat and mass transfer relations to track chemical species in detail – air, water vapor, HF, and polymerized HF states – as functions of downstream position. Also, liquid droplet trajectories were followed until what didn't evaporate hit the ground. Actually, HF rainout to the ground is insufficient to stop evaporation unless the HF is then diluted with water.

The Mobil researchers assumed droplet sizes of ordinary subcooled liquid atomization (hundreds of microns), and did not include the case of flash atomization. "In what follows, we will restrict to situations where such flash atomization does not occur."[2] The ARF and rainout models from the 1990s were not valid for flash atomization. For sufficiently superheated conditions, these models would incorrectly predict large HF capture fractions, when actually there would be no capture at all.

Flashing Criteria

Flashing liquid jets were reviewed by Witlox and Bowen[4] for the UK Health and Safety Executive, specifically with regard to hazardous fluids such as HF. They recommended a correlation by Kitamura, Morimitsu and Takahashi[5] that matched the relevant data. The Kitamura correlation predicts superheat for which droplets of a given diameter will shatter into smaller droplets. This correlation accounts for – the vapor bubble growth corresponding to the superheat, the surface tension holding droplets together, and the pressure forces on a droplet at jet velocities corresponding to the tank pressure. Technical details of this correlation in its use with HF and MHF properties are given in the Appendix at the end of this report.

MHF used at refineries in Torrance and Wilmington is 90% HF and 10% sulfolane by weight. Given that sulfolane has six times the molecular weight of HF, this is a molecular or mole fraction of 98.2% HF and 1.8% sulfolane. While the boiling point of HF is 67°F, that for MHF is 73°F, due to its 11% decrease in vapor pressure.[6] Otherwise, MHF fluid properties that impact the superheat for flash atomization will be very close to those for HF.[7,8] The superheat to flash atomize HF (and MHF) can be added to the boiling point of MHF to predict flash atomization or maximum droplet sizes.

The maximum droplet size from flash atomization of an MHF jet is shown in Figure 1 as a function of tank temperature and pressure. A leak from a tank at a given pressure (specific curve in Figure 1), with MHF initially at a given temperature (on the horizontal axis), will flash to droplets smaller than those indicated on the vertical axis. For example, MHF leaking from a tank with pressure 60 psi above atmospheric (the dark blue curve), initially at 95°F, would flash to droplets smaller than 10 μm. None of these droplets would rainout or be trapped by a barrier. MHF is used in alkylation operation at temperatures of 105°F [9] and pressures above 100 psi, where flash atomization would be to submicron sizes.

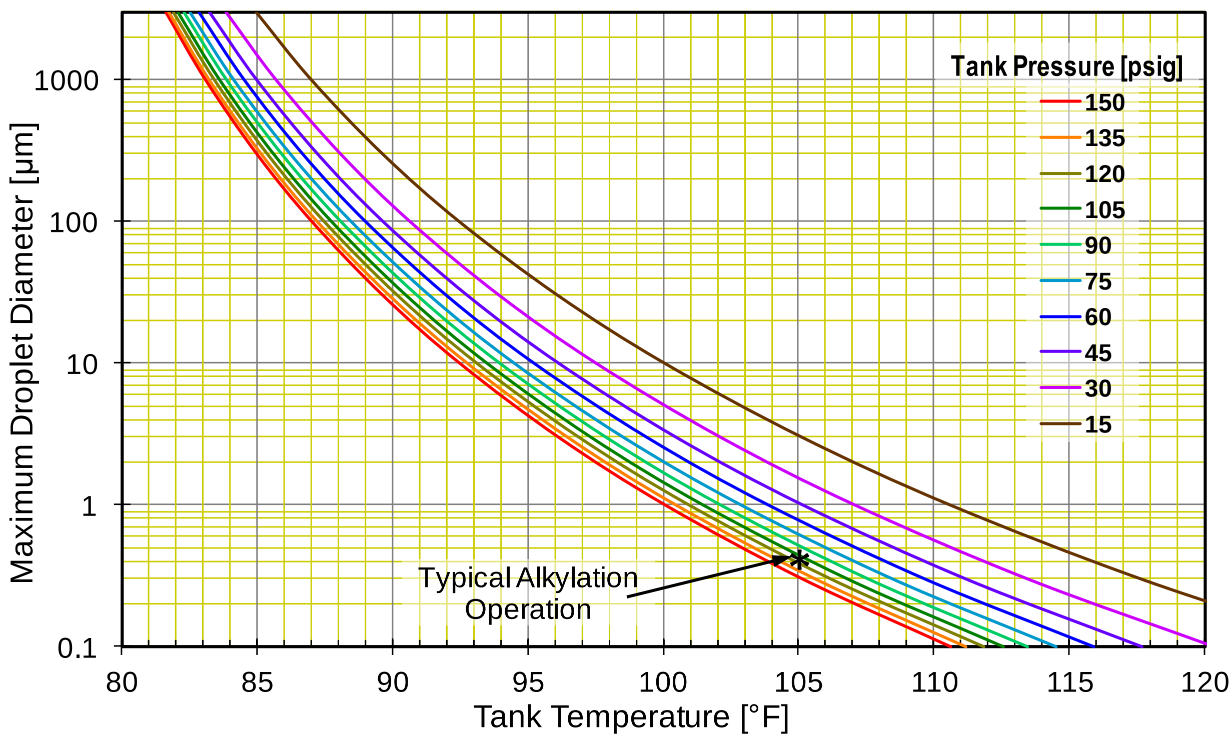

Figure 1 – Maximum droplet size from flash atomization of MHF

References

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3. R. Muralidhar, G.R. Jersey, F.J. Krambeck, "A two-phase model for subcooled and superheated liquid jets," International Conference and workshop on modeling and mitigating the accidental releases of hazardous materials, AIChE, CCPS, New Orleans, LA, 189-224, September 26-29, 1995

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5. Y. Kitamura, H. Morimitsu, and T. Takahashi, "Critical Superheat for Flashing of Superheated Liquid Jets," Ind. Eng. Chem. Fundamentals, 25(2), 207-211 (1986)

6. G. Harpole, "HF and MHF – Equivalent Ground Hugging Fog Hazards," http://bit.ly/2ck2l8G

7. Honeywell Specialty Chemicals, Hydrofluoric Acid Properties (2002) http://www3.imperial.ac.uk/pls/portallive/docs/1/7276108.PDF

8. Solvay, Hydrogen Fluoride Anhydrous, Technical Data Sheet, AHF#3324 (05/2014) http://www.solvay.us/en/binaries/AHF_TDS-237448.pdf

9. Consent Decree Safety Advisor Steve Maher presented a chart titled "AHF/MHF" which listed "Typical settler temperature 105°F" at the 10/13/2015 City of Torrance Workshop regarding ExxonMobil's use of MHF catalyst.

Appendix – Technical Details

The relevant HF fluid properties used in calculating the curves in Figure 1 were obtained from references 7 and 8, and are as follows – liquid density, ρ_L = 930 kg/m^3; vapor density, ρ_V = 0.8 kg/m^3; liquid specific heat, $c_{p,L}$ = 2680 J/kg-K; heat of vaporization, h_{fg} = 3.4x10^5 J/kg; and surface tension, σ = 0.0086 N/m. The air density is ρ_A = 1.16 kg/m^3.

Correlations in fluid mechanics and heat and mass transfer are often formulated in terms of dimensionless variables that are ratios of competing forces or energy governing the phenomena. Some of these ratios are named after historic figures in engineering research. The Kitamura correlation uses the Jakob number, *Ja*, and the Weber number, *We*. The definitions of these are as follows.

$$We = \frac{\rho_A u^2 d}{\sigma} \quad \text{and} \quad Ja = \left(\frac{c_{p,L}\Delta T_{SH}}{h_{fg}}\right)\left(\frac{\rho_L}{\rho_V}\right)$$

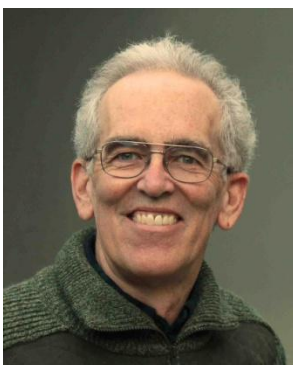
where *u* is the liquid velocity relative to the air, *d* is the droplet diameter, and ΔT_{SH} is the superheat above the boiling point. The Weber number is a ratio of the pressure difference forces on the droplet to the surface tension forces holding it together. The first factor of the Jakob number is mass fraction of liquid with potential to vaporize due to the superheat, and the second factor represents the inverse of volume factor increase due to that vaporization. The Kitamura correlation for flash atomization is as follows.

$$\left[1-\exp\left(-2300\frac{\rho_V}{\rho_L}\right)\right]Ja = \frac{100}{We^{1/7}}$$

The liquid jet velocity, u, is related to the tank pressure above atmospheric, ΔP, as follows.

$$\Delta P = \frac{\rho_L u^2}{2}$$

This relation can be used to replace the u^2 in the Weber number with $2\,\Delta P/\rho_L$. Then, given the fluid properties and tank pressure, the Kitamura correlation predicts the maximum stable droplet diameter as a function of the superheat. This relation allows the calculation of the curves in Figure 1.



George Harpole holds a Ph.D. in Engineering from the U.C.L.A. School of Engineering, Chemical, Nuclear, and Thermal Engineering Department. He has been Chief Engineer of two chemical laser systems at Northrop Grumman Corporation. His current assignment is thermal analysis for the James Webb Space Telescope. He is the inventor, or co-inventor, of 14 U.S. Patents. He received two TRW Chairman’s Awards. George Harpole lives in Torrance.