THE IMPORTANCE OF MULTIPHASE AND MULTICOMPONENT MODELING IN CONSEQUENCE AND RISK ANALYSIS

David W. Johnson and Jeffrey D. Marx

Presented At
Mary Kay O'Conner Process Safety Center
2002 Annual Symposium
October 29-30, 2002
Texas A&M University
College Station, Texas

Printed in
Journal of Hazardous Materials
Vol. 104, Issues 1-3: pp. 51-64
November, 2003

Presented By
Quest Consultants Inc.®
908 26th Avenue N.W.
Norman, Oklahoma 73069
Telephone: 405-329-7475
Fax: 405-329-7734
E-mail: info@questconsult.com
URL: http://www.questconsult.com/

THE IMPORTANCE OF MULTIPHASE AND MULTICOMPONENT MODELING IN CONSEQUENCE AND RISK ANALYSIS

David W. Johnson and Jeffrey D. Marx
Quest Consultants Inc.
908 26th Avenue N.W.
Norman, Oklahoma 73609

The ability to accurately predict the consequences of a hazardous fluid release is dependent on three things: the knowledge of the modeler, the quality of the model that is used, and the quality of the input parameters. One of the most difficult problems in consequence modeling is the prediction of post-release multiphase behavior, especially when a multicomponent mixture is involved. Releases from gas/oil wells often fit this description. The wellstream will produce a light crude oil and a gas stream when flashed into a separator. If accidentally released to the atmosphere, the gas, aerosol, and liquid fractions rarely match the phase separations in the separator, or the expectations of the modeler. And, since the wellstream has a wide range of hydrocarbon components, the need to accurately predict the multicomponent behavior becomes more important. Over the years, modelers have used several "rules of thumb" to provide the source term input parameters for modeling multiphase/multicomponent releases and subsequent dispersion. These modeling assumptions can lead to hazard predictions that are very different from reality. The biggest problem with rules of thumb is their inability to account for thermodynamics; thus, they cannot approximate the phase splits and composition changes that do occur. The aim of this paper is to improve the knowledge of the modeler by providing some insight into the selection of the proper input parameters for multiphase releases of multicomponent fluids. The application of a multiphase release model with multicomponent thermodynamics to a wellstream release is used to illustrate the importance of good modeling techniques.

INTRODUCTION

Why do refineries have so many distillation columns, batch stills, and extraction columns? The answer is obvious: because almost every stream in a refinery is a complex mixture of hydrocarbons. By separating these hydrocarbons, useful products can be made and sold at a profit. Many other industries also operate with streams that consist of many components. This means that when consequence analysis or risk analysis studies are performed, we are likely to have to deal with multicomponent streams.

The use of a consequence model capable of handling multicomponent fluids would seem to be a standard requirement for the modeler. However, most consequence models are *not* designed to handle multiple component mixtures. Only a very few consequence models have true multicomponent/multiphase capabilities. Why is this so? The answer is relatively straightforward: the thermodynamic and physical

---

property components of multicomponent models are orders of magnitude harder to develop than pure component models.

What are the differences between multicomponent and pure component thermodynamics? When can pure components be used to accurately model multicomponent systems? When *must* multicomponent models be used? These questions will be discussed in the remainder of this paper. To provide a level field for comparison, all calculations were made using the CANARY by Quest® consequence model [Chang, et al., 1998]

COMPARISON OF MULTICOMPONENT AND PURE COMPONENT THERMODYNAMICS

Do multicomponent mixtures behave differently than pure components? Of course they do! You can't distill a pure component and get something other than the pure component. For comparative purposes, consider a simple mixture containing 50 mole percent methane and 50 mole percent pentane. This mixture has a molecular weight of 44.1, the same as pure propane. One of the most often used approximations for mixtures is to choose a pure component of the same molecular weight. So for this example, we can compare the methane-pentane mixture with propane.

Figure 1 shows the vapor pressure curve for pure components—methane, propane, and pentane. The propane vapor pressure curve falls between methane and pentane. Does this mean that propane would be a good thermodynamic substitute for the methane-pentane mixture? Figure 2 is a computed phase envelope for the methane-pentane mixture superimposed over the three vapor pressure curves of Figure 1. As Figure 2 shows, propane's pressure-temperature properties do not adequately represent the methane-pentane mixture. The vapor pressure curve of propane can be represented with a simple equation involving only temperature, pressure, and a couple of constants. The area of temperature and pressure that falls to the right of the curve represents vapor, and the area to the left is liquid. The area above the curve is commonly referred to as the supercritical region.

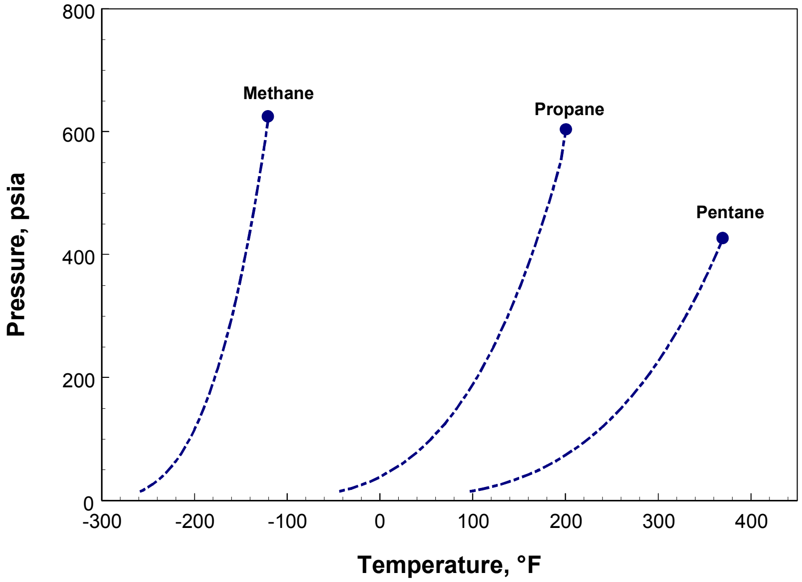

Figure 1
Vapor Pressure Curves for Methane, Propane, and Pentane

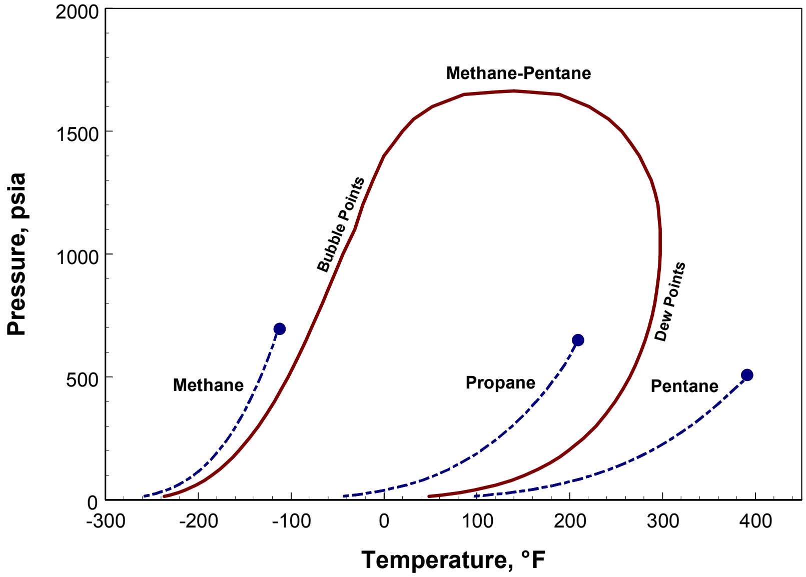

Figure 2
Methane-Pentane Mixture Phase Diagram

The behavior of the methane-pentane mixture cannot be represented by such a simple relationship. This diagram for the mixture is known as a phase envelope because a change from vapor to liquid (or liquid to vapor) does not happen at one temperature as with a pure component. At a constant pressure, there is a temperature range (envelope) that must be traversed to complete the phase change. Figure 3 shows this behavior for the methane-pentane mixture at a constant pressure of 400 psia. As the temperature of the mixture increases, the phase of the mixture is liquid until a temperature of –118°F is reached. From –118°F to 250°F, the mixture boils, changing from all liquid, to liquid and vapor, and finally to all vapor. Since methane preferentially distills from the liquid, the pentane concentration in the liquid increases. This causes an increase in the boiling temperature of the liquid. When the system temperature reaches about 250°F, all of the liquid is gone and only vapor remains.

This difference in phase behavior between a mixture and a pure component can result in other property differences. Consider the case of the two fluids described above, flowing in a pipeline at an initial pressure of 2,000 psia and an initial temperature of 60°F. As the fluid flows, frictional forces cause a reduction in pressure. Figure 4 shows the change in vapor quality (fraction of vapor in the fluid) with the change in system pressure. The methane-pentane mixture reaches its bubble point (point of initial production of vapor) at a pressure of around 1,400 psia. At this pressure, the methane-pentane mixture would begin to flow as a two-phase fluid. The amount of vapor would continue to increase as the pressure drops in the pipeline. At atmospheric pressure, the fluid flowing in the pipeline would consist of about 56 weight percent vapor. The propane would not reach its bubble point until the pressure had dropped to 108 psia. At atmospheric pressure, the propane flowing in the pipeline would contain about 33 weight percent vapor.

As each fluid reaches its bubble point, vapor is produced and the combined phase density of the fluid may begin to change rapidly. This can result in a rapid change in the velocity of flow in the pipe. Figure 5 shows the combined phase density of each fluid as it flows in the pipeline. At pressures below 1,400 psia, there are significant differences in the combined phase density.

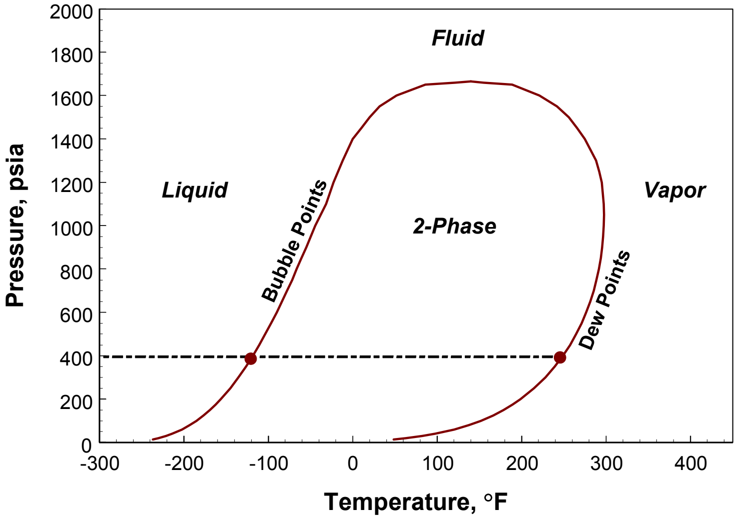

Figure 3
Boiling Range for Methane-Pentane Mixture

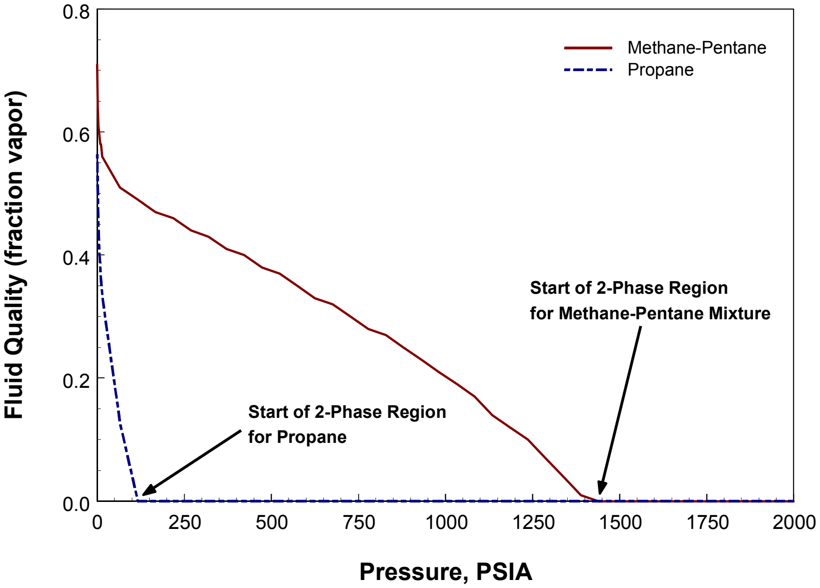

Figure 4
Fluid Quality Versus Pressure
for Propane and Methane-Pentane Mixture

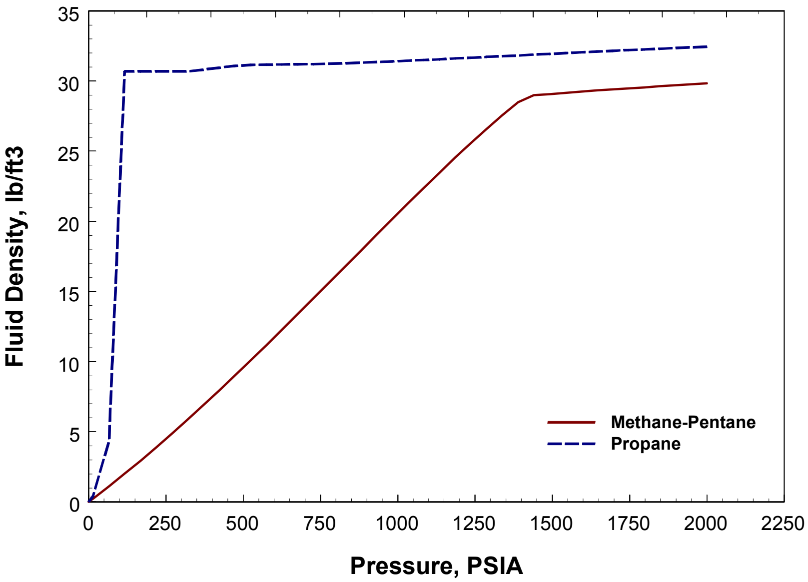

Figure 5
Fluid Density versus Pressure
for Propane and Methane-Pentane Mixture

Do differences in fluid properties have an effect on consequence analysis? The answer is YES. The important question is how much effect they have and when the effect is small and can be ignored. The problem that often arises is that you cannot determine the importance of these effects until you compute the changes in physical properties between a pure component and a mixture; and that requires a multicomponent model.

How can the modeler determine when he can model a multicomponent mixture by using a pure component and when is true multicomponent consequence modeling necessary? Let's take a look at a fairly simple example to see if there are any differences in the consequence analysis results when we simulate a mixture by using a pure component.

A Simple Example

As a consequence analysis specialist, you need to determine the distance to the LFL for a release from a tank containing a 50-50 mole percent mixture of methane and pentane. The project is in the early feasibility stage and only a few process conditions are known. The tank contains liquid stored at a pressure of 2 psig. A breach is assumed to occur in a 4-inch line located at the bottom of the tank. Facility operating personnel are assumed to isolate the breach within 10 minutes. The tank has a volume of 40,000 m^3 (10 million gallons). The spilled liquid is directed to a curbed area (bund) 100 ft in diameter with a concrete floor and wall. Local ambient atmospheric conditions are 80°F, 70% relative humidity, 4.5 mph (2 m/s) wind speed, and Pasquill F stability. The bund surface is assumed to be at 80°F.

The stored liquid is approximated using a pure component with the same molecular weight. A 50-50 mole percent methane and iso-pentane mixture has a molecular weight of 44.1, so propane is chosen as the pure component to use.

Table 1 summarizes the physical scenario and Table 2 summarizes the calculated release results for the propane.

Table 1
Summary of Physical Scenario for Simple Case

Item	Value
Storage pressure, psig	2.0
Release duration, min.	10.0
Ambient temperature, °F	80.0
Ambient relative humidity, %	70.0
Wind speed, mph	4.5
Atmospheric stability	F
Bund diameter, ft	100.0
Substrate material	Concrete

Table 2
Computed Scenario Results

Item	Propane
Release rate, lb/s	92
Maximum rate of vapor production, lb/s	22
Average vapor production for first 5 min., lb/s	18
Distance to LFL, ft	900

The calculations made using propane as a substitute fluid seem reasonable and indicate that a zone of 900 ft will be required to provide public safety.

Even though the actual fluid is only a two-component mixture and the molecular weight of the substitute fluid is a good match, there are still some nagging doubts in the back of your mind regarding the substitution of a pure component for this mixture. Those doubts may be justified because computing the distance to the LFL using the same consequence model in a multicomponent analysis shows that the distance required for public safety is 600 ft. Using propane as a substitute for the methane-pentane mixture overpredicts the distance to the LFL by almost 50 percent. Does this company want to buy the extra 300 ft of safety zone?

The liquids have the same molecular weight, the bunds are the same size and material of construction, the storage pressure, pipe diameter, release duration, and atmospheric conditions are identical. The release rates are similar. What causes the difference? The answer, of course, is that the two liquids have some physical properties that are quite different. What are these differences and how do they affect the results?

One difference is the storage temperature of the two liquids. The methane-pentane mixture must be cooled to –244°F before it becomes a liquid at 2 psig pressure. The propane is stored at about –39°F. When you specify a 2 psig storage pressure, the propane temperature will be –39°F, while the actual methane-pentane liquid temperature is –244°F. The percent flash of either liquid is small and does not contribute appreciably to the vapor production. The lower temperature methane-pentane liquid boils at a higher rate when spilled into the bund. Figure 6 shows the rate of vapor evolution from the bund for each liquid.

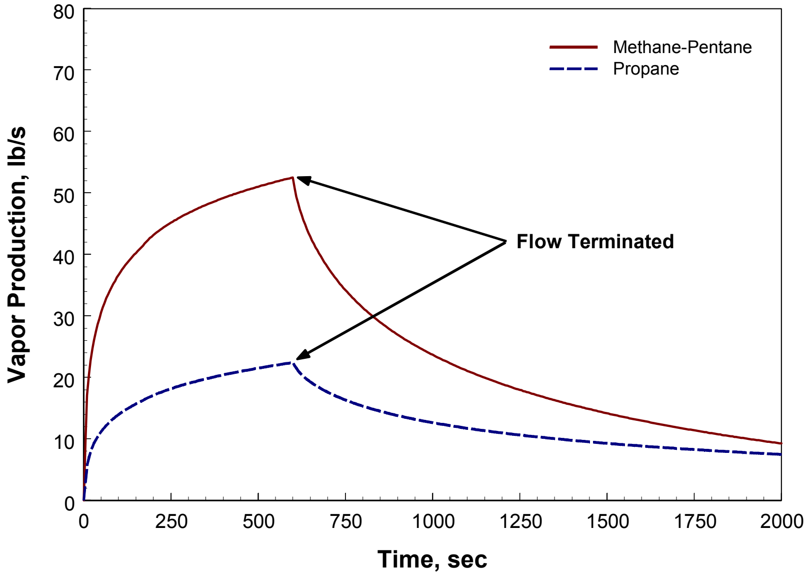

Figure 6
Vapor Production Rate
for Propane and Methane-Pentane Pools

Based on Figure 6, the methane-pentane spill should have a larger consequence zone since this spill results in a higher vapor production rate. However, the methane-pentane spill has a shorter hazard zone. Why is this? Another significant difference is found in the Lower Flammability Limit (LFL) of the vapor evolving from each liquid pool. The LFL of vapor from the propane pool is 2.1 mole percent, the LFL of pure propane. For a considerable period of time, the vapor from the methane-pentane pool is almost all methane and has an LFL of 5.0 mole percent. Thus, the propane vapor, with its lower LFL, would be expected to produce a longer flammable cloud.

The relative ratios of vapor production and LFL would seem to compensate for each other, yet the propane travels 50 percent further. The explanation may lie in the density of each evolving vapor. Although colder, methane vapor is not as dense as propane vapor. As the methane vapor warms, it becomes lighter than air, eventually lifting and rising. The propane vapor never becomes lighter than air, remains a ground hugging cloud, and travels further downwind to the LFL.

While these differences may seem obvious to the seasoned modeler, hazard calculations are often done by those not familiar with thermodynamics and phase equilibria. Even a seasoned modeler must resort to some form of multicomponent thermodynamic calculation to determine the storage temperature, composition, and density of the evolving vapor.

We have been looking at a simple two-component mixture. Think of the difficulties that would occur if the stored liquid had been a ten-component mixture. It seems obvious that, even for this relatively uncomplicated example, we can easily get into serious trouble by ignoring the multicomponent nature of the system.

A More Difficult Scenario

Consider a 2-inch diameter gathering line that transports fluid from a gas/oil well to a separator 500 ft away. The line receives fluid from the reservoir at 920 psig and 100°F. The flow line is ruptured just upstream of the separator which is operating at 200 psia. We will assume that an operator is able to activate the well shutdown in 30 minutes. The release is directed vertically upward under ambient atmospheric conditions of 4.5 mph (2 m/s) wind, Pasquill F stability, and 80°F air temperature. This scenario presents a more difficult problem when attempting to use a pure component to simulate a mixture.

Table 3 gives the compositions of the two fluids used in the analysis. The reservoir fluid is a ten-component mixture simulating fluid flowing from a gas/oil well. This fluid has a molecular weight of 114.2, so *n*-octane (MW=114.2) was chosen as a suitable pure component to use as a substitute for the mixture.

Table 3
Reservoir Fluid Compositions in Mole Percent

Component	Reservoir Fluid	Octane
Methane	28.9	
Ethane	7.8	
Propane	5.4	
i-Butane	4.8	
n-Hexane	4.3	
n-Heptane	5.7	
n-Octane	2.0	100.0
n-Decane	4.0	
Tridecane	8.0	
Heptadecane	29.1	
Average molecular weight	114.2	114.2

Figure 7 shows the release rate of each fluid with respect to time. Only the first two seconds of the release are shown since a steady flow is established very quickly. Both calculations were made using the same consequence model; the differences in the results are due to the use of pure or multicomponent thermodynamics.

Why does the reservoir fluid have a lower release rate than the octane? The answer lies in the thermodynamic behavior of each fluid. At 100°F, *n*-octane is a liquid at all pressures above 0.54 psia (*n*-octane vapor pressure at 100°F). The reservoir fluid becomes two-phase at any pressure below 919 psia. When its flow becomes two-phase, the reservoir fluid will have a higher pressure drop per unit of mass flow, higher fluid velocities, and lower phase density. Translated into simple terms, this means that the flashing reservoir fluid cannot sustain the high mass flow rates of the *n*-octane fluid given the same pressure level in the reservoir.

Figure 7 does not show the entire story. At the instant of the breach, most of us would expect a high initial rate of liquid that might produce a vapor/aerosol cloud. However, this high initial flow would only last a short time. The flow would rapidly decay, reaching an almost steady-state condition within a second or two.

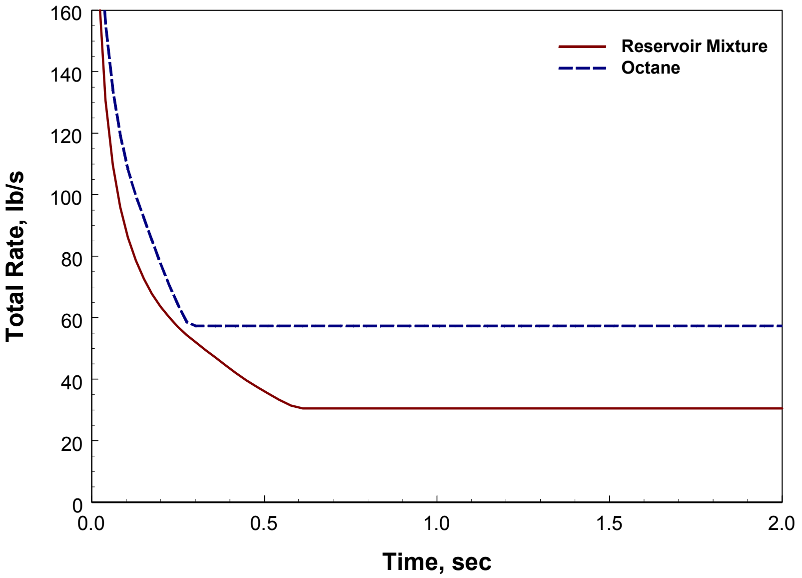

Figure 7
Release Rate versus Time
for Well Fluid and Octane Cases

For octane, as the flow rate declines, there is much less potential to form an aerosol, and the piping will simply dump liquid to the ground. However, the reservoir fluid would continue to flash in the piping and exit the breach as a high velocity two-phase aerosol cloud. Figure 8 shows the computed amounts of aerosol produced by each fluid, and Figure 9 shows the computed amounts of liquid reaching the ground for each fluid.

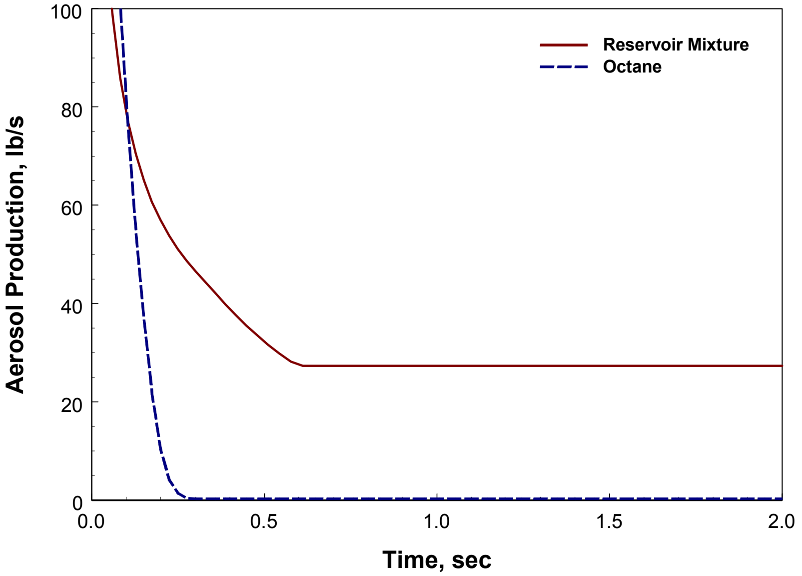

Figure 8
Aerosol Rate versus Time
for Well Fluid and Octane Cases

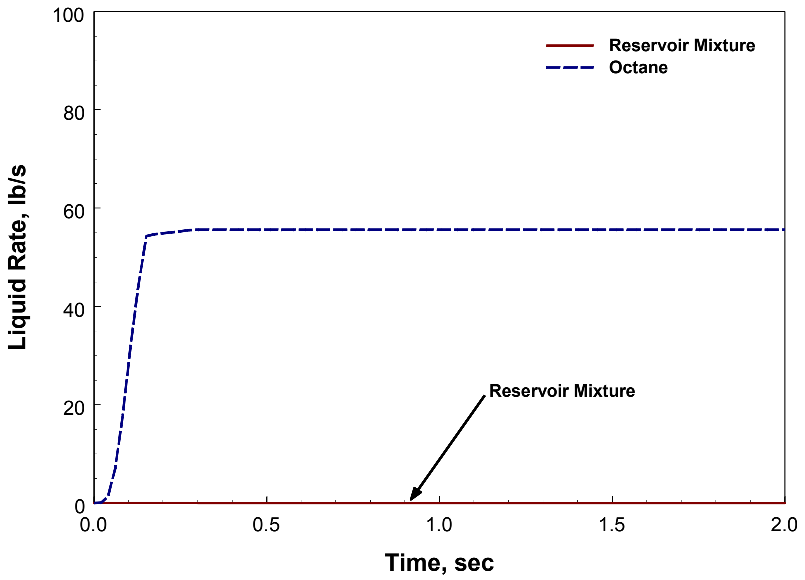

Figure 9
Liquid Rate versus Time
for Well Fluid and Octane Cases

As these figures show, the release behavior of these two fluids is different. The octane will produce a liquid pool and a heavy gas cloud. The reservoir fluid will produce a vapor/aerosol momentum jet cloud. Table 4 summarizes the results of the vapor dispersion portion of the consequence analysis.

Table 4
Summary of Calculated Release Results for Pipeline Rupture

Item	Reservoir Fluid	Octane
Maximum release rate, lb/s	250	260
Steady-state release rate, lb/s	30	57
Steady-state liquid rate, lb/s	0	55
Steady-state vapor/aerosol rate, lb/s	30	2
Distance to LFL, ft	360	40*
Cloud height at LFL, ft	0	0

*The flammable zone remains within the liquid pool boundary.

At 100°F, the maximum octane concentration directly above the liquid pool is approximately 3.5 mole percent. The wind mixes with and dilutes the vapor above the pool to below the LFL (1.1 mole percent) before the vapor leaves the perimeter of the pool.

Using *n*-octane to simulate a release of the reservoir fluid is not a good idea. Certainly, the calculations show significant differences in the hazard zone.

Are there other ways to use a single component to simulate this reservoir fluid? Perhaps. The modeler could look at the vapor portion of the system and assume that the released vapor would contain a large fraction of the lighter components. Table 5 summarizes a possible vapor stream composition based on the components found in the reservoir fluid (Table 3).

Table 5
Vapor Composition in Mole Fraction

Component	Mole Fraction
Methane	0.72
Ethane	0.15
Propane	0.08
i-Butane	0.05

The average molecular weight of the vapor stream is approximately 22.5. The modeler must make a choice between using methane, which has a lower molecular weight (MW=16), or ethane, which has a higher molecular weight (MW=30). For this analysis, the modeler has chosen ethane, assuming that the higher molecular weight vapor will produce the largest hazard zone. A "rule of thumb" that some modelers have used in analyzing a release of this type is to apply the Gas Oil Ratio (GOR) in the separator as a reliable indicator of what will happen when the fluid is released to the atmosphere. The GOR is simply the volume ratio of vapor to liquid. With this assumption, the simulated release will result in a vapor stream jetting into the air and a liquid stream pooling on the ground.

For this system, the GOR at 200 psia (separator pressure) is about 3.1. This means that for every 1.0 ft^3 of liquid collecting in the separator, 3.1 ft^3 of vapor is produced. For this particular fluid, a GOR of 3.1 translates into a vapor *mass* fraction of 0.30. Of course, this doesn't help the modeler determine the actual vapor flow rate. Normally, some estimate of the open hole flow characteristics of the well are available and can be used as the worst-case release rate. For this well, the open hole flow rate has been found to be the equivalent of 180 lb/s. Based on a GOR of 3.1, the rate of vapor release will be 53 lb/s.

Introducing this information into a model with ethane as the vapor and a set of atmospheric conditions and release orientation similar to our previous analysis results in a computed downwind distance to the LFL of 90 ft at a height above grade of 130 ft. The multicomponent analysis found a downwind distance to the LFL of 360 ft at grade. Figure 10 compares the results of the ethane vapor computation with the previous multicomponent calculation.

The dispersion results are strikingly different. The differences are due to the way in which the pure component model and the multicomponent model characterize the fluid entering the atmosphere. The pure component model treats the fluid as a vapor (ethane), while the multicomponent model treats the fluid as a liquid/vapor mixture. The primary driving force for the multicomponent fluid is its density. Due to the presence of liquid in the vapor, the multicomponent fluid is considerably heavier than air and quickly slumps to the ground. Once on the ground, the fluid disperses like a heavy gas rather than a high velocity release of vapor. This results in a less vigorous entrainment of air and longer distances to the LFL.

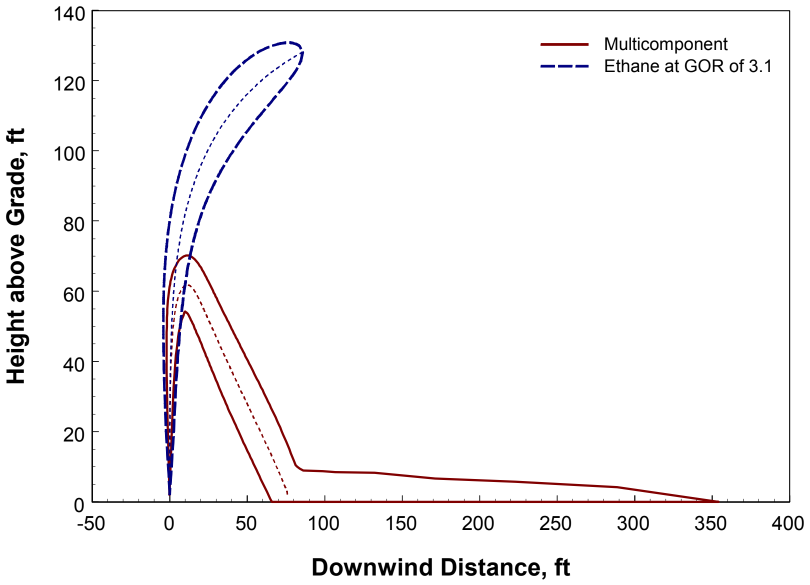

Figure 10
Comparison of Multicomponent
and Single Component Dispersion

Can Consequence Analysis be Performed Adequately Using a Pure Component Analysis?

Is there any consequence analysis scenario that allows the use of a pure component to simulate a mixture? What about a vapor release? Consider a release of methane-pentane vapor from a large vessel operating at 50 psig and 150°F, and a release of pure propane at the same conditions. The release will come from a 6-inch diameter hole made in the side of the vessel. The release is angled 45° above horizontal. The release rate will be relatively constant since pressure and temperature in the large vessel will change slowly with time.

Table 6 summarizes the computed results and Figure 11 shows the LFL contours. With the many uncertainties within which modelers work, the agreement is good. Thus, it appears possible to model releases of vapor mixtures using pure component data.

Table 6
Summary of Calculated Release Results for a Vapor Release

Item	Propane	C1-C5
Vapor production, lb/s	35	35
Distance to LFL, ft	100	100
Height above grade at LFL, ft	100	100

The good agreement between the mixture and pure component calculation is not an unexpected result, since the LFLs are similar and we do not have to deal with phase equilibrium in this calculation.

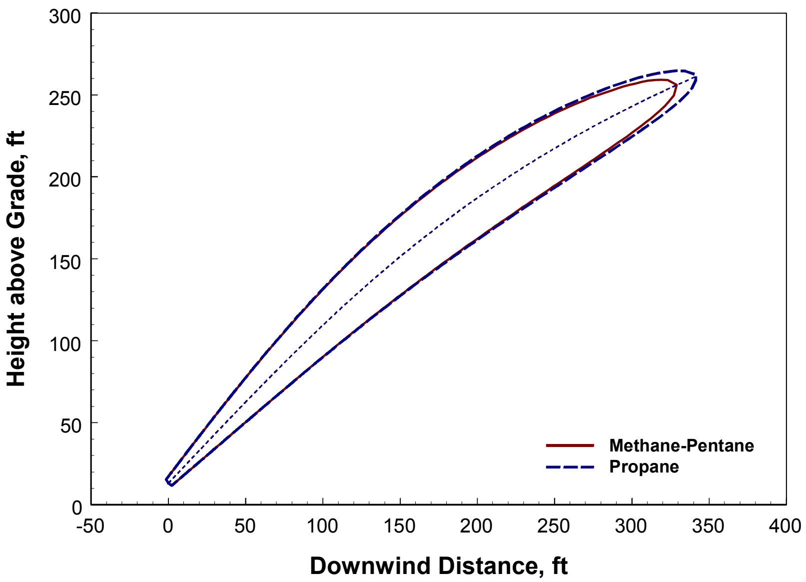

Figure 11
Dispersion of Vapor Releases to the Lower Flammable Limit

CONCLUSIONS

The examples developed in this paper illustrate that the simulation of a mixture via the use of pure component consequence modeling will not always provide accurate predictions. Use of a multicomponent consequence model is always recommended when the potential for the formation of a two-phase system exists. The use of a pure component consequence model may produce accurate results under conditions where only a vapor is released and the LFL of the pure component and mixture are similar.

The most reliable use of a single component consequence model results when the single component simulates the behavior of the multicomponent fluid over all potential conditions, from storage conditions to ambient atmospheric conditions. Naturally, this involves an intimate knowledge of the thermodynamic behavior of the mixture. This information can only be determined through the use of a multicomponent thermodynamic model. Computation of the large amount of information needed to simulate a multicomponent mixture and subsequent integration of that information into the pure component model can be a time-consuming and tedious task. Why not just use a multicomponent model from the start?

Since the multicomponent model is always preferred, one might wonder why single component models are used at all. The reason is simple and straightforward. Single component models are much easier to develop, generally run faster, and often are more reliable than multicomponent models. Additionally, there are several publicly available compilations of pure component properties. Reid, Prausnitz, and Poling [1987], Yaws [1999], and The Center for Chemical Process Safety (CCPS) [1985] have developed and provided to the public at reasonable cost, very complete sets of equations and constants for the calculation of pure component thermophysical properties.

Sadly, no such information is publicly available for the prediction of multicomponent thermophysical properties. The development of such a calculation procedure would greatly aid the consequence modeling community.

REFERENCES

CCPS, *Data Compilation Tables of Properties of Pure Compounds*. Center for Chemical Process Safety of the American Institute of Chemical Engineers, 345 East 47th Street, New York, New York, 1985.

Chang, Joseph C., Mark E. Fernau, Joseph S. Scire, and David G. Strimaitis (1998), *A Critical Review of Four Types of Air Quality Models Pertinent to MMS Regulatory and Environmental Assessment Missions*. Mineral Management Service, Gulf of Mexico OCS Region, U.S. Department of the Interior, New Orleans, November, 1998.

Reid, R., C., J. M. Prausnitz, and B. E. Poling (1987), *The Properties of Gases and Liquids* (Fourth Edition). McGraw-Hill Book Company, New York, New York, 1987.

Yaws, Carl L. (1999), *Chemical Properties Handbook*. McGraw-Hill Book Company, New York, New York, 1999.