A thermodynamic analysis of fuel vapor characteristics in an aircraft fuel tank ullage [☆]

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Abstract

As a prerequisite to a comprehensive analysis of aircraft fuel tank fire and explosion hazards, a vapor–liquid equilibrium thermodynamic analysis was developed to assess the fuel vapor behavior in an aircraft fuel tank ullage. The analysis was based on the Peng–Robinson equation of state and the extended corresponding-states method. Jet-A fuel was treated as a pseudo-single-component fluid and as a binary mixture. The calculated fuel/air mass ratios from the binary-mixture model followed the trend observed in previous measurements more closely than those from the pseudo-single-component model. The calculated results also demonstrated that for a given amount of fuel, increasing the tank temperature could potentially cause an initially non-flammable fuel/air vapor in the ullage to become flammable.
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1. Introduction

On July 17 1996, a Trans World Airlines Boeing 747 (TWA Flight 800)[1] tragically exploded in mid-air and plummeted into the Atlantic Ocean near East Moriches, New York. The **US** National Transportation Safety Board (NTSB) determined that the probable cause of the accident was an explosion of the center wing tank (CWT),

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[1] This identification is for historical accuracy only.

Nomenclature

M	mass
M_w	molecular mass
N	number of moles
P	pressure
R	universal gas constant
T	temperature
T_b	normal boiling point
v	molar volume
V	volume
V_t	tank volume
x	mole fraction in liquid phase
y	mole fraction in vapor phase
z	bulk mole fraction
ρ	molar density
ω	acentric factor

Subscript and superscript

a	air
c	critical state
f	fuel
j	jth component in the mixture
l	liquid phase
v	vapor phase

resulting from ignition of the flammable fuel/air mixture in the tank [1]. The tragedy of that flight has since initiated extensive examination of the problems related to the flammability of fuel vapor in the CWT of aircraft. The US Federal Aviation Administration and NTSB have since sponsored research to study fuel vapor characteristics in CWT for various in-flight conditions [2–6]. Early studies in aircraft fuel tank explosion and fire hazard assessment can be found, for example. in Ref. [7]. In this paper. we apply vapor liquid equilibrium thermodynamics to examine the fuel vapor concentration in the fuel tank ullage and hope to provide a theoretical framework to understand the fuel vapor behavior in the tank. Our primary focus is to study the effect of fuel mass loading in the tank on the fuel vapor concentration in the ullage since fuel mass loading is an important factor in determining the vapor composition in the ullage [2,3,8]. The present study differs from previous work [3,7], in that detailed vapor liquid equilibrium calculations are performed without resorting to the assumption of ideality in either or both phases (liquid or/and vapor). The experimental measurements from two recent studies [2,4] are used to compare with the thermodynamic calculations.

2. Analysis

As a *first* step toward a comprehensive assessment of fuel tank fire and explosion hazards, we examine a situation wherein an initially empty fuel tank with a volume V_t is charged with a known amount of fuel (M_f) or known volume (V_f) at a temperature T and a pressure P. Since the fuel tank is not evacuated before refueling, air is always present in the tank. We want to calculate the fuel vapor concentration and the mass ratio of fuel/air in the ullage as a function of the tank temperature.

In the analysis, the fuel vapor is assumed to be at equilibrium with the liquid fuel at the prevailing temperature. This conservative assumption is considered acceptable for all phases of the flight [8]. No venting of fuel vapor from the tank and no fuel consumption are considered in the present analysis, that is, the fuel tank is treated as a closed system, and the amount of fuel in the tank is constant. In addition, it is assumed that there is no spatial variation in fuel vapor concentration in the ullage.

Jet-A is a complex mixture of hydrocarbon fluids including branched and linear alkanes, alkenes, cycloalkanes, alkyl-aromatics, and naphthalenes [5], the composition of which varies from batch to batch. For the purpose of this work, we use two different methods of treating the fuel: a simplified model where the fuel is treated as a pseudo-single-component fluid with an averaged set of physical properties, and as a binary mixture of two hydrocarbons selected to approximate Jet-A. Both the pseudo-single-component approach [9] and the binary-mixture approach [3] have been used before for undefined petroleum fractions such as Jet-A. In this paper, we modeled a specific Jet-A fuel with a molar mass of the vapor phase of 132.4g/mol [4] and the vapor pressure curve reported in Ref. [3] for a loading of $3kg/m^3$. Air was assumed to be a binary mixture with a nitrogen mole fraction of 0.78 and an oxygen mole fraction of 0.22.

For the pseudo-single-component method, the critical pressure (P_c), critical volume (V_c), normal boiling point (T_b), and acentric factor *(w)*, estimated by scaling (using the molar mass) between normal nonane and normal decane, were 2235 kPa, 0.564l/mol, 430.8 K, and $w = 0.457$, respectively. The critical temperature ($T_c = 637.9$ K) was adjusted to achieve vapor pressures consistent with Ref. [4] at $3kg/m^3$. There are other methods to obtain the various parameters in a pseudo-single-component model [9]; however, for this work we selected a simple method to emphasize the reproduction of Jet-A vapor pressures at temperatures near 323 K due to its importance in modeling the fuel tank ullage.

The second method of representing Jet-A is to approximate the fuel as a binary mixture. Many choices are possible; we selected a mixture of 0.35 mol fraction of nonane with 0.65 mol fraction of hexadecane. This mixture was selected because it has a wide boiling range (424–560 K), has a vapor-phase molar mass of approximately 129g/mol for the temperatures and mass loadings of interest here, and is in good agreement with the vapor pressure curve at $3kg/m^3$ reported in Ref. [3].

The calculation procedure for properties of the fuel/air mixture is analogous to the one that we have developed for fire suppressant/dissolved nitrogen mixtures [IO]. The phase equilibrium is determined using the Peng–Robinson equation of state (EOS)

[11], an equation widely used in industry for vapor liquid equilibrium calculations of mixtures of hydrocarbons and non-polar fluids. The Peng Robinson equation is given by

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)},$$

where a and b are the parameters, the expression of which can be found in Ref. [11].

The thermodynamic properties at a given state point are then found using the extended corresponding states method (EXCST), with propane as a reference fluid. The EXCST offers improvements over the Peng Robinson EOS for fluid properties, especially liquid densities. The central idea of extended corresponding states is that all points on the PVT surface of any fluid may be represented by scaling the PVT surface of a reference substance. Due to its very long saturation boundary, and the availability of a high-accuracy EOS and non-polar nature, propane has been used successfully as a reference fluid in EXCST models developed for noti-polar hydrocarbon fluids ranging up to 24 carbons [12]. Details of the EXCST method can be found in Refs. [12,13], and it is the basis for a computer program available from the Standard Reference Data Program of the National Institute of Standards and Technology [14].

To begin the calculations, it is required that the amount of fuel, the tank temperature, the tank size, and the total pressure be known. The calculation is essentially a flash calculation at fixed T and P. Briefly described, given a mixture, in this case fuel/air, whose bulk compositions (z_j) are known at T and P, determine x_j, y_j, and fraction vaporized (α), where x is the liquid mole fraction, y is the vapor mole fraction, and the subscript j represents the component: Jet-A, nitrogen or oxygen. A detailed discussion can be found in Prausnitz et al. [IS] and Walas [16]. A flow chart of the calculation procedure to find the fuel/air mass ratio is given in Fig. 1. If there is so little fuel present that it all vaporizes, the flash calculation will return only a single phase. In this case, the fuel mole fraction is simply the partial pressure of fuel vapor divided by the total pressure of the tank.

3. Results and discussion

In the following, the results are presented in terms of fuel/air mass ratio (F/A). This quantity has been suggested to be a convenient way for defining the lean flainmability limits of fuel/air mixtures because the ratios at the lean flammability limits for a wide range of fuels remain relatively constant with a value close to 0.03 at sea level air [8]. Fig. 2 shows a comparison of the thermodynamic calculations with the experimental results from Summer [2]. Note that the fuel/air mass ratios reported in Summer's work are approximated values, and experimental uncertainties were not stated. The predicted fuel/air mass ratios show the same trend of a rapid rise at low fuel volume as the experimental measurements. For these particular experimental conditions ($V_t = 2497.841$, $T = 324.82$ K, $P = 101.325$ kPa), the calculations made with a pseudo-single-component fuel show that as long as the fuel tank contains
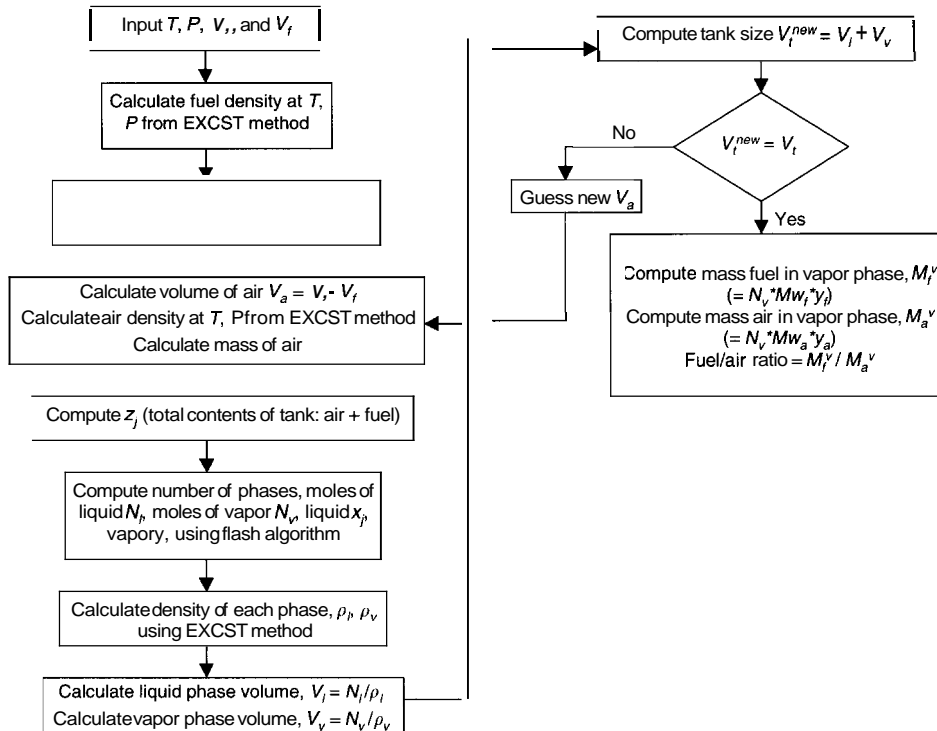
Fig. 1. Flow diagram of the calculation procedure for obtaining fuel/air mass ratio.

more than 0.111 of fuel, the fuel/air mass ratio is constant at 0.035. For a "pure" fluid, the fuel/air mass ratio is mainly dependent on the vapor pressure of the fuel, which does not depend on how much fuel is in the tank, as long as enough fuel is present so that a liquid phase exists. If the fuel amount is under that threshold, all of the fuel that is put in the tank will be in the vapor phase, and as more fuel is put in, more ends up in the vapor phase. Once a liquid phase forms, additional fuel simply raises the liquid level and does not change the equilibrium fuel composition in the vapor phase of the tank.

The calculations made with Jet-A modeled as a binary mixture illustrate some interesting differences due to the nature of a mixture instead of a "pure" (pseudo-single-component) fluid. The binary-mixture curve approaches the same value as the pseudo-single-component model, due to the fact that the parameters for Jet-A in both cases were selected to match the same vapor pressure data. The shapes of the curves are different, however. The binary-mixture representation approaches its limiting value much more slowly than the pseudo-single-component model, and also better mimics the behavior of the experimental observation.

The applicability of the thermodynamic equilibrium model to examine the flammability of fuel vapor in the fuel tank ullage is demonstrated in Fig. 3, where the calculated fuel/air mass ratios as a function of fuel loading at various tank
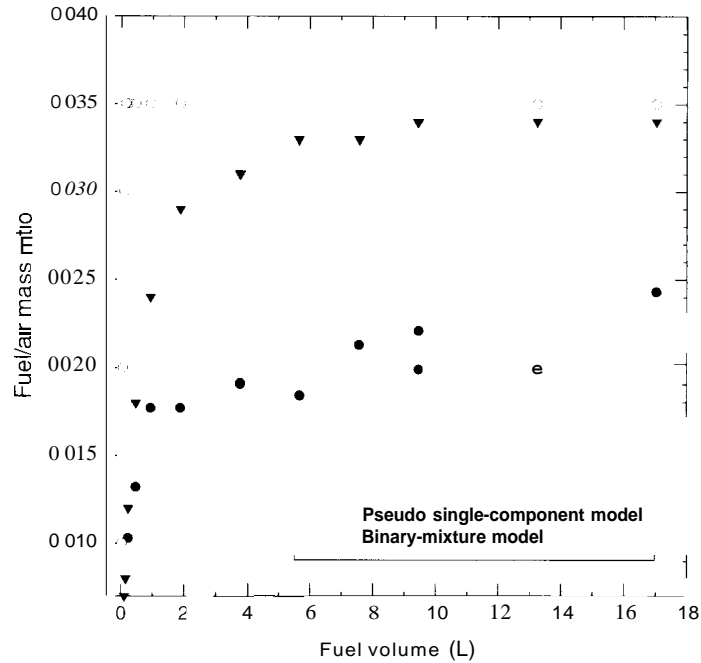
Fig. 2. The effect of fuel loading on fuel/air mass ratio in the fuel tank ullage ($T = 324.82$ K. $V_t = 2497.84$ l. $P = 101.325$ kPa).

temperatures (fi-om 233 to 330 K) are plotted. The calculations were obtained using the same fuel tank volume as in Fig. 2 and the binary-mixture model. Fig. 3 shows that irrespective of the tank temperature, the fuel/air mass ratio reaches an asymptotic value. as explained in the above paragraph. when the amount of fuel in the tank exceeds a certain threshold. If a fuel/air mass ratio of 0.03 is assumed to represent the lean flammability limit of the fuel vapor air mixture in the ullage [8], increasing the tank temperature can potentially cause an initially non-flammable mixture (i.e., $F/A < 0.03$) to become flammable (i.e., $F/A > 0.03$) for a given amount of fuel in the tank. as indicated in Fig. 3.

Thermodynamic calculations were also performed to compare with the experimental results from Sagebiel [4] using both the pseudo-single-component and binary-mixture representation of Jet-A. Table 1 shows the comparison. The pseudo-single-component and the binary-mixture models show similar F/A ratios because the same vapor **pressure** data was used to obtain the model parameters. Both models tend to somewhat underpi-edict the F/A ratio at the lower pressures.

4. Concluding remarks

A detailed vapor liquid equilibrium thermodynamic analysis ⱥas been developed to predict the fuel/air mass ratio in a fuel tank ullage. The Peng Robinson EOS and
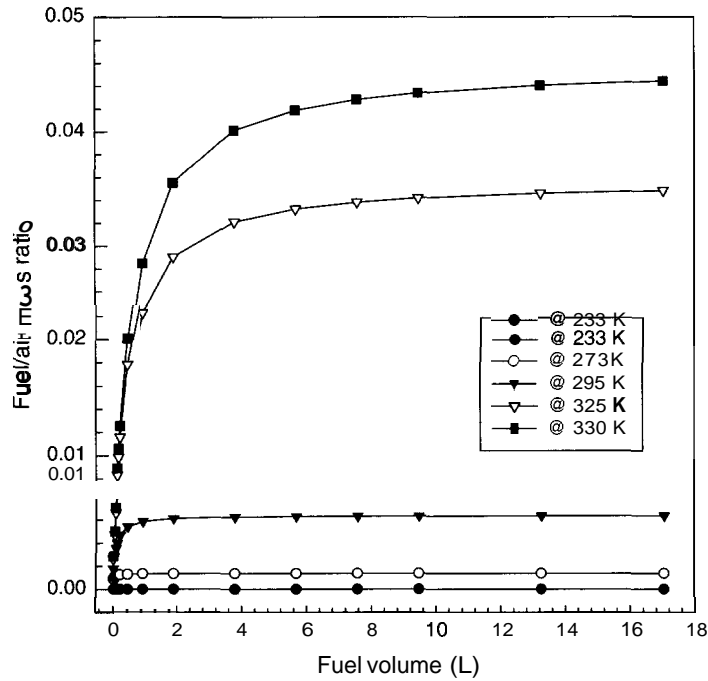
Fig. 3. Calculated fuel/air mass ratios in ullage as a function of fuel loading at various tank temperatures using the binary-mixture model.

Table I
Comparison of the calculated fuel/air mass ratios (F/A) with the measured values taken from [4]

T (K)	P (kPa)	F/A from [4]	F/A pseudo-single-component model	F/A binary-mixture model
322.03	100.0	0.030	0.030	0.029
318.71	69.7	0.045	0.036	0.036
319.82	58.5	0.049	0.045	0.045
323.71	100.0	0.034	0.033	0.032
319.26	69.7	0.046	0.037	0.037
320.37	58.5	0.054	0.046	0.046
318.71	100.0	0.028	0.025	0.025
315.93	69.7	0.036	0.030	0.031
315.37	58.5	0.048	0.035	0.036

the EXCST method are used in the algorithm. The thermodynamic calculations, especially from the binary-mixture model, capture the fuel vapor behavior in the ullage. In modeling these systems, it is important to have accurate representations of the vapor pressure of the fuel, since this is a major factor in calculating the fuel mass/air ratio. Accurate measurements of the fuel/air mass ratios are also needed, complete with estimates of the uncertainties of the quantities. In our future modeling

effort. the assumption of a closed system will be relaxed, and an *open* system will be considered in the analysis. The behavior of dissolved air in fuel. fuel evaporation, fuel vapor venting from the ullage, and fuel consumption will be taken into account in the problem formulation.

References

[1] In-flight breakup over the Atlantic Ocean Trans World Airlines Right 800 Boeing 747-131, N93119 near East Moriches. New York. July 17, 1996. National Transpot-tation Safety Board Aircraft Accident Report, NTSB AAR-00 03. Washington, DC: National Transportation Safety Board. 23 **August** 2000.

[2] Summer SM. Mass loading effects on fuel vapor concentrations in an aircraft fuel tank ullage. Department **of** Transportation, DOT FAA AR-TN99 65 US Federal Aviation Administration. September 1999.

[3] Shepherd JE. Krok JC, Lee JJ. Jet **A** explosion experiments: laboratory testing. Docket No. **SA-5**16. Exhihit No. 20D. Waahington, DC: National Ti-ansportation Safety Board, Novemher 1997.

[4] Sagebiel JC Sampling and analysis of vapors from the center wing **tank of** a test Boeing 747-100 aircraft, Docket No. SA-516, Exhibit No. 20G. Washington. DC: National Transportation Safety Board. November 1997.

[5] Woodrow JE, Seiber JN. The laboratory characterization of jet fuel vapor under simulated flight conditions. Docket No. SA-516. Exhibit No. ?OH. Washington. DC: National Transportation Safety Board. Novemher 1997.

[6] Summer SM. Cold ambient temperature effects **on heated** fuel tank vapor concentrations. Department of Transportation. DOT FAA AR-TN99 93. US Federal Aviation Administration, July 2000.

[7] Kosvic TC, Zung LB, Gerstein M. Analysis of aircraft fuel tank fire and explosion hazards. Technical Report AFAPL-TR-71-7. OH: Air Force Aero Propulsion Lahot-ator). Wright Patterson Air Force Base. March 1971

[8] Fuel Flammability Task Group. A review **of** the flammability hazard of jet A fuel vapor in civil transport aircraft fuel tanks. US Deportment of Transportation, DOT FAA AR-98 26. Federal **A**viation 4dministration, June 1998.

[9] **Rupprecht** SD. Faeth **GM**. Investigation of air solubility in jet a fuel at high pressures. NASA Contractor Report 3422. NASA. Lewis Research Center. 1981.

[10] Yang JC'. Vázquez I. Boyer CI, Huber ML. Weber L. Meastired and pi-edicted thermodynamic properties of selected halon alternative nitrogen mixtures. Int J Refrig 1997:20(2):96 105.

[11] Peng DY. Robinson DB. **A new** two-constant equation of state. **Ind Eng Chem** Fundam 1976;15:59 64.

[12] Huber ML, Hanley **HJM**. Transport properties from extended corresponding states. Transport properties of fluids. Cambridge: Cambridge University Press. 1996 [Chapter 10].

[13] Huber ML. Ely JF. **A** predictive corresponding states model for pure and mixed **refrigerants** including a new equation of state for R134a. Int J Refrig 1994:17(1):18 31.

[14] NIST Thermophysical properties of hydrocarbon mixtures (NIST4, Version 3.01). Gaithersburg. MD: National Institute of Standards and Technology. 1999.

[15] Prausnitz JM, Anderson TF, Grens EA. Eckert CA, Hsieh R. O'Connell JP. Computer calculations for multicomponent vapor liquid and liquid liquid equilibria. New Jersey: Prentice-Hall, 1980.

[16] Walas SM. Phase equilibrium in chemical engineering. Boston: Butlet-north. 1985.