

ANOMALOUS EFFECTS OF WATER IN FIREFIGHTING: INCREASED FIRE INTENSITIES BY AZEOTROPIC DISTILLATION EFFECTS

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INTRODUCTION

The greatest single effect of water in fire extinguishing applications is its great cooling capacity, particularly when used in fog or mist form. There are several well-known situations, however, in which application of water actually serves to intensify a fire:

1. When applied to very hot oil or grease fires, water will flash into steam, with possible spattering effects that can spread the area of a fire.
2. Direction of a vigorous jet of water from a fire hose into burning liquid fuel can also increase the area of a fire by mechanical “digging” effects.
3. Air entrained in water jets, sprays, or mists can feed oxygen to a fire.
4. Water reacts explosively with active metals such as sodium, or with other water sensitive energetic materials such as strong acids or bases.
5. Previous work by this group [1] and confirmed by others [2] has shown that high humidity facilitates autoignition by lowering hot surface ignition temperatures.
6. “Boilover” can result from formation of a heat wave progressing downward through burning fuel floating on water, finally reaching the water and causing it to come to a rapid boil with forcible ejection of burning fuel upward from the surface. This occurs only for burning fuel mixtures made up of both high and **low** density components (as the lighter components volatilize, the heavier species tend to sink). Thus, this effect is not observed for pure liquids; the fuel mixture must be floating on water, and the effect requires several hours of build-up time before it is observed [3,4].
7. “Sloper” is a related effect, in which water being applied from fire hoses heats to its boiling point as it passes through the heat wave en route to the bottom of the burning fuel. The resulting steam bubbles, entrained and rising in the body of the fuel, then can cause fire expansion by a frothing effect within the fuel [3].

None of these is involved in any way in the azeotropic effects to be described in this report. (An inference can be drawn from material in this report that azeotropic effects may be peripherally related to “boilover” and “sloper” once these two phenomena occur, neither of these two effects is in itself an element of azeotropy.)

AZEOTROPIC EFFECTS OF WATER ON FIRE INTENSITIES

Although azeotropy has thus far not been considered in fire research work, it can be shown to pose at least as serious a problem for firefighting considerations. Azeotropy is a well-known and well-described phenomenon, forming the basis of what is termed “steam distillation,” practiced on a large industrial scale as a means of performing distillations at relatively low temperatures for what would ordinarily be very low volatility, high boiling point liquids [5,6]. A brief description of this effect is provided below.

As shown in Figures 1 – 3 for benzene, xylene, and water, the boiling point of any liquid or mixture of liquids is that temperature at which the vapor pressure of the liquid system exactly equals the atmospheric pressure (standard atmospheric pressure being 760 mm of mercury). Benzene and xylene were chosen for this work, since these have boiling points analogous to boiling points of volatile JP-4 (B.P. 70 – 200 °C) [7], and less volatile JP-8 and Jet A-1 fuels, respectively (B.P. 125 – 250 °C) [7]. Moreover, by using pure hydrocarbon fuels, possible “boilover” effects were avoided. In Figure 1, benzene boils at 80 °C [7]; in Figure 2, xylene boils at 139 °C [7]; and in Figure 3, water boils at 100 °C—each at 760 mm.

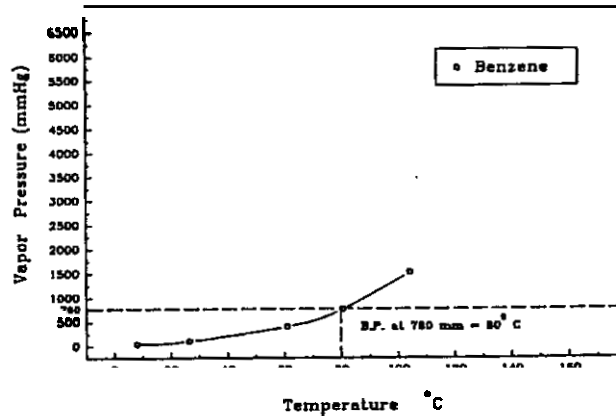


Figure 1. Vapor pressure/temperature diagram for benzene.
(Data from *Handbook of Chemistry and Physics* [8].)

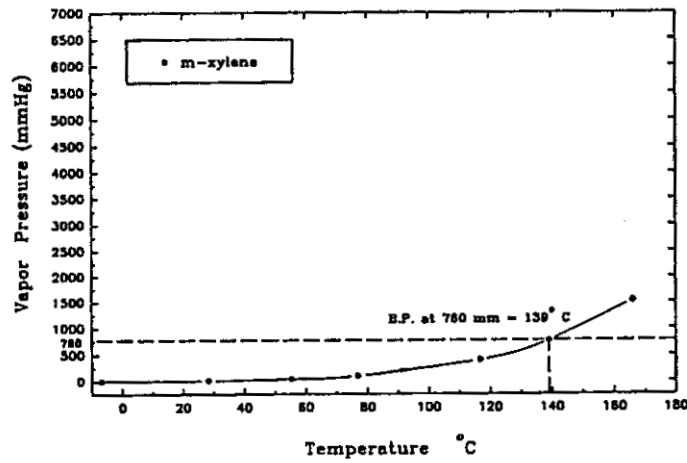


Figure 2. Vapor pressure/temperature diagram for xylene [8].

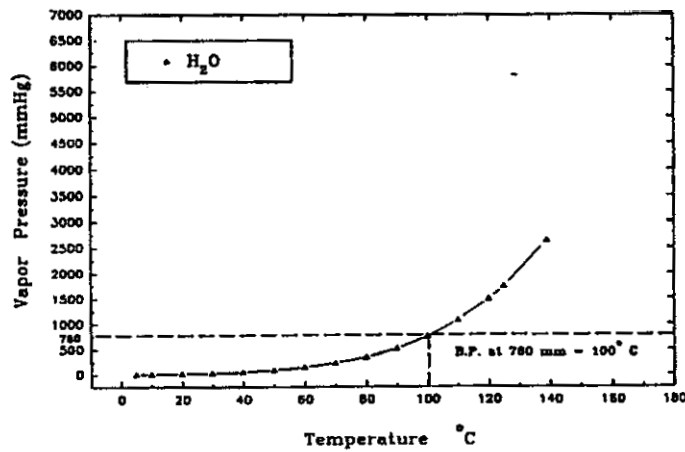


Figure 3. Vapor pressure/temperature diagram for water [8].

If two liquids are insoluble in each other (as is the case for benzene and water, and xylene in water, and jet fuels in water), each phase exerts its own vapor pressure at a given temperature. The total pressure is then the sum of the vapor pressures for each liquid at that temperature. Figures 4 and 5 show azeotropic effects when two insoluble liquids such as these hydrocarbon fuels are mixed.

For the insoluble mixture of benzene and water (Figure 4), at 69°C the vapor pressure of benzene is 533 mm, and of water, 227 mm. Since the total pressure is 760 mm, the mixture will boil at this lower temperature, 11 °C (20 °F) lower than the boiling point of pure benzene.

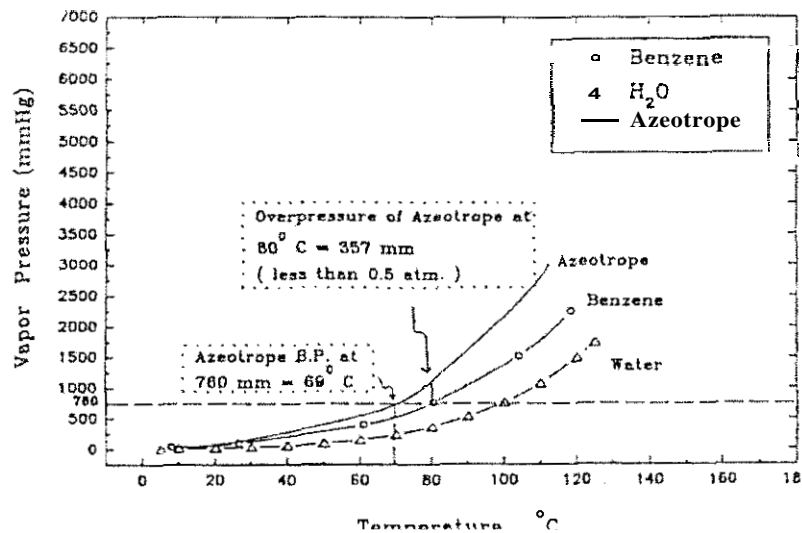


Figure 4. Azeotropic vapor pressure/temperature diagram for benzene/water [8]

The effect is even more pronounced for higher boiling hydrocarbon fuels, as seen in Figure 5 for the insoluble mixture of xylene and water. At 94.5 °C the vapor pressures of the xylene and water phases total **one** atmosphere – *some 45°C, or 80 °F cooler than for xylene alone!*

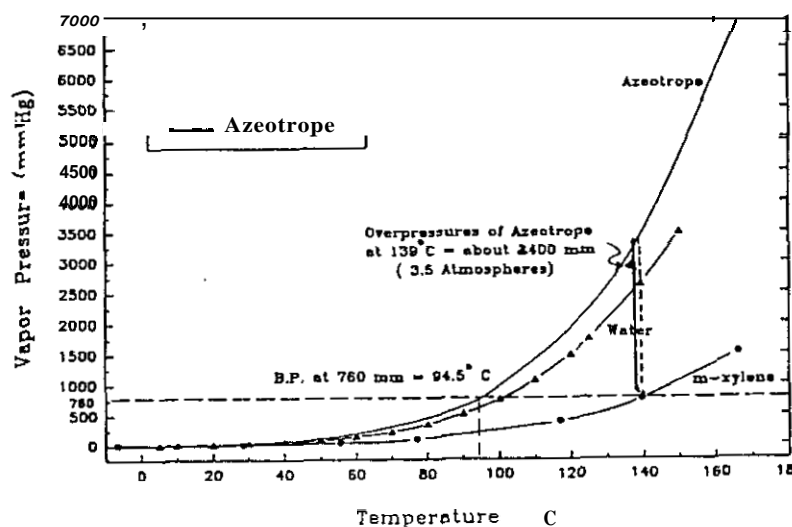


Figure 5. Azeotropic vapor pressure/temperature diagram for xylene/water [8].

Figures 4 and 5 introduce another term, azeotropic overpressure. In a liquid fuel fire, the fire plume above the surface is of course at a very high temperature; the surface of the boiling liquid is at its boiling point; and, although there will be a temperature gradient below the surface, a significant portion of the fuel beneath the flaming surface will be at or close to the boiling point of the fuel. If a water-based extinguishing agent (mist, fog, AFFF, solid stream, etc.) is then applied to this fire, the incoming water will be greatly heated as it passes through the flame and into the burning liquid.

In Figure 4, benzene is shown as an example of a high volatility fuel, corresponding to the volatility of the major components of JP-4. If this is heated to its boiling point (80 °C) and water is added at a rate such as to allow it to be heated to the same temperature, the vapor pressures of the water (157 mm) and of the benzene (760 mm) now total to 1117 mm. This is an overpressure of 357 mm (about 0.5 atmosphere) in vapor pressure, which has suddenly been installed in what had been a gently boiling liquid. The effect will be similar to that of benzene heated to 92 °C in a closed pressure cooker, which would now show a pressure of about 7 psig or 0.5 atmosphere on its dial. If the pressure cooker is suddenly opened, the contents will boil off more rapidly than would have been the case if there had been no pressure release. This same effect would be observed, then, upon addition of water to burning benzene (or JP-4 type fuel) without a pressure cooker; and somewhat of an increase in fire intensity may thus be observed.

Figure 5 illustrates a low volatility for xylene, with volatility representative of major components of JP-8 or Jet A-1 fuels. If this is heated to its boiling point (139 °C), and water is added at a rate to allow it to be heated to the same temperature, the vapor pressures of water (2640 mm) and of the xylene (760 mm) now total to 3400 mm – an overpressure of 2640 mm, *or about 3.5 atmospheres in vaporpressure!* The effect is thus similar to that of xylene heated to 200 °C in a closed pressure cooker, which would indicate a pressure of about 52 psig (3.5 atmospheres) on the dial. On sudden rupture of the pressure cooker, the contents would erupt in very violent boiling; the same effect will be thus observed upon addition of heated water to flaming JP-8 or Jet A-1 fuels, with a potentially extremely greatly pronounced increase in fire intensity. Thus, azeotropic effects may have serious implications in the flammability of hydrocarbon fuels in contact with water.

EXPERIMENTAL WORK

Experimental determinations were performed in an apparatus and with procedures as shown in Figure 6.

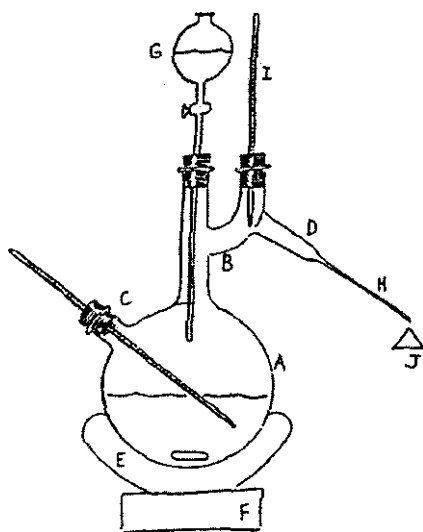


Figure 6. Ignition Flask

- A. 500-ml round bottom, with
- B. Two-necked Claisen head;
- C. Pot thermometer well; and
- D. Side arm extending from Claisen head.
- E. Electric heating mantle.
- F. Magnetic stirrer.
- G. Addition funnel for adding water.
- H. Capillary extension tube from side arm tube.
- I. Head, pot temperature thermometers.
- J. Igniter.

Not shown: Aluminum foil insulation around assembly; nitrogen tank for purging air from assembly; heating tape for side arm tube; emergency fire extinguishers.

PROCEDURES

1. Add 100ml fuel to flask, with magnetic stirring bar.
2. Purge air from assembly with nitrogen tank.
3. Set controls for heating mantle and heating tape to 20 °C above boiling point of fuel.
4. When fuel begins to distill from capillary extension, light distillate with igniter.
5. Add 1 ml water from addition funnel; observe flame growth (if any) at capillary extension.

RESULTS OF AZEOTROPIC EXPERIMENTS

For both benzene and xylene experiments, distillation rates were achieved (prior to adding water), which provided just enough fuel at the capillary extension tube to sustain a small flame upon application of the igniter.

1. For distilling benzene, addition of one or two small drops of water did not materially increase the magnitude of the flame, upon application of the igniter.
2. For distilling xylene, addition of one or two small drops of water resulted in a huge increase in flame size and magnitude of the flame, upon application of the igniter.
3. For distilling benzene or xylene when floating on a surface of water in the distillation flask, addition of drops of water resulted in no change at all in flame size and magnitude of the flame, upon application of the igniter.
4. In work performed by other, it has been noted that addition of water spray to fully developed wood and furniture (**Class A**) fires also resulted in a huge increase in flame size and magnitude of the fire.* This indicates that azeotroping effects may not be limited to liquid fuel system fires.

RAMIFICATIONS OF WATER AZEOTROPING EFFECTS FOR OPERATIONAL FIREFIGHTING CONSIDERATIONS FOR LOW VOLATILITY, HIGH BOILING POINT

JP-8 AND JET A-1 FUEL FIRES

No previous attention appears to have been directed to the possibility of increased flammability hazards arising from azeotroping effects from application of water systems to hydrocarbon fuel fires. Statements to the contrary have been encountered in responsible fire manuals:

“...water...entrained in fuel is not particularly significant from a fire hazard standpoint...”[9].

This **is** certainly valid for firefighting implications for pre-existing entrainments of water in fuels, for high volatility fuels such as AVGAS or JP-4, or for any type of fuel floating on water (except for “boilover” effects as previously discussed in this paper). **As** we have demonstrated, however, this is not valid for water being applied to large-scale fires involving low volatility JP-8, Jet **A-1**, JP-5, or similar high boiling point fuels. At least one instance in the firefighting literature may now possibly be reinterpreted in the light of a possible water/fuel azeotroping effect.

On **26 May 1981**, an EA-6B crashed into several F-14s while landing on the US Navy carrier *NIMITZ* (CVAN 68). In the ensuing fire, 14 men were killed and 42 injured, with \$60 M damages to the carrier and its planes. Firefighting efforts commenced immediately, using water hoses and AFFF washdown systems (although AFFF itself was not deployed until well into the firefighting effort). It was noted that immediately after initiation of the firefighting effort, a very great increase in fire intensity ensued, at least momentarily. In a subsequent investigation it was suggested that possibly there had been contamination of nonvolatile JP-5 fuel in the Navy aircraft by volatile JP-4 fuel as a result of refueling from a USAF tanker, resulting in a reduction in flash point by the possible admixture with the more volatile JP-4 [10].

* Videotaped research results, Forest Products Laboratory US Dept. of Agriculture (Madison, WI), (ca. 1992).

It could also be speculated, however, that an increased volatility of fuel resulted from the introduction of water into the hot environment in the blazing running fuel fire.

In work previously conducted at the fire research facilities at the New Mexico Engineering Research Institute (Albuquerque, NM), and at the Air Force Fire Research Labs (Tyndall AFB, FL), there were several occasions in which an increased fire intensity resulted upon initial introduction of AFFF into running fuel fires. There have also been anecdotal comments about this same type of observation in the Stapleton Airport fire (Denver, CO).

RAMIFICATIONS OF WATER AZEOTROPING EFFECTS FOR FIRE PIT FIREFIGHTING TRAINING EXERCISES, AND FOR FIRE PIT FIRE RESEARCH ACTIVITIES

For many typical firefighting training exercises, and for many fire research activities, natural gas fired simulators are utilized, in which the amount of gas can be varied to produce varying fire intensities. This type of fire scenario is totally incapable of reproducing the azeotroping effects that can accompany water extinguishment.

In other situations, a large fire pit is partially filled with water to provide a flat surface on which the liquid fuel can be layered to a depth of an inch or so over the water. Many of these facilities are being phased out due to environmental smoke problems, but there are still many in existence. The flat water surface minimizes fuel volume requirements, and also serves to cool the fire pit and thus minimize maintenance and pit replacement costs. Although this type of training and research facility does indeed provide much more real life fire characteristics than does the natural gas simulator, it also will not provide any kind of capability for reproducing the azeotroping effects that can accompany water extinguishment, for reasons described below.

Thus, our work has shown that for high volatility fuels such as aviation gasoline and JP-4, there is little or no effect on fuel volatility on fuel volatility when water is added, whether or not either the fuel or water is preheated. When water is added to hot non-volatile fuels (JP-8, Jet A-I, JP-5 etc.), there ~~is~~ is a serious increase in volatilization rate and a corresponding increase in fire intensity for the burning fuel.

It is therefore not surprising that azeotroping effects have not heretofore been observed in training or research fire pit assemblies, since for fuels floating on water there is a very sharp temperature gradient in the very thin layer of burning fuel floating on the fire pit pool of water (Figure 7). Above the burning surface the flame temperatures are quite high (around 650 °C), which will considerably heat water being introduced into the flame area. At the burning surface, the fuel is at its boiling point (in the case of JP-8, about 225 °C). An inch or less below this, however, the fuel temperature has dropped to ambient water temperatures, perhaps ca. 25 °C. Therefore, almost all of the fuel will be at a temperature far below the azeotropic boiling point of ca. 94 °C.

Thus, even for the most nonvolatile hydrocarbon fuels such as JP-5, when floating on water, no increase in the rate of volatilization of the fuel will be observed when water-based extinguishing agents are applied to the fire.

Thus, no significant increase in rate of volatilization will be observed for fuel floating on water surfaces.

SUMMARY

1. Application of water onto burning fuels, which are insoluble in water, will result in an increased rate of volatilization of the fuel, and, at least momentarily, an increased fire intensity.
2. The effect is particularly pronounced for less volatile "fire-safe" fuels, such as JP-8, Jet A-I, and JP-5.

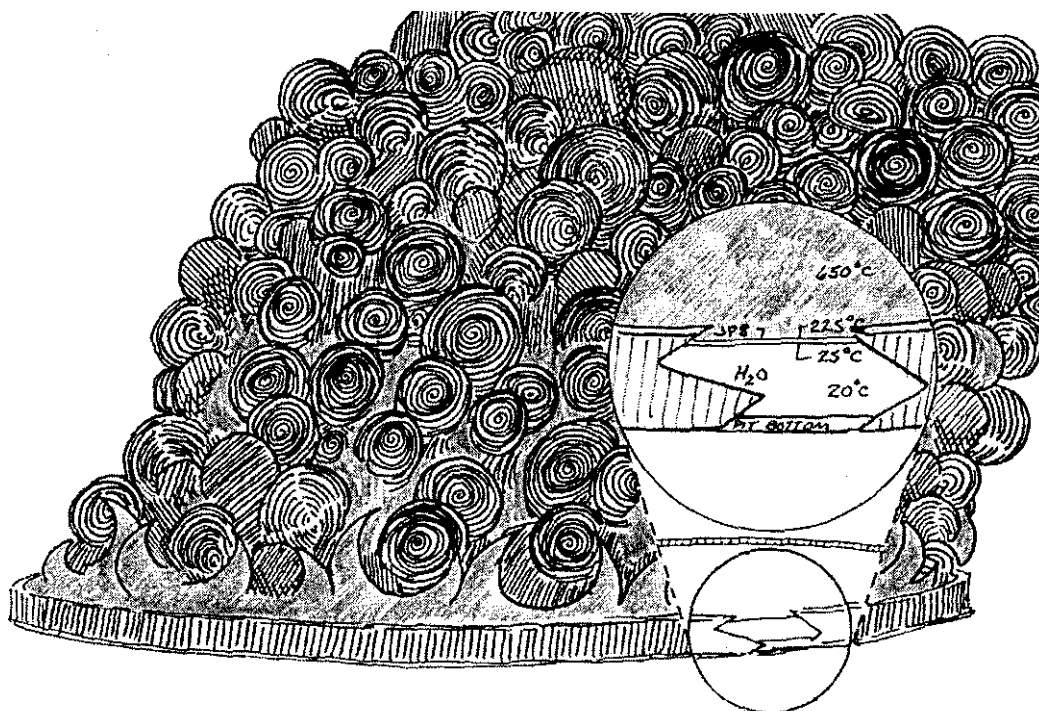


Figure 7. Non-azeotropes for typical fire pit assemblies: average fuel temperature: ca. 35 °C; azeotrope distills at 94 °C.

3. Water suspended in or vicinal to the fuel before the fire will not materially affect the flash point or flammability of the fuel.
4. This phenomenon should be examined in more detail as water misting becomes more attractive in fire extinguishing systems.
5. A need may exist for fire training and fire research pits that do not require pools of water for flotation of the burning fuel.

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