STUDY ON COMBUSTION PROPERTY OF CRUDE OIL  
- A JOINT STUDY BETWEEN NIST/CFR AND FRI- 

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ABSTRACT 

In order to understand the combustion properties of crude oil pool fires, an experimental study was done in Fire Research Institute (FRI) large scale test facility. The radiative output, burning rate, and the concentrations of CO, CO₂, and smoke (above the flame tip) were measured during the burning of Arabian light crude oil. Several different size tanks were used to study the scale effect. Crude oil burned less rapidly and gave off less thermal radiation compared with heptane, but when water boiling occurred the burning rate and thermal radiation increased by a factor of two or more. Water boiling is a kind of boilover phenomenon and which intensity is most related with tank size and fuel layer thickness. 

INTRODUCTION 

Because of the wide abundance of crude oil in various storage facilities, it is important to study crude oil burning concerning fire safety. The smoke emission from the burning of crude oil has become a subject of concern in regard to the proposed burning of certain crude oil spills. While it is recognized that the burning of crude oil is a serious safety issue, regarding huge smoke emission and boilover phenomenon, there has been relatively little research on this topic. Therefore a joint study between Center for Fire Research (CFR) of National Institute of Standards and Technology (NIST) and Fire Research Institute (FRI) was performed in the FRI large scale test facility. This paper introduces this US-Japan joint study briefly.

EXPERIMENTAL 

In Figure 1, a schematic of the experimental setup is shown. Tanks were placed at the center of the test facility which is 24m × 24m and 20m high. Wind effects were small compared to outdoor tests, but still there were effects from the outside wind for some of the tests. We burned Arabian light crude oil in 0.6m, 1m and 2m diameter circular pans and in 2.7m square pan. We measured burning rate, external radiation, smoke
emission, concentrations of CO and CO$_2$ above the flame tip. Near the end of the combustion process, water boiling and splashing was observed. We call this phenomenon "thin layer boilover" to distinguish the boiling effects in our test from the hot zone boilover discussed by Hasegawa$^{11}$. Burning rate was measured with a float-type level meter connected with the piping of the tank. So the burning rate was represented as fuel level regression rate. When thin layer boilover occurred, splashing water to outside of tank gave errors in the calculation of burning rate, but we obtained net value by canceling this effect from the water level difference during the experiment.

Radiation from the entire flame to surroundings was measured by three thermopile-type radiometers which cover a wide angle. They were oriented toward the flame axis and located at L/D=3 and L/D=5 where D is the tank diameter and L is the radial distance from the tank center to the radiometer. Smoke, CO and CO$_2$ were collected above the flame tip. The gas flowed through a cold trap and flow meter before entering the CO, CO$_2$ analyzer.

The temperatures inside and near the flame and in the fuel and water were measured using 0.3 mm diameter Chromel-Alumel thermocouples sheathed with a 1.6 mm diameter stainless steel tube. Two thermocouples were embedded in the fuel and one was in the water. Each thermocouple bead was placed along the centerline of the pan. The outputs of these sensors were corrected of error by radiation, and recorded on a pen-type recorder and/or digital data acquisition system.

RESULTS AND DISCUSSION

Burning rate
Figure 2(a) shows the time history of a 0.6m tank fire. About one minute after ignition, the burning rate is in quasi-steady state. In the later period it increased to about four times as much as that of steady state condition due to thin layer boilover.

Figure 3 shows the relationship between burning rate and tank diameter, D. With a square tank, D was calculated with the equation: $D=\left(\frac{4}{\pi}\right)^{1/2} \cdot W$. Here W is the length of one side. For reference, Mulholland et al.'s small scall tests data$^5$ and others large scale tests data$^6$-$^8$ are shown. These data were obtained by several different investigators, but gave almost one
Figure 2 An example of time history
(0.6 m crude oil fire)
Figure 3 Relationship between burning rate and tank diameter

Figure 4 Relationship between radiative output and tank diameter

Figure 5 Relationship between smoke yield and tank diameter
In these size tanks, the burning rate increased with increasing tank size up to maximum at about 10-20 m in diameter.

Radiative outputs
Figure 2(b) shows the time history of radiative outputs at L/D=3 and 5 in the same test of Figure 2(a). When thin layer boilover occurred, radiative outputs also increased, but not as much as the burning rate.

Figure 4 shows the relationship between radiative output at L/D=5 and the tank diameter. For reference, some others data are shown including heptane data. While the burning rate is constant for tank diameter greater than 2m, it appears that the radiation decreases for tank diameter greater than 2m. This indicates smoke blockage effect on external radiation is large but smoke blockage on internal radiation is small in crude oil and heptane flame. Radiation from heptane fire is larger than that of crude oil in any size tanks, and does not decrease as rapidly as does the radiation from the crude oil fires at large scale.

Radiative fraction
Radiative fraction, X, is represented as:

\[ X = \frac{Q_{rad}}{Q_{tot}} \]

Here, \( Q_{rad} \) is the total radiative power output. Assuming isotropy it is simply the flux times the spherical surface area:

\[ Q_{rad} = 4\pi L^2 q \]

where \( q \) is the irradiance measured by the radiometer at L/D=5. \( Q_{tot} \) is the net calorific potential of the flame assuming complete combustion.

In steady state burning, \( X \) is about 0.3-0.4, but when thin layer boiling occurred it went down to about 0.2. This change is large compared to measurement errors associated with the splashing of the water. The reason for the decrease in the radiative fraction is a slight reduction in the temperature caused by the water vapor, which has a high specific heat.

Smoke emission
Smoke was collected above the flame tip. At this height the averaged temperature was about 100°C. A useful measure of smoke emission used by Mulhollanand et al. is smoke yield, \( \varepsilon \), which is defined as the mass of smoke aerosol generated per mass of fuel consumed. We calculated the smoke yield, \( \varepsilon \), by the carbon balance method:

\[ \varepsilon = Y_s \cdot F_c \]

Here \( Y_s \) is the carbon mass in the smoke aerosol, as a fraction of the carbon mass in the total combustion products (CO\(_2\), CO and smoke aerosols) and \( F_c \) is the mass fraction of carbon in the fuel, measured as 0.838 by elemental analysis. Figure 5 shows the relationship between smoke yield, \( \varepsilon \), and tank diameter. Mulholland et al's data shows \( \varepsilon \) of the large scale fire are similar to the small scale one, but the results indicates that the larger the tank is, the larger smoke yield is. Future testing is needed to verify this difference. We also have found the difference with Bard et al data. They proposed the volume fraction method in the flame, which is larger than our current and previous data. Their data is larger than us, because
they ignored some soot oxidation occurs in the upper portion of the flame. Still intermittent region of the flame, oxidation reaction has continued. We also collected smoke for observation with a transmission electron microscope (TEM). TEM photographs gave similar value in size distribution to Evans et al. 21.

Concentration of CO and CO₂ above the flame tip
The CO and CO₂ were collected along with the smoke just above the flame tip. The concentration of CO₂ was about 0.3%-0.5%, and that of CO was about 50-500 ppm. Figure 2(c) shows the time history of the ratio of CO and CO₂ concentrations. When thin layer boilover occurred, this ratio possibly due to the flame quenching on the probe. The ratio of CO/CO₂ is a measure of combustion efficiency.

Figure 6 shows the relationship between the ratio of CO/CO₂ and tank diameter. Data is limited but it indicates that the ratio increased with tank diameter. So the combustion efficiency decreased with increasing tank size as shown by an increase in smoke and CO. In 1m diameter crude oil tank fire, it was about 90%, and it decreased to 75% in 2.7 square tank fire.

Temperature in the liquid
Figure 2(d) shows time history of temperature in the fuel and water. In 0.6m tank fire, initial free board was 1 cm, and the fuel level decreased after ignition. The upper thermocouple was just above the fuel surface, and it recorded the initially, rapidly increasing gas temperature just above the fuel. When the thin layer boilover occurred, the temperature at this point fluctuated by a sizable amount as the boiling water/oil contacted the thermocouple.

Thin layer boilover phenomenon
Water boilover was found to occur near the end of the combustion process, and a considerable amount of oil spilled over the rim of the test tank. The burning rate and radiative output increased when the boiling occurred. The magnitude of the boiling effects, ψ, was defined as:

\[ \psi = \frac{V_{bo}}{V_{s1}} \]

\( V_{s1} \) means the burning rate in steady state condition, and \( V_{bo} \) means the maximum burning rate in boiling occurred.

Figure 7 shows the relationship between ψ and tank diameter. According to Evans et al. 21, fuel thickness is an important factor in regard to the boiling effect, so here in every test we set it at 2 cm in first series. The boiling effect, ψ, decreased with increasing tank size. We did not observe a significant boiling effect in the largest test. According to Arai et al. 31, boiling occurs for fuels with boiling point temperature higher than that of water. To test their results, we burned kerosene (bp: about 150-300°C), toluene (bp: 111°C) in the same condition with crude oil (tank diameter: 1m, fuel thickness: 2cm). Figure 8 shows the time history of burning rate in kerosene and toluene 1m diameter tank fires. We did not observe boiling phenomenon for these fuels. This indicates that the cause of the boiling effect is not simply controlled by the boiling temperature of the fuel. Not only boiling point of fuel, we believe that a second condition necessary for boilover is that the steady state burning rate, \( V_{s1} \), should be less than the hot zone regression rate, \( V_{hz} \) sufficiently because of lip effect. We varied the fuel thickness in the various size tank fire to determine the influence of fuel layer thickness on the intensity of thin layer boilover. Figure 9 shows the relationship between ψ and fuel thickness. The thicker fuel
Figure 6 Relationship between CO/CO₂ and tank diameter

Figure 7 Relationship between \( V_{st}/V_{bo} \) and tank diameter

Figure 8 Time history of burning rate

(a) kerosene  
(b) toluene
Figure 9 Relationship between $V_{bo}/V_{st}$ and fuel thickness

Figure 10 Relationship between time to occur thin layer boilover and fuel thickness
layer is, the more violent thin layer boilover is. Figure 10 shows the relationship between boilover time and initial fuel thickness. The thicker the fuel layer is, the longer the time for the hot zone to reach the water layer, and at the same time, the thicker the hot zone has grown. The hot zone model for "real boilover" developed by Hasegawa\textsuperscript{11} maybe helpful in modeling this process, and Saito\textsuperscript{11} simple model can not be applied in this phenomenon. Following Hasegawa, we obtained $v_{h2} = 31(\text{mm/min})$ in the range of our experiment. Therefore, when burning rate is much larger than 3.1mm/min, boilover should not be occurred.

CONCLUSIONS

1. In steady state condition, burning rate and radiation in crude oil fire are less for crude oil than for heptane. The burning rate increases with tank size up to about 3m at which point the burning rate is independent of tank size. The thermal radiation at a position of five pool diameters from the center of the pool increases for increasing tank size up to 2m and then decreases for larger tanks due to smoke blockage effect.

2. In the end of combustion process, water boiling occurred for crude oil. Burning rate and radiative output increased, but in larger tanks, a boiling effect was not observed. In thick crude oil layer tank fire, we found intensity of thin layer boilover is stronger and changes to "real boilover".

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REFERENCES

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