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Comparison of Combustion Characteristics of Crude oils using Cone Calorimeter

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ABSTRACT

Small-scale free-burning pool fire experiments were conducted in a Cone Calorimeter to obtain the combustion characteristics of 14 different crude oils. Measurements included heat release rate based on oxygen consumption calorimetry, mass loss rate, radiative heat flux from the flame to a nearby target, liquid fuel temperature and CO2 and CO concentrations in the exhaust duct. The effective heat of combustion, radiative heat loss fraction, and smoke yield were calculated on the basis of the measured data. It was found that heat release rate, flame radiation, and smoke yield had relation to the type of crude oil. The effective heat of combustion, radiative heat loss fraction, and extinction coefficient were nearly constant for the range of crude oils evaluated in this program. Heat release rate, mass loss rate, flame radiation, and smoke yield appeared to correlate well with crude oil density.

INTRODUCTION

Fire hazard assessment of crude oil storage facilities is generally based on generic characteristics of the fuel. However, the physical and chemical properties of crude oils, such as density and specific heat, are known to depend on the region of origin and the production lot [1], and crude oil combustion characteristics may therefore vary accordingly. If these variations are significant, fire protection measures based on generic properties may, in some cases, be inadequate. There is little information in the literature concerning combustion characteristics of crude oils. Due to the difficulty of obtaining consistent crude oil samples, only a few systematic studies have been conducted [2,3]. The combustion of crude oil is very complex because it is a mixture of many hydrocarbons, and its composition changes constantly as combustion progresses. It would be very convenient if the combustion characteristics of a crude oil could be predicted on the basis of a simple physical property of the fuel. The development of such correlations is one of the objectives of this paper.

The purpose of the research presented in this paper is to get a feel for the magnitude of the variations in burning behavior of crude oils on the basis of small-scale data. If the variations are significant, additional intermediate or large-scale experiments will be needed to enable the development of improved methods for fire protection of crude oil storage facilities and suppression of crude oil tank fires.

Cone calorimeter data were obtained for 14 crude oils and kerosene, and are presented in the following sections. Combustion characteristics were calculated on the basis of the small-scale data. Correlations were developed to predict the combustion characteristics as a function of density. Crude oil density was chosen as the independent variable since it is easily determined, and because it is directly related to the composition of the fuel.

EXPERIMENTAL

Materials

Samples of 14 different crude oils were examined. In addition, kerosene was used as a benchmark. The names of the crude oils evaluated in the experiments, and their density are given in Table 1. The crude oils used in the experiment were sampled from several storage facilities maintained by the Japan National Oil Corporation for emergency use. They belonged to light or medium density crude oils. High-density crude oils are available in Japan, but they were not examined in this study. Water was removed from the samples to prevent boilover during the experiments.

Cone Calorimeter

The experiments were conducted in the Cone Calorimeter at Southwest Research Institute (SwRI) in San Antonio, Texas. This Cone Calorimeter was constructed in accordance with the specifications in ASTM E 1354-97, "Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products using an Oxygen Consumption Calorimeter". However, some modifications were made to the standard protocol, so that small circular pans filled with liquid fuel could be evaluated. A schematic of the apparatus is shown in Figure 1. The fuel pans were 90 mm in diameter, and 18 mm in depth. The initial freeboard (the distance between liquid surface and the top of pan) was approximately 1 mm. Fuel was not replenished during the experiment. All experiments were conducted without external heat flux from the cone heater. The heat release rate (HRR, in kW/m^2) was determined on the basis of oxygen consumption calorimetry [4]. The mass loss rate (MLR, in g/s) was measured with a load cell. CO_2 and CO concentrations (in volume %) in the exhaust duct were obtained with Non Dispersive InfraRed (NDIR) analyzers. The extinction coefficient (k, in 1/m) was determined on the basis of the absorption by the smoke of a 0.5 mW HeNe laser beam. A personal computer and data acquisition system was used to obtain the signals of all transducers and instruments at a sampling rate of two seconds.

Additional instrumentation was provided to measure the radiative heat flux from the flame, and the temperature of the liquid fuel. Flame radiation was measured by a thermopile type radiometer. The radiometer was positioned so that it faced the experiment sample at a distance of 0.36 m from the center of the pan, at a height slightly above the top surface of the pan. Liquid temperatures were measured using a 0.3 mm diameter type K sheathed thermocouple positioned in the center of the pan. The tip of the thermocouple was submerged in the liquid at the start of the experiment, and located at 5 mm from the bottom of the pan.

After 30 seconds of baseline data were collected, a butane lighter flame was applied to the liquid surface until the fuel ignited. All crude oils ignited almost immediately after application of the flame, but it took several minutes of preheating to ignite the kerosene samples. All crude oil experiments were conducted in duplicate. The first experiment was terminated at 30 min, and the second experiment was terminated at 20 min. The kerosene was also experimented in duplicate, and both experiments were terminated at flameout.

RESULTS AND DISCUSSION

Experimental Results

Iranian Light crude oil is widely used in Japan. Iranian Light crude oil data are shown in Figure 2, as a typical example of the experimental results that were obtained. The shape of the curves is similar for the other crude oils that were experimented, but there are some significant quantitative differences. The results of the duplicate experiments were nearly identical for almost all the samples. The repeatability of experiments was very good.

Data Analysis

The burning rate of a liquid pool fire is controlled by the radiation heat transfer from the diffusion flame to the liquid fuel surface. The combustion regime corresponding to a 90 mm diameter fuel pan is not fully turbulent. Therefore, the conclusions drawn from this work may not be valid for large scale pool fires. However, it is expected that the results can at least be used to compare and rank the various crude oils.

Given a certain incident heat flux at the surface, the mass loss rate (and therefore heat release rate) of a liquid fuel is controlled by the ratio of the heat of combustion to the latent heat of vaporization [6]. In the present program, this characteristic ratio could not be determined, because the heat of vaporization could not be available. As an alternative, an attempt was made at correlating some of the measured burning characteristics against a physical or chemical property of the crude oil. The density was chosen as the independent variable since it is easily determined, and because it is directly related to the composition of the fuel. The resulting correlations are shown in Figure 3, and provide a reasonably accurate method to predict crude oil burning characteristics.

Heat Release Rate

The heat release rate (HRR) rapidly reaches a maximum value at approximately 50 seconds after ignition. Subsequently, the HRR decreases gradually and reaches a steady value. The HRR of some crude oils has the tendency to gradually rise again at approximately 1500 seconds after ignition. This is attributed to the boiling of a small amount of water trapped at the bottom of the fuel pan.

The average HRR values (HRR_{avg}) were calculated over a 1170 second period starting at ignition (30 seconds). HRR_{avg} of Kafji is the lowest of all the crude oils experimented. HRR_{avg} of Marib Light is the highest, and approximately 1.5 times the value for Kafji. The HRR of all crude oils varies within this range. A correlation was established between HRR and density, which shows that higher HRR correspond to lower densities. The maximum HRR values (HRR_{max}) show the same trend as the HRR_{avg} values. The ratio of HRR_{max} to HRR_{avg} is approximately 1.5.

It is interesting to compare the effective heat of combustion ($\Delta H_{c,eff}$) of different crude oils. $\Delta H_{c,eff}$ was calculated as the ratio of the total heat released during the first 20 min of a experiment to the total mass loss over the same period. $\Delta H_{c,eff}$ is nearly constant for the crude oils that were experimented, and appears to be independent of density. The combustion efficiency is defined as the ratio of $\Delta H_{c,eff}$ to the net heat of combustion. The net heat of combustion of Umm Shaif, Murban and Kafji was known, and the resulting combustion efficiencies are 0.82, 0.80 and 0.83 respectively.

Mass Loss Rate

The average mass loss rate over a given period is equal to the ratio of mass loss over the period to the length of the period. The average mass loss rate in 60 seconds interval from ignition was calculated (see Figure 2). The mass loss rate rapidly reaches a maximum value. Subsequently, the mass loss rate decreases gradually and reaches a steady value. This can be explained by the fact that initially, due to the short freeboard height, almost the entire amount of heat transferred from the flame to the fuel pan contributes toward evaporation of fuel, while in the later stages part of the heat is lost to the edges of the pan. In addition, the lighter components of the fuel burn at a faster rate, and are consumed in the initial stages of the experiment. • The average mass loss rate (MLR) over the period between ignition and 1170 seconds was correlated against density. The correlations are similar to those between HRR_{avg} and density, although the density effect on the MLR appears to be slightly more pronounced (see Figure 3).

Flame Radiation

The heat flux from the flame to the radiometer quickly reaches a maximum value at approximately 60 seconds after ignition. Shortly thereafter, the heat flux drops to a lower steady value. The relative difference between the maximum and steady values is not as pronounced as for the HRR. The heat flux of some crude oils gradually increases toward the end of the experiment, concurrently with a rise of the HRR.

Average heat flux values were calculated over a 1170 second period starting at ignition (30 seconds). The average heat flux of Kafji is the lowest of all the crude oils experimented. The average heat flux of Marib Light is the highest, and approximately 1.3 times the value for Kafji. The heat flux of all crude oils varies within this range. The maximum heat fluxes show the same trend as the average fluxes. The ratio of maximum to average heat fluxes is approximately 1.3. Flame radiation is related to the heat of combustion and the mass loss rate and the radiative heat loss fraction [7]. The heat of combustion had relation to heat release rate. Consistent with the HRR_{avg} correlations, the average heat flux decreases with increasing density. Since heat release

rate was a function of crude oil density, it was no surprise to find a good correlation between heat flux and density.
It is instructive to examine whether and how the radiative heat loss fraction varies for the different crude oils that were experimented. In this paper, the radiative heat loss fraction is defined as the ratio of heat that is transferred from the flame to its surroundings in the form of radiation to the total heat released. A point source flame model was used to calculate the radiative heat loss fraction from the measured heat release rate and heat flux data:

$$\chi_r = \frac{4 f\hat{I} L^2 \dot{q}_f''}{HRR \times A_s} \qquad (1)$$

where

χ_r = radiative heat loss fraction (-)
L = distance from the center of the pan to the radiometer (m)
q_f = heat flux from the flame measured with the radiometer (kW/m^2)
A_s = exposed sample area (0.0064 m^2)

The radiative heat loss fraction is a useful variable when comparing the combustion characteristics of different fuels. χ_r was found to be nearly independent of density. This follows from Equation (1), because both q_f and HRR vary with density in a similar fashion.
Averaged χ_r ranges from 0.60 to 0.67 for the crude oils that were experimented. The actual heat release rate was used in the denominator of Equation (1). These values are higher than those defined by the theoretical amount of energy released for the whole because the actual heat release rate was lower than the theoretical heat release rate. Based on a combustion efficiency of 0.82, the radiative heat loss fraction values based on the common definition ranged from 0.49 to 0.55. Reference [8] gives a value for crude oil of χ_r = 0.57, on the basis of heat release rate measured by the oxygen depletion measuring equipment. A value for crude oil of χ_r is regarded as 0.47 on the common definition in [8]. This could be explained by the fact the more smoke was made and covered radiation from the fire, since the value in [8] was based on measurements for 0.4 and 0.6 m diameter pans.

Smoke Obscuration
The smoke yield (Y_s) was used to quantify smoke emissions in the crude oil experiments. Y_s is equal to the ratio of the mass of soot particulates generated to the mass loss of the fuel. It can be calculated as follows:

$$Y_s = \frac{\int_{t_1}^{t_2} \frac{k\dot{V}_s}{k_m} dt}{m(t_1) - m(t_2)} \approx \frac{\sum_{t_1}^{t_2} \frac{k\dot{V}_s}{k_m} \Delta t}{m(t_1) - m(t_2)} \qquad (2)$$

where Y_s is the smoke yield (in kg/kg), k is the extinction coefficient (in 1/m), V_s is the volumetric duct flow rate at the smoke meter (in m^3/s), k_m is the ratio of the extinction coefficient to the mass concentration of soot (7600 m^2/kg based on [3]), m(t_1) is the sample mass at time t_1 (kg), m(t_2) is the sample mass at time t_2 (kg), Δt is the scan interval (s). The extinction coefficient is calculated from:

$$k = \frac{1}{l} \ln\left(\frac{I_0}{I}\right) \qquad (3)$$

where l is the diameter of the duct (in m), I_0 is the light intensity of the laser light source, and I is the intensity of the beam that is transmitted through the smoke stream in the exhaust duct. The extinction coefficient is proportional to the concentration of soot particulates in the exhaust flow. To obtain the mass concentration of soot, k is divided by k_m.
A correlation was established between Y_s and crude oil density. The smoke yield increases with

density. This is due to the fact that the MLR decreases with increasing density, while k is nearly independent of density.

It was assumed that the amount of residual carbon after distillation of a crude oil affects the smoke yield. A correlation was established between residual carbon and smoke yield. It was found that higher density crude oils include more residual carbon and also have higher smoke yields.

Burning Characteristics of Kerosene

Kerosene was burned as a reference material. It took approximately four minutes to ignite kerosene with a small butane flame. Kerosene has a higher HRR_{avg} (632 kW/m^2), MRL (0.11 g/s), q_f (1.30 kW/m^2), and k (2.58 1/m) than any of the crude oils. However, the smoke yield (0.064) is lower. This can be explained• by the fact that the MRL is approximately two times higher than for the crude oils, while the difference in k values is much smaller.

CONCLUSIONS

Small-scale free-burning pool fire experiments were conducted to obtain the combustion characteristics of various crude oils. The main results are as follows.

(1) The effective heat of combustion, radiative heat loss fraction, and extinction efficient is almost constant for the range of crude oils experimented.

(2) Heat release rate, mass loss rate, flame radiation, and smoke yield appear to correlate well with crude oil density.

Additional intermediate or large scale tests are needed to extend the validity of these correlations to real size fires, so that they can be used to develop improved methods for fire protection of crude oil storage facilities and suppression of crude oil tank fires.

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