

Comparison of Combustion Characteristics of Various Crude Oils

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ABSTRACT

Small-scale free-burning 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, extinction coefficient, 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 was nearly constant for the range of crude oils evaluated in this program. Heat release rate, mass loss rate, flame radiation, radiative heat loss fraction, and smoke yield appeared to correlate well with crude oil density. Tendency of boilover was also discussed with mass loss rate and fuel temperature.

KEYWORDS: crude oil, cone calorimeter, burning rate, radiation, smoke yield, boilover

1. INTRODUCTION

Fire hazard assessment of crude oil storage facilities is generally based on generic characteristics of the fuel. However, 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 complicate because it is a mixture of lots of 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 information 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 including boilover 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. Boilover may be dependent with burning scale and fuel characteristics.

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.

2. EXPERIMENTAL

2.1 Materials

Samples of 14 different crude oils were examined, and kerosene was used as a reference material. The names of the crude oils evaluated in the experiments, and their density are shown 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. Mostly they are belonged to light or medium density crude oils. High-density crude oils are also available in Japan, but they were not examined in this study. Water was removed from the samples to prevent boilover during the experiments, but still small amount of water existed in the samples.

Table 1 List of the samples

	Fuel	Origin	Density (kg/m ³)
1	Iranian Light	Iran	856
2	Umm Shaif	UAE	840
3	Marib Light	Yemen	804
4	Suez Blend	Egypt	874
5	Zakum	UAE	829
6	Upper Zakum	UAE	852
7	Murban	UAE	827
8	Kafji	Neutral Zone	884
9	Hout	Neutral Zone	854
10	Arabian Light	Saudi Arabia	852
11	Arabian Light*	**	852
12	Dubai	UAE	872
13	Attaka	Indonesia	812
14	Sarukawa	Japan	869
15	Kerosene	US	790

* Fuel used in 20 m tank fire experiment [5]

** Zakum 40.3 %, Rostam 26.8 %, Kuwait 27.5 %, Arabian Heavy 2.3 %, Arabian Extra Light 1.5 %, Umm Shaif 0.9 %, Murban 0.4 %, Kafji 0.3 %

2.2 Cone Calorimeter

The experiments were conducted in a cone calorimeter at Southwest Research Institute (SwRI) in San Antonio, Texas, USA. 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 burning pan was 90 mm in diameter, and 18 mm in depth. The initial freeboard (the distance between the 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/m²) was determined on the basis of oxygen consumption calorimetry [4]. The mass loss rate (MLR, in g/s) was measured with a load cell. CO₂ and CO concentrations (in volume %) in the exhaust duct were obtained with Non Dispersive Infra-Red (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 He-Ne 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. 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 temperature was 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 twice. The first experiment was terminated at 30 min, and the second one was terminated at 20 min. Kerosene was also experimented twice, and both experiments were terminated at flameout.

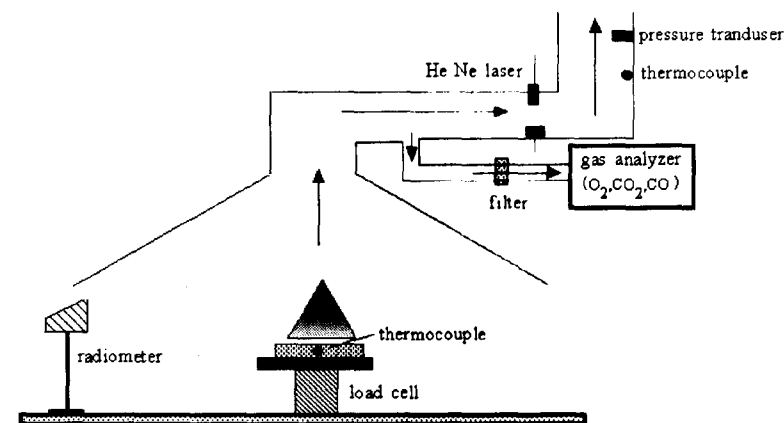


Figure 1. Experiment apparatus

3. RESULTS AND DISCUSSION

3.1 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 samples. The repeatability of experiments was very good.

3.2 Data Analysis

The burning rate of a liquid pool fire in 90 mm diameter pan is controlled by the radiation and the convective 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 in literature.

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 fuel density was chosen as an 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.

(1) 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 rise gradually again at approximately 1500 seconds after ignition. This may be 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 the ignition (30 seconds). HRR_{avg} of Kafji crude oil is the lowest of all crude oils experimented. HRR_{avg} of Marib Light is the highest, and approximately 1.5 times as much as the value of Kafji. The HRR of all crude oils varies within this range. A correlation was established between HRR and fuel 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.

To compare the effective heat of combustion ($\Delta H_{c,eff}$) of different crude oils was made. $\Delta H_{c,eff}$ was calculated as the ratio of the total heat released during the first 20 min of an 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.

(2) Mass Loss Rate (Fuel Burning Rate)

The average mass loss rate over a given period is equal to the ratio of mass loss over

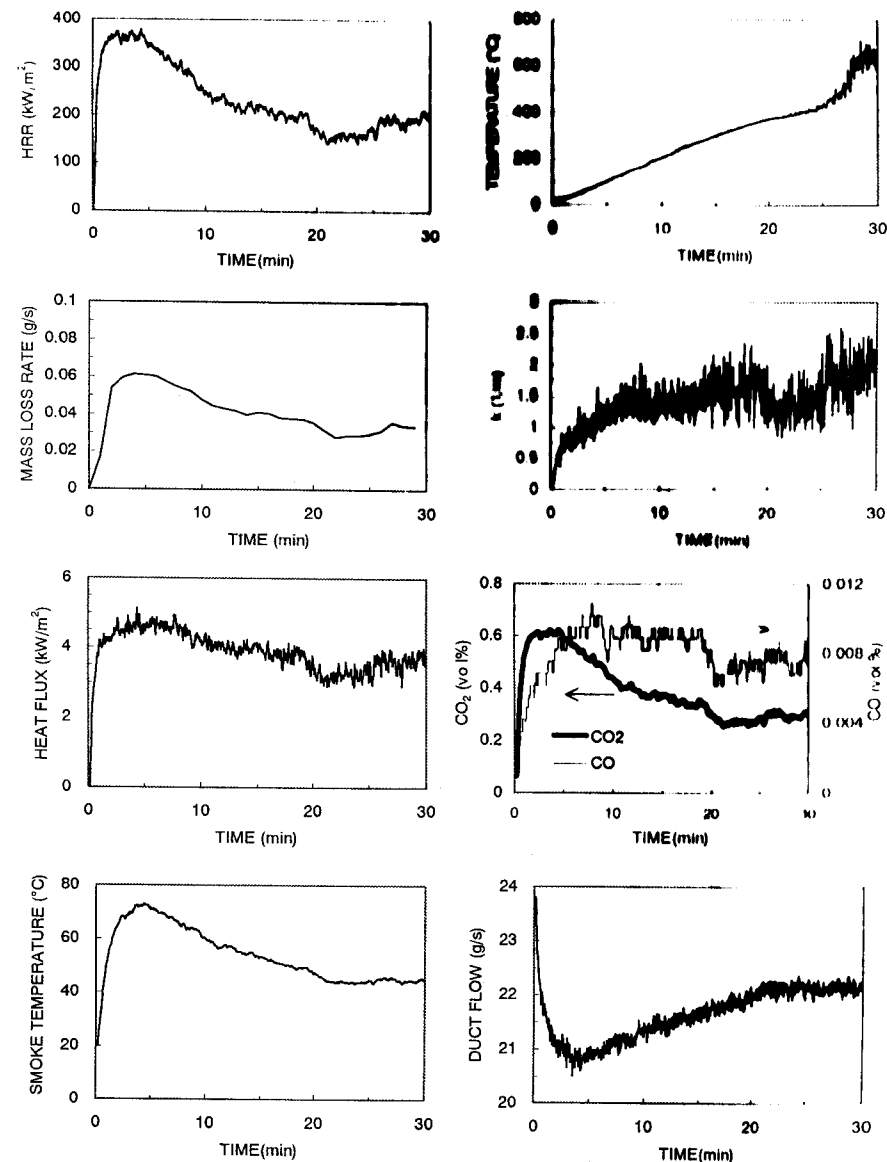


Figure 2. Typical results of Iranian Light crude oil

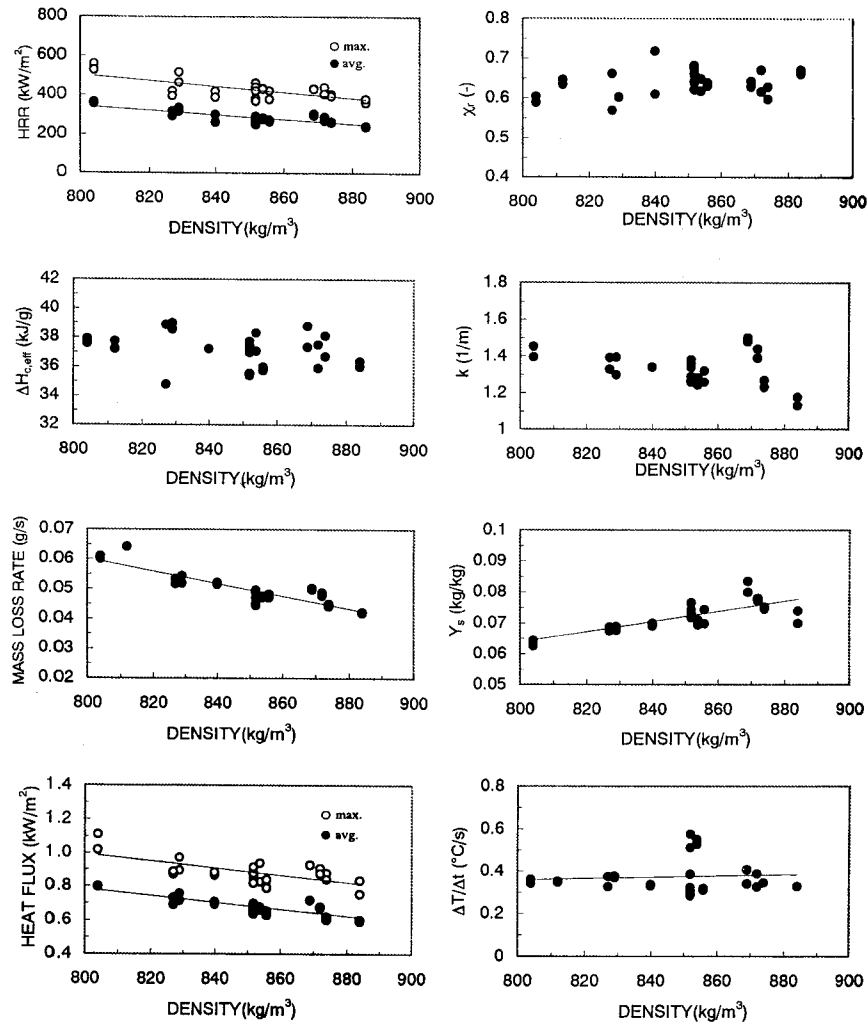


Figure 3. Relationship density and each characteristic of crude oil

the period to the length of the period. The average mass loss rate in 60 seconds interval from ignition was calculated. 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 mass loss rate was regarded as almost constant during the experiment on the basis of the straight line in the mass loss vs. time graph. Crude oils burn almost constantly during the experiment although crude oils have the multi-component system. 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 (Figure 3).

(3) Flame Radiation

The heat flux from the flame to the radiometer quickly reaches a maximum value at approximately 50 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 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.

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 increases with density. Since heat release rate was a function of crude oil density, it was found that it was 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 [7] was used to calculate the radiative heat loss fraction from the measured heat release rate and heat flux data:

$$\chi_r = \frac{4 \pi L^2 \dot{q}_f''}{HRR \times A_s} \quad (1)$$

where

- χ_r = radiative heat loss fraction (-)
- L = distance from the center of the pan to the radiometer (m)
- \dot{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 \dot{q}_f'' and HRR vary with density in a similar

fashion. 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 $\chi_r = 0.57$, on the basis of heat release rate measured by the oxygen depletion measuring equipment. 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.

(4) 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:

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

where Y_s is the smoke yield (in kg/kg), k is the extinction coefficient (in 1/m), \dot{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 ($7600 \text{ m}^2/\text{kg}$ 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:

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

where l is the diameter of the duct (in m), I_0 is the light intensity if 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 increasing. 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.

(5) Liquid Fuel Temperature and Tendency of Boilover

Boilover is a violence burning which might be occurred after long burning of the crude oil or multi-component fuels like to fuel oil. Therefore to understand boilover phenomenon is important in studying combustion properties of crude oil. When a hot zone (isothermal zone) is made and then it reaches water layer, which may exist in the tank bottom, an onset of boilover may start. Potentiality and intense of boilover of crude oil fires may be controlled by the depth of hot zone and the hot zone temperature. Both parameters are related

with distillation property of each crude oil. It may be expected that the former is related with the temperature difference of IBP (Initial boiling point) and the end of boiling point, and the latter is related with the end of boiling point.

Among the experimental data obtained here, the depth of hot zone related with temperature slope, and the hot zone temperature related with the crude oil temperature. The crude oil temperature increases as a function of time at a nearly constant rate, for example, in Iranian Light crude oil (see Figure 2). The temperature slope was defined as the averaged increase rate ($\Delta T/\Delta t$) from ignition to the end of burning in this paper. The temperature slope (in $^\circ\text{C}/\text{s}$) was calculated by dividing the crude oil temperature increase from the ignition to the end of burning by the burning time. There were differences in the temperature slope among the crude oils experimented in this paper, but was independent with the fuel density. The density of crude oil might not be related with tendency of boilover.

There is possibility that the temperature slope has relation to the crude oil temperature when crude oil is vaporized during distillation. The 50 %-distilled temperature was defined as the oil temperature when 50 % volume of crude oil is vaporized during distillation in this paper. Relationship between the 50 %-distilled temperature and the temperature slope is shown in Figure 4. Each number in Figure 4 indicates the crude oil number in Table 1. The data of the 50 %-distilled temperature of some crude oils could not be obtained from reference[9]. The higher rate of increasing temperature had tendency to correspond to the higher 50 %-distilled temperature, excluding Suez Blend crude oil and Arabian Light crude oil, which belonged to the high-density crude oil among the crude oils experimented in this paper, and they might have high hot core temperature. Hoot crude oil and Arabian Light* crude oil indicated the high value of the 50 %-distilled temperature and the temperature slope. Therefore both crude oils might have strong tendency of violence boilover on these basis of the results of the small-scale experiment. These results should be examined with experiments with the larger-scale pan.

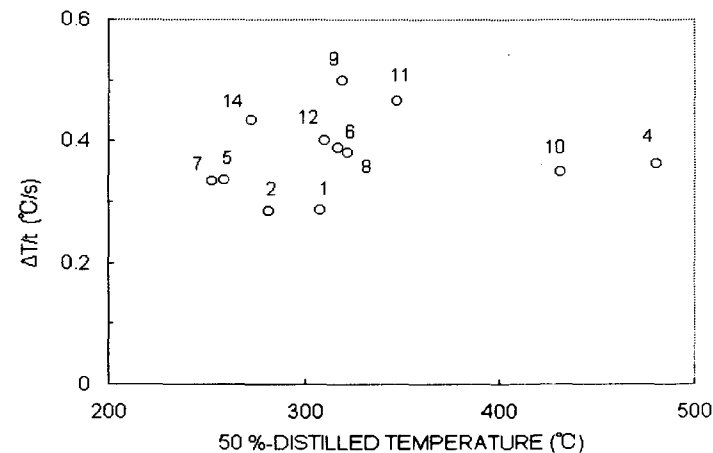


Figure 4. Relationship between 50 %-distilled temperature and the temperature slope. Each number indicates the crude oil number in Table 1.

(6) Burning Characteristics of Kerosene

Kerosene was burned as a reference material. Kerosene has a higher HRR_{avg} (632 kW/m²), MRL (0.11 g/s), \dot{q}_f (1.30 kW/m²), 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 of kerosene approximately two times higher than those of experimented crude oils, while the difference in k values is much smaller. The correlations between different combustion characteristics and density established on the basis of the crude oil data can be extended to kerosene.

4. 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) Heat release rate, radiant heat flux from the flame, and smoke yield are a function of the type of crude oil and appear to correlate well with crude oil density. The effective heat of combustion is almost constant for the range of crude oils experimented.
- (2) Tendency of boilover is dependent with distillation property of crude oil.

Additional intermediate or large scale experiments 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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A Study of Full-scale Flammability Test of Flame Retardant and Non-Flame Retardant Curtains

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ABSTRACT

Fabric products such as curtains and bedclothes play an important role for fire propagation in an early stage of fire. However the flame retardant standard test currently used in Japan for such fabric material pays more attention to ignitability than flammability and any other characteristics of combustion. In this study, the full-scale burning test of curtains was conducted by using a room calorimeter to obtain basic information for future flammable test development associated with fabric products. Prior to the experiment, a set of ignition heat source model is introduced from wastebasket fire tests, i.e. 50kW for 5 min and 30kW for 10 min. The heat release rate of various kinds of curtains are examined under different ignition heat source conditions. Some discrepancies of test results between the full-scale and the present standard flame retardants test are found. These are caused by thermal characteristics of fabric material such as melting and shrinking. To develop new evaluation test methods, these characteristics should be taken into account.

KEYWORDS: flammability, fire, fabric material, full-scale test, curtain, combustion, flame retardant

INTRODUCTION

In the beginning of building fires especially for residential fires, fabric products such as curtains and bedcloths play an important role for fire propagation because of latent risk of ignitability, flammability and its large surface area which causes fire propagation widely. Some of those fabric material are processed with various flame retardant (FR) treatments, and adoption of these FR material in certain locations such as in high-rise buildings is enforced by the Japanese Fire Service Law. However the present flame retardant standard tests in Japan for such fabrics mainly evaluate ignitability by using a small pilot flame like a tobacco but hardly evaluate flammability, fire propagation, heat release rate and combustion products etc. From the viewpoint of fire safety, performance of FR fabrics