Twenty-Sixth Symposium (International) on Combustion/The Combustion Institute, 1996/pp. 1445–1452

THE EFFECT OF POOL DIAMETER ON THE PROPERTIES OF SMOKE PRODUCED BY CRUDE OIL FIRES

G. W. MULHOLLAND
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899, USA

W. LIGGETT
Information Technology Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899, USA

H. KOSEKI
Fire Research Institute
Mitaka, Tokyo, 181, Japan

The smoke production from the burning of crude oil was investigated for a 1-m-diameter pan and for a 2.7- × 2.7-m pan, which is the largest pan used within a fire test facility for smoke characterization. The smoke yield was measured using the carbon balance method by two different procedures: one involved continuous sampling to gas analysis equipment, and the second used a portable, airborne-smoke-sampling package (ASSP). The advantages and limitations of the carbon balance method are addressed. The smoke yield increased by ca. 50%, from 0.100 to 0.148, as the pan size increased. These results are compared with other studies ranging in scale from a pool diameter as small as 8.5 cm to those as large as the 12-m crude oil "spill" fires and the 100-m pool fires set during the 1991 war in Kuwait. Possible causes for the factor-of-5 lower yield measured for the Kuwait oil-well fires, compared to the larger pool fires measured in this study, are examined. The primary sphere size of the smoke was measured by transmission electron microscopy (TEM). It was found that the diameter of the primary spheres increased by ca. 80%, from 58 nm to 106 nm, as the pan size increased. This scale dependence of the primary sphere size is discussed in light of recent studies concerning smoke formation.

Introduction

The production of smoke from the burning of hydrocarbon fuels has ramifications for public health, the environment, and the climate. The accidental burning of crude or processed oil in storage tanks creates both a life safety threat from the flames and a longer-range health impact from the inhalation of smoke. In the case of an oil spill, there may be circumstances in which the burning of the crude oil produces less of a threat to the environment compared to other methods of cleanup [1].

A second concern about large-scale crude oil fires is the potential climatic effect arising from the blocking of sunlight by the smoke. The smoke generated by the burning of crude oil was a major component of the light absorbing smoke in the "nuclear winter scenario" [2,3]. There was concern in 1991 that the burning oil fields in Kuwait could have at least a local climatic impact.

Until recently, most published smoke-yield data for petroleum products and crude oil were based on small-scale tests with the diameter of the pan containing the fuel less than ca. 0.5 m [4–7]. In one study [4], it was found that small and larger samples have the same smoke yield if the specific burning rate is matched by increasing the burning rate of the smaller sample; in a second study [7], it is shown that if the residence time is ca. 10 times longer than that for a laminar, smoke-point flame, the smoke yield approaches an asymptotic value.

This study is directed at extending the database for quantitative smoke yield for the burning of crude oil within an enclosure to include a 1-m pan diameter and a 2.7- × 2.7-m pan. The experiments were performed at the large-scale fire facility at the Fire Research Institute in Japan. A previous study [8] based on a single, large pool burn suggested that the smoke yield increased by more than 50% as the pan size was increased from 1 to 2.7 m. To ensure reli-

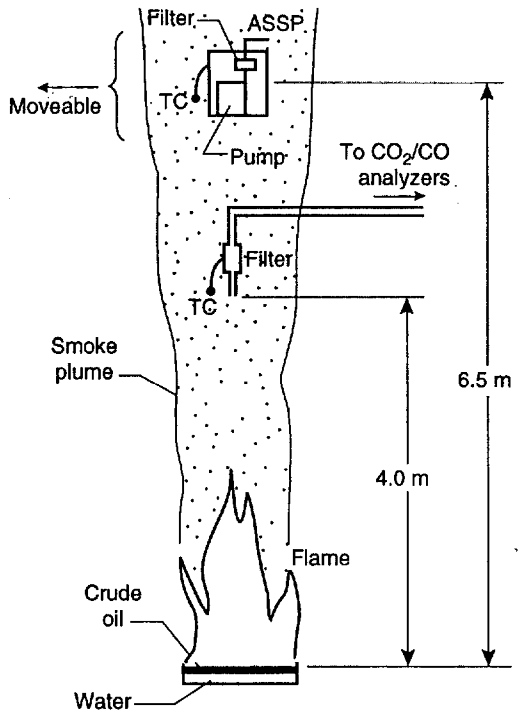

FIG. 1. Schematic diagram of the location of the smoke-sampling equipment relative to the location of a 1-m crude oil pool fire. The gas-sampling bag for the airborne smoke sampling package (ASSP) is not shown.

able results in the present study, triplicate tests were performed at both scales and two measurement approaches were employed. A key feature of the study is the use of the carbon-balance method for the quantitative measurement of smoke yield.

A second objective of the present study was to determine the effect of pan size on the primary sphere size of the smoke, which is made up of clusters of primary spheres. Previous measurements of primary sphere size for a wide range of hydrocarbon fuels extend from 30 to 50 nm for fires ranging in size from 2 to 20 kW [9]. For large fires, there appears to be no systematic study of the primary sphere size of the smoke.

The results are compared with other studies involving smaller and larger pool fires as well as the oil-well fires in Kuwait. The effect of pan size on the primary sphere size is discussed in light of a recent study on soot precursor particles [10].

Experimental Approach

Figure 1 shows a schematic of the experimental setup. A mixture of 80% murbane and 20% Arabian crude oil was burned in pans placed at the center of the test facility, which has an open area 24 × 24 m under a 20-m-high ceiling. The crude oil was burned in both a 1-m-diameter circular pan and a 2.7-m-square pan with an oil layer of 2 cm floating on water. In this study, we focused on the smoke property measurements, whereas in earlier studies [8,11], the burning rate and radiant output before and during boil-over were measured.

The major experimental focus was on the application of the carbon-balance method [4,12] in the measurement of the smoke yield, defined as the mass of smoke particulate produced per mass of fuel consumed. This method requires a determination of the ratio of the smoke mass in a given volume to the total mass of carbon in the form of gas or particulate in the same volume. This is accomplished by dividing the smoke mass collected on a filter by the sum of the smoke mass and the mass of carbon contained in the forms of CO and CO_2. The equation for calculating smoke yield, ε, as expressed in terms of CO_2 and CO concentrations, is given by

$$\varepsilon = \frac{f\, m_s}{[m_s + 0.012 n_t(\Delta X(\mathrm{CO}) + \Delta X(\mathrm{CO_2}))]} \quad (1)$$

The quantity f is the carbon mass fraction of the fuel (0.855 for the crude oil blend used in this study); m_s is the mass of the smoke sample collected on a filter; n_t is the number of moles of air sampled; and the constant 0.012 represents the molar mass of carbon in kilograms. The quantities $\Delta X(\mathrm{CO})$ and $\Delta X(\mathrm{CO_2})$ are the mole fractions of CO and CO_2 of the gas sample taken during the test minus the ambient background concentrations of these gases. In this equation, the other carbon-containing gases are neglected on the basis of observations from laboratory-scale, open burns that these other species made up 2% or less of the total carbon emitted by the flame [4]. One other approximation is that the smoke collected is pure carbon. In fact, the smoke is mainly "graphitic" carbon with an estimated carbon content by weight of 95% or greater. This, together with the fact that m_s is small relative to the other terms in the denominator of Eq. (1), less than 20% of the total, leads to, at most, a 1% uncertainty in the value of the smoke yield for this approximation.

The carbon-balance method has the advantage of not requiring that all the smoke produced be collected. It is becoming widely used for field sampling by tethered, helium-filled balloons [1,13–15] and aircraft [16–20] for large fires. The method has been validated in laboratory-scale measurements (agreement within ±10%) in which the carbon-balance result is compared to the measurement of the total smoke produced and the total amount of fuel burned [4]. The smoke yield was also found to be insensitive to the radial location of the sampling point above the fire as long as sampling was performed within the visible plume [15].

Two different procedures, both based on the carbon-balance method, were used for measuring the smoke yield. In one, a sampling probe was positioned 4 m above the pan for the 1-m fire, and in the exhaust duct of the facility for the case of the 2.7-m-square pan. The smoke/gas entered a 6.5-mm-diameter sampling probe at near isokinetic velocity of about 5 m/s for the smaller pan and about 10 m/s for the larger pan. The smoke particulate was collected on a ceramic filter while the gases flowed to a CO-CO_2 nondispersive infrared analyzer. The nominal average values were 2000 ppm for CO_2, 40 ppm for CO, and 90°C for both the 1- and the 2.7-m pans. For the 1-m pan, near the end of the typically 10-min. burn, boil-over occurred, resulting in enhanced burning and increased temperature by about 150°C.

The second method used an airborne-smoke-sampling package (ASSP) originally designed to be flown suspended below a tethered, helium-filled balloon or helicopter [13]. The basic components of the device are a filter, a diaphragm pump, and a gas-sampling bag. In this case, a fraction of the gas sampled by the pump is directed into the sampling bag throughout the sampling period. After the test is completed, the CO and CO_2 content of the gas is determined by gas chromatography. The ASSP is suspended above the sampling probe for the 1-m-diameter pan fire and positioned off-center in the smoke layer for the larger fire. The ASSP is lowered to the side late in the test just before boil-over occurs. The CO_2 concentration is about 1200 ppm for both tests; the temperature is about 40°C for the 1-m pan and about 80°C for the 2.7-m pan. Transmission electron microscopy (TEM) grids were attached to the aluminum surface of the ASSP using double-stick tape for subsequent analysis of the size and structure of the smoke agglomerates. The agglomerates are deposited by thermophoresis because the metal surface is cooler than the air. Sedimentation and diffusion also contribute to the deposition of the smoke.

Results

Smoke Yield

The average smoke yields obtained by the two methods for the 2.7-m-square pan agree well, 0.148 ± 0.012 (three tests for the ASSP) versus 0.149 ± 0.015 (three tests for the continuous sampling). The average yield for the 1-m pan is 0.100 ± 0.008 (four tests for the ASSP) versus 0.061 (two tests for the continuous sampling). One reason for the lower value for the continuous sampling is that the smoke is collected throughout the burn, including the boil-over period during which the yield is reduced [21]. The smoke is not collected during boil-over by the ASSP to prevent damage to the plastic components (collection bag, plumbing, and pump housing). A difference in yield for the two approaches is not expected for the larger pan because the boil-over effect is minimal. The key observation is that the smoke yield increases by ca. 50% as the pan size is increased from 1 to 2.7 m. The corresponding burning rates for the two pan sizes are ca. 0.022 and 0.26 kg/s.

Primary Sphere Size

In Fig. 2, we show representative micrographs of the smoke collected from the 1-m and 2.7-m pans. The most striking feature is the apparent bimodal size distribution of large (100–150 nm) and smaller (30–70 nm) primary spheres for the larger pan. Furthermore, the larger spheres are grouped together, as are the smaller ones.

The particle-size analysis for each fire size is based on ca. 20 TEM micrographs taken at randomly selected locations on a single grid. A total of 404 spheres were sized for the 1-m-diameter pan and 483 spheres for the 2.7- × 2.7-m pan. The spheres selected for sizing for each photograph are determined from a transparent template with 100 randomly selected points. In the case in which a point appears in a region of overlapping primary spheres, the closest identifiable sphere is sized. This procedure was chosen over sizing every primary sphere to obtain a broader sampling selection and to avoid the ambiguity of regions where individual spheres are difficult to enumerate. The overlap is more prevalent for the larger spheres. Also, as explained later, this method provides a more accurate volume distribution than obtained by sizing every sphere in a photograph.

The TEM photographs are taken at a magnification of 30,000×, and enlargements (ca. 2.4×) are prepared for sizing. The primary spheres are measured manually from the glossies to the nearest 0.1 mm using a 6× measuring reticule. The spheres are then binned with the first bin, 0.25–0.75 mm, with the second, 0.75–1.25, and so forth.

The procedure we have used to randomly select the spheres is biased toward the choice of larger spheres. The probability of hitting a sphere of diameter D with coordinates chosen at random is proportional to the cross-sectional area of the sphere. Therefore, the empirically determined distribution, $Y(D)$, is related to the number distribution by the following expression:

$$Y(D) = CD^2n(D) \tag{2}$$

where C is a proportionally constant.

Our interest is in the volume distribution, $V(D)$, of the primary spheres because the optical properties and the health impact are better correlated with the volume or mass distribution rather than the number distribution. The volume distribution is pro-

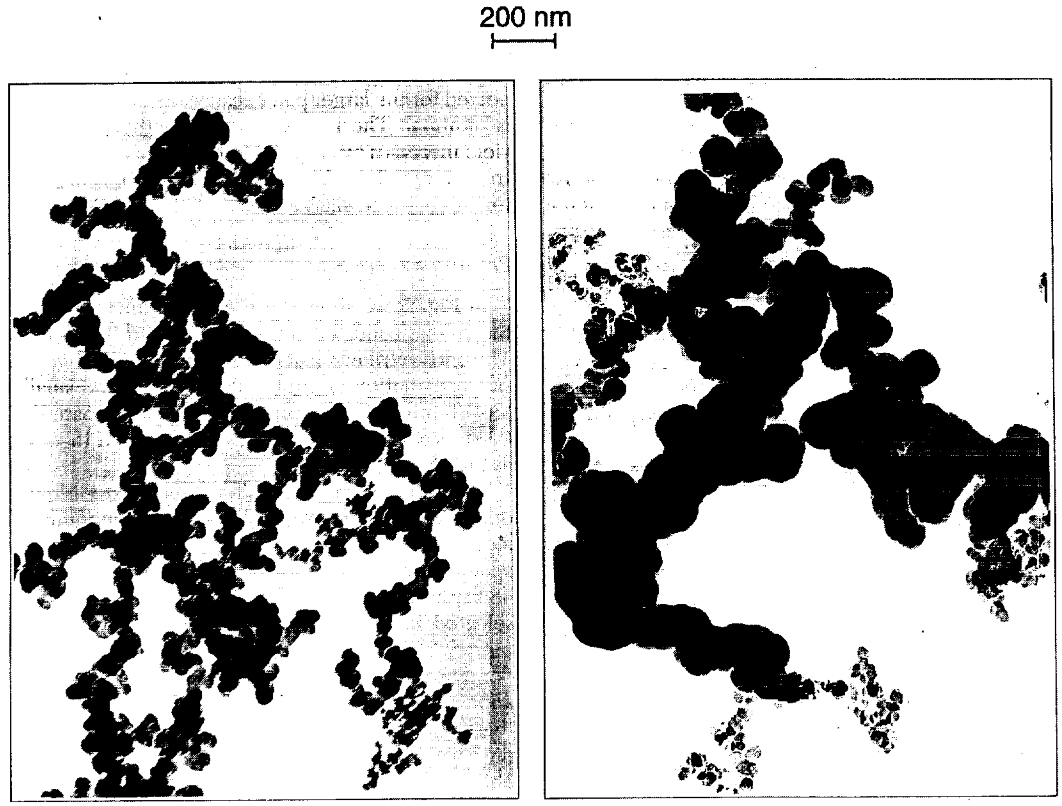

FIG. 2. TEM photographs of smoke collected from crude oil fires for 1-m-diameter pan (left) and 2.7- × 2.7-m pan (right).

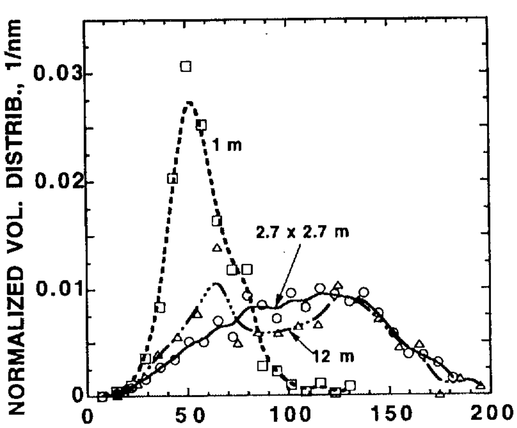

FIG. 3. The normalized volume distribution of smoke from crude oil fires for a 1-m-diameter pan, a 2.7-m- × 2.7-m pan, and a 12-m-diameter pan.

portional to $D^3n(D)$. Therefore, multiplying $Y(D)$ by D gives a result proportional to the volume distribution. This method gives a more accurate measurement of the volume distribution than counting every particle on a fewer number of micrographs (fixed number of particles sized), because the volume distribution is more similar to $Y(D)$ than to $n(D)$ (first power of D multiplicative factor versus third power). This is especially true for the large fires in which a relatively small number of large spheres contributes a large fraction of the volume distribution.

It is convenient to define a normalized volume distribution, $V^1(D)$, where the integration over particle diameter gives unity:

$$V^1(D_i) = \frac{D_i Y(D_i)}{\sum D_i Y(D_i) \Delta D} \tag{3}$$

In Fig. 3, the volume distribution is plotted for the primary spheres for the 1-m-diameter pan, the 2.7- × 2.7-m pan, and a 12-m-diameter pan (317 points). A limited data set (83 spheres sized) for a 0.1-m-diameter pan is similar to the 1-m-diameter pan result. In the case of the 12-m pan, the fuel was Baton

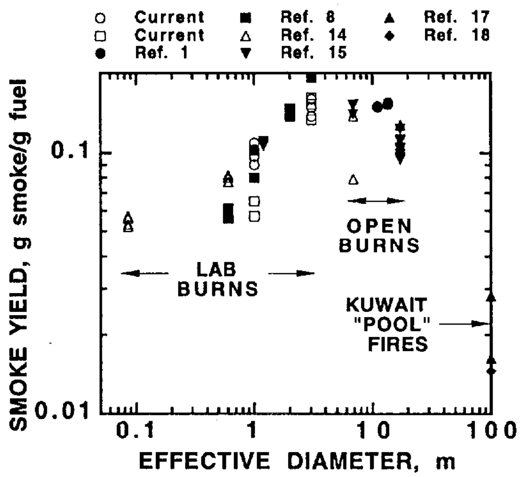

FIG. 4. The effect of pan diameter on the smoke yield of burning crude oil.

Rouge crude and the smoke was collected by the ASSP approximately 200 m from the flame tip [14]. The bimodal character apparent in the micrographs from the larger fire is more apparent for the 12-m pan than for the 2.7-m pan. Apparently, slight changes in mean sizes from sample to sample wash out the structure for the 2.7-m pan. From the volume distribution, the volume mean diameter, D_v, is found to be 58 nm for the 1-m-diameter pan, 106 nm for the 2.7- × 2.7-m pan, 101 nm for the 12-m-diameter pan, and 51 nm for the 0.1-m-diameter pan.

Discussion

Smoke Yield

In Fig. 4, the smoke yield is plotted versus pool diameter. We define the effective diameter of the 2.7-m-square pan as the diameter of a circle (3.05 m) with area equal to the square pan. Figure 4 includes other crude oil fires with "pan sizes" ranging from 0.085 m to 100 m [1,8,14,15,17,18]. The pan sizes of 1 m and 3.05 m in the present study match two of the sizes used in a previous study [8]. The average yields obtained by the ASSP in the present study are 0.148 and 0.100 compared to 0.194 (one test) and 0.087 (three tests) obtained in the previous study [8] for the 3.05-m and 1-m pans, respectively. Our present experiments confirm the trend of increasing smoke yield with increasing pan size though the magnitude of the increase, ca. 50%, is less than the more limited results of the previous study [8].

The data from pans sized at 2–15 m based on five studies ([1,8,14,15] and the present study) with five types of crude oils (murban, Arabian light, Louisiana crude, murban–Arabian light, and Newfoundland crude), appear to be independent of size; with one exception, the data fall in the range 0.13–0.16. For the pans larger than 3 m, the burns were performed outside where the ambient wind may affect the smoke yield.

The results from two series of tests with 17.2-m pans are significantly lower than the results from pans sized at 2–15 m. One was a series of tests [15] with results ranging from 0.101 to 0.111 with a mean of 0.107, whereas the other was a single test with a value of 0.127 [14]. The cause for an apparent decrease is not known.

Figure 4 also contains the results obtained from sampling smoke produced by individual oil-well fires in Kuwait [17,18]. The University of Washington's Convair C-131A research aircraft was used for sampling in the plume for one study [17], and a Royal Saudi Air Force UH1N helicopter fitted with a NASA smoke-sampling package was used in the other [18]. For the fixed-wing aircraft [17], smoke samples were collected in the plume of two large pool fires with estimated diameters of 100 m. The carbon-balance method was used for determining the yield for graphitic carbon particulate, organic carbon particulate, salts, and gaseous species. We have taken the smoke yield as the sum of the organic and elemental carbon mass, which resulted in yields of 0.018 and 0.031.

We believe these values significantly underestimate the true value for two reasons. First, the total particle yield, 0.043 and 0.052, is about twice the smoke yield, 0.018 and 0.031. We surmise that the total particle yield is a better estimate of the smoke yield than the actual smoke measurements, in part because no other major component was found in the particulate besides the smoke. There were small amounts of inorganics collected on the filter, salts, and sulfates, corresponding to a total of 11% of the total particulate in one case and 5% in the other [19].

Secondly, the sampling methods could affect the results. The aircraft fills the sampling bag with ram air and subsequently draws from the bag through a 3.5-μm-diameter cyclone separator into a filter. The ASSP sampling involves a tethered, helium-filled balloon positioned in the smoke plume drawing a flow of 3 m/s through a 10-cm section of tubing to the filter. In an oil burn test in Canada [20], both methods were used in the same test, with the ASSP giving an average yield of 0.151 compared to the aircraft yield of 0.073 for the carbonaceous component of the particulate (including elemental carbon and organic carbon) and 0.087 for the total particulate yield. These results suggest that sampling is an issue, though the exact collection method used in Canada was not quite identical to the one used in Kuwait.

The measurement method used by Cofer et al. [18] for the particulate yield is similar to that of

Laursen et al. [17] except the velocity of the helicopter is much lower than that of the fixed-wing aircraft. The average particulate yield [18] based on 24 samples from 5 oil-pool fires was 0.014 using the helicopter, compared to an average yield of 0.048 for two oil-pool fires sampled by the fixed-wing aircraft.

The Kuwait results appear to be inconsistent and inconclusive. It is possible that the yield from the Kuwait fires is appreciably different from the smaller-scale tests because of the high salt content of the oils, different fuel conditioning resulting from many days of burning versus a short burn (less than an hour) of oil floating on water, and possibly higher wind velocity.

Primary Sphere Size

Our observation that the volume mean diameter of the primary sphere increases by more than 80% (58 nm versus 106 nm) as the pan diameter increases from 1 to 3.05 m appears to be new. This change is expected to affect both the optical and the aerodynamic properties because for a 106-nm sphere, the optical size parameter, $\pi D/\lambda = 0.7$ for wavelength $\lambda = 0.5\,\mu$m, and the Knudsen number, 1.2, are both approaching the value 1, which marks a change from Rayleigh scattering to Mie scattering and from free molecular dynamics to continuum dynamics.

How do these sizes compare with other fuels studied? The geometric mean sphere diameter and the geometric standard deviation were measured for the smoke produced by burning seven fuels as buoyant turbulent diffusion flames with a burner diameter of 5–25 cm [9]. The volume mean diameter derived from these measurements extends from 33 to 56 nm for fuels ranging from the least sooting, isopropanol, to the most sooting, toluene. This result suggests that a large fire is needed to obtain a large volume mean diameter for a buoyant diffusion flame at ambient conditions.

There are limited data for large-scale fires. Our result for the volume mean diameter for a 12-m pool fire, 101 nm [14], is similar to the result for the 2.7- × 2.7-m pan fire, 106 nm. Radke et al. [16] also observed large primary spheres for smoke collected from the burning of a 30-m-diameter pool of aviation fuel. They comment that "most of the particles in the smokes consisted of two types of chain aggregates: one comprised of fairly uniform spheres with approximately 30 nm diameter and the others of spheres with approximately 150 nm." Johnson et al. [22] report a primary sphere size of about 100 nm on the basis of SEM of the smoke from the burning wells in Kuwait. Even if smaller-diameter primary spheres in the range of 30–60 nm were present, they would not be measurable by the scanning electron microscope.

How can we account for the increased primary sphere size? The study of Dobbins et al. [10] shows that individual microspheres composed of polycyclic aromatic hydrocarbons (PAHs) are formed low in a laminar diffusion flame. These microspheres grow by a surface process as well as by coagulation followed by coalescence. The microspheres low in the flame have a high content of PAHs. As they reach into the high-temperature region of the flame, they carbonize, leading to particles with a much lower mole fraction of hydrogen, 0.15 high in the flame versus 0.36 low [10]. Once this happens, the particles no longer coalesce upon contact but rather form aggregates. This scenario suggests that the primary sphere size can be increased by decreasing the flame temperature or by increasing the residence time in the lower-temperature region of the flame. The preceding suggestion is consistent with the well-known result in the carbon black industry that a decreasing temperature produces a larger primary sphere size [23].

Is this scenario also consistent with thermal-temporal analysis of large flames? Steady-state temperature measurements [24,25] for heptane burning in the same-size pans, 1 m and 2.7 × 2.7 m, indicate an *increase* in temperature on the centerline with increasing pan size. This appears to be inconsistent with the earlier scenario.

The residence time in the flame is estimated to increase from 0.7 to 1.1 s as the diameter is increased from 1 to 3.05 m on the basis of the residence time correlation of Koylu and Faeth [7]. Lahaye and Prado [26] observed only about a 10% increase in particle diameter as the residence time in a pyrolysis reactor was increased from 0.3 to 1.0 s. So, the cause of the increase in particle size is still a puzzle, though one suspects that the particle trajectory for the larger flame passes through a lower-temperature region even though the peak temperature of the larger flame is higher.

One is left with a related question about why the primary sphere size is approximately constant for pan sizes ≤1 m and for pan sizes ≥3 m.

Conclusions

1. Smoke yield increases as the pan diameter increases up to a value of 0.14–0.15 at a pan diameter of 2–3 m and stays relatively constant up to a pan diameter of about 15 m. The reported yields from the Kuwait oil-well fires, 0.02–0.03, are likely to be underestimates because of difficulties in particle sampling and analysis.
2. The volume mean diameter of the primary spheres of smoke produced from the burning of crude oil increases by about 80% from 58 to 106 nm as the pan size increases from 1 to 3.05 m. The limited results available for larger pool fires are similar to the results for the 3.05-m pan. The large and small primary spheres are segregated

on separate agglomerates or subsections of agglomerates.

Acknowledgments

The electron microscopy was performed by Dr. Hashimoto from Tokyo Science University.

REFERENCES

1. Walton, W., Twilley, W., McElroy, J., and Evans, D., *Proceedings of the Seventeenth Arctic and Marine Oil Spill Program Technical Seminar* Vol. 2, Ministry of Supply and Services Canada 1994, pp. 1083–1098.
2. Crutzen, P. J., Galbally, I. E., and Bruhl, C., *Clim. Change* 6:323–364 (1984).
3. Penner, J. E., *Nature* 324:222–226 (1986).
4. Mulholland, G. W., Henzel, V., and Babrauskas, V., *Proceedings of the Second International Conference on Fire Safety Science* (Wakamatsu, T., Hasemi, Y., Sekizawa, A., Pagni, P. J., and Grant, C. E., Eds.), Hemisphere Publishing, New York, 1989, pp. 347–357.
5. Tewarson, A., *SFPE Handbook of Fire Protection Engineering*, National Fire Protection Association, Quincy, MA, 1988, pp. 1–179.
6. Patterson, E. M., Duckworth, R. M., Wyman, C. M., Powell, E. A., and Gooch, J. W., *Atmospheric Environment* 25A:2539–2552 (1991).
7. Koylu, U. O. and Faeth, G. M., *Combust. Flame* 87:61–76 (1991).
8. Koseki, H. and Mulholland, G. W., *Fire Technology* 27:54–65 (1991).
9. Koylu, U. O. and Faeth, G. M., *Combust. Flame* 89:140–156 (1992).
10. Dobbins, R. A., Fletcher, R. A., and Lu, W., *Combust. Flame* 100:301–309 (1995).
11. Koseki, H., Kokkala, M., and Mulholland, G. W., *Proceedings of the Second Fire Safety Science International Symposium* (Cox, G. and Langford, B., Eds.), Elsevier, London, 1991, pp. 865–874.
12. Ward, D. E., Nelson, R. M., and Adams, D. F., *Proceedings of the Seventy-Seventh Annual Meeting of the Air Pollution Control Association*, Air and Waste Management Assoc., Pittsburgh, 1979, Pap. 079-6.3.
13. Lawson, J. R., Mulholland, G. W., and Koseki, H., *Fire Technol.* 30:155–173 (1994).
14. Evans, D., Walton, W., Baum, H., Notarianni, K., Lawson, J., Tang, H., Keydel, K., Rehm, R., Madrzykowski, D., Zile, R., Koseki, H., and Tennyson, E., *Proceedings of the Fifteenth Arctic and Marine Oil Spill Program Technical Seminar*, Ministry of Supply and Services Canada, 1992, pp. 593–657.
15. Walton, W., Evans, D., McGratten, K., Baum, H., Twilley, W., Madrzykowski, D., Putorti, A., Rehm, R., Koseki, H., and Tennyson, E., *Proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar*, Ministry of Supply and Services Canada, 1993, pp. 679–734.
16. Radke, L. F., Lyons, J. H., Hobbs, P. V., and Weiss, R. E., *J. Geophys. Res.* 95:14,071–14,076 (1990).
17. Laursen, K. K., Ferek, R. J., Hobbs, P. V., and Rasmussen, R. A., *J. Geophys. Res.* 97:14,491–14,497 (1992).
18. Cofer, W. R. III, Steven, R. K., Winstead, E. L., Pinto, J. P., Sebacher, D. I., Abdulraheem, M. Y., Al-Sahafi, M., Mazurek, M. A., Rasmussen, R. A., Cahoon, D. R., and Levine, J. S., *J. Geophys. Res.* 97:14,521–14,525 (1992).
19. Ferek, R. J., Hobbs, P. V., Herring, J. A., and Laursen, K. K., *J. Geophys. Res.* 97:14,483–14,489 (1992).
20. Ross, J. L., Ferek, R. J., and Hobbs, P. V., *J. Air Waste Management Assoc.*, 46:251–259 (1996).
21. Benner, B. A., Bryner, N. P., Wise, S. A., Mulholland, G. W., Lao, R. C., and Fingas, M. F., *Environ. Sci. Technol.* 24:1418–1427 (1990).
22. Johnson, D. W., Kilsby, C. G., McKenna, D. S., Saunders, R. W., Jenkins, G. J., Smith, F. B., and Foot, J. S., *Nature* 353:617–621 (1991).
23. Donnet, J. B. and Voet, A., *Carbon Black Physics, Chemistry, and Elastomer Reinforcement*, Marcel Dekker, Inc., New York, 1976, p. 8.
24. Koseki, H. and Yumoto, T., *Proceedings of the Second International Conference on Fire Safety Science* (Wakamatsu, T., Hasemi, Y., Sekizawa, A., Pagni, P. J., and Grant, C. E., Eds.), Hemisphere Publishing, New York, 1989, pp. 231–240.
25. Yumoto, T. and Koseki, H., "Effect of Tank Diameter on Combustion Characteristics of Heptane Tank Fires," Report of Fire Research Institute of Japan (in Japanese) 55:71 (1983).
26. Lahaye, J. and Prado, G., in *Particulate Carbon Formation during Combustion* (Siegla, D. C. and Smith, G. W., Eds.), Plenum Press, New York, 1981, p. 143–175.

COMMENTS

I. Glassman, Princeton University, USA. The various general results on the degree of soot formation would appear to correlate well with the fundamental results on simple laminar diffusion flames. First, it appears apparent that soot nucleates at similar temperatures regardless of the fuel. Further, the mass and size of soot are controlled by growth on nucleated particles. Thus mass and size are determined by the time from nucleation to that entering the flame zone. More appropriately, the distance from the nucleation point to flame surface controls. This distance is related to the depth of the thermal wave since a stable diffusion flame is essentially a quasi-steady moving boundary heat transfer case.

The depth of the thermal wave is the ratio of the thermal diffusivity over the gaseous fuel velocity. In the Kuwaiti case the liquid spout has large velocities and thus small depth of thermal wave and thus less soot. You also mentioned, that when the case is such that the fuel is hot, there is greater soot. This too is consistent with the thermal concept since when the flame temperature is fixed, as is the nucleation temperature, then increasing the initial temperature increases the depth of the thermal curve and therefore greater soot growth. Some of these concepts can also be applied to your results when you increase the size of the pool.

Author's Reply. The comment about the decreasing thermal wave for a liquid spout may be relevant to the smoke emission for many of the Kuwaiti oil well fires; however, the data reported in this paper were restricted to oil well "pool" fires rather than liquid jet fires.

The paper states that the centerline flame temperature increases with pan size for heptane fuel. The data (cf. Koseki et al. (1989), Yumoto et al., and [1]) show an increase in the temperature with increasing pan size for the upper portion of the flame, but do not indicate a pan size effect low in the flame where the pyrolyzing fuel would be located. The paper speculates that for the larger pan the particle trajectory passes through a *lower* temperature region compared to the smaller pan even though the peak temperature for the larger pan is higher.

We do agree with the comment that fundamental results on laminar diffusion flames are relevant to smoke properties for large flames. Unfortunately, there has been little research on what controls the primary sphere size for smoking laminar diffusion flames.

REFERENCE

1. Baum, H. R. and McCaffrey, B. J., *Proceeding of the Second International Conference on Fire Safety Science*, (T. Wakamatsu, Y. Hasemi, A. Sekizawa, P. J. Pagni, and C. E. Grant, Eds.), Hemisphere Pub., New York, 1989, pp. 129–148.

•

M. A. Delichatsios, FMRC, USA. Mass flux (i.e. burning rate) from a liquid turbulent pool fire increases with size to an asymptotic value. Soot formation rates increase as mass flux rate increases because dilution of fuel by N_2 near the surface decreases, so that the issuing fuel mixture becomes more smoky (smoke-point decreases). Therefore, unburnt soot (= smoke yield) will increase for possibly an asymptotic value. Can you comment on this interpretation of your data?

Author's Reply. Both the mass burning rate per area and smoke yield increase with pan diameter up to a plateau region. For the smoke yield, the plateau begins at a pan diameter of about 2 m, while for the burning rate it begins around 6 m (cf. Koseki et al., 1991 and Walton et al., 1993). So the burning rate does not account, at least directly, for the smoke yield approaching a plateau at the smaller pan diameter.