

NISTIR 6030

**THIRTEENTH MEETING OF THE UJNR
PANEL ON FIRE RESEARCH AND SAFETY,
MARCH 13-20, 1996**

VOLUME 1

Kellie Ann Beall, Editor

June 1997
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899



U.S. Department of Commerce
William M. Daley, *Secretary*
Technology Administration
Gary R. Bachula, *Acting Under Secretary for Technology*
National Institute of Standards and Technology
Robert E. Hebner, *Acting Director*

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

G.W. Mulholland and W. Liggett
National Institute of Standards and Technology
Gaithersburg, MD 20899

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

ABSTRACT

The smoke production from the burning of crude oil was investigated for a 1 m diameter pan and for a 2.7 m \times 2.7 m pan, which is the largest pan size used within a fire test facility for smoke characterization. The smoke yield, as measured by two procedures both based on the carbon balance method, increased by about 50% as the pan size increased. Analysis of the smoke by transmission electron microscopy showed that the volume mean diameter of the primary spheres increased by about 80% 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 as large as 12 m crude oil "spill" fires and 100 m pool fires set during the 1991 war in Kuwait.

INTRODUCTION

This study is directed at extending the data base for quantitative smoke yield for the burning of crude oil within an enclosure to include a 1 m pan diameter and a 2.7 m \times 2.7 m pan. The experiments were performed at the large scale fire facility at the Fire Research Institute in Japan. A previous study [1] based on a single large pool burn suggested that the smoke yield increased by at least 50% as the pan size was increased from 1 to 2.7 m. To ensure reliable 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 diameter for a wide range of hydrocarbon fuels extends from 30 to 50 nm for fires ranging in size from 2 to 20 kW [2]. For large fires, there appears to be no systematic study of the primary sphere size of the smoke.

EXPERIMENTAL APPROACH

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 m \times 24 m under a 20-m high ceiling. The crude oil was burned in a 1-m diameter circular pan and in a 2.7 m square pan with an oil layer of 2 cm floating on water. In this study we focussed on the smoke property measurements, while in earlier studies [1,3] the burning rate and radiant output before and during boilover were measured.

The major experimental focus was on the application of the carbon balance method [4] in the measurement of the smoke yield, defined as the mass of smoke particulate produced per mass of fuel consumed. This is accomplished by dividing the smoke mass collected on a filter to the sum of the smoke mass and the mass of carbon contained in the forms of CO and CO₂. The equation for calculating smoke yield, ϵ , as expressed in terms of CO₂ and CO concentrations is given by:

$$\epsilon = \frac{f m_s}{[m_s + 0.012n(\Delta X(\text{CO}) + \Delta X(\text{CO}_2))]} \quad (1)$$

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 , is the number of moles of air sampled, and the constant 0.012 represents the molar mass of carbon in kilograms. The quantities $\Delta X(\text{CO})$ and $\Delta X(\text{CO}_2)$ are the mole fractions of CO and CO₂ of the gas sample taken during the test minus the ambient background concentrations of these gases.

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/CO₂ nondispersive infrared analyzer.

The second method utilized an airborne smoke sampling package (ASSP) originally designed to be flown suspended below a tethered helium-filled balloon or helicopter [5]. 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 CO₂ content of the gas is determined by gas chromatography. Transmission electron micrograph (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 as a result of the metal surface being cooler than the air. Sedimentation and diffusion also contribute to the deposition of the smoke.

RESULTS

Smoke Yield

The results of all the tests are summarized in Table 1. The average smoke yields obtained by the two methods for the 2.7 m square pan agree well, 0.148 vs 0.149. The coefficients of variation, standard deviation/average, equal 0.081 for the ASSP and 0.101 for the continuous sampling. The average yield for the 1 m pan is 0.100 for the ASSP and 0.061 based on continuous sampling. One reason for the lower value for the continuous sampling is that the smoke is collected throughout the burn including the boilover period during which the yield is reduced [6]. The smoke is not collected during boilover by the ASSP to avoid 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 boilover effect is minimal. The key observation is that the smoke yield increases by about 50% as the pan size is increased from 1 m to 2.7 m. The corresponding burning rates for the two pan sizes are approximately 0.022 and 0.26 kg/s.

Primary Sphere Size

In Fig. 1 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 and the smaller ones are also grouped together.

The particle size analysis for each fire size is based on the analysis of a single TEM grid. For each grid on the order of 20 locations were selected at random and photographs were taken. The size distribution is based on 10-30 primary spheres from each photograph for a total of 404 spheres for the 1 m diameter pan and 483 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. From the size 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. Limited data sets were also analyzed for an 0.1 m diameter pan with the same crude oil and a 12 meter diameter pan involving the burning of Baton Rouge crude [8]. The values of D_v are 101 nm and 51 nm for the 12 m and 0.1 m pans, respectively.

DISCUSSION

Smoke Yield

In Fig. 2 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. Fig. 2 includes other crude oil fires with "pan sizes" ranging from 0.085 m to 100 m [1, 7, 8, 9, 10, 11]. The present study with pan sizes of 1 m and 3.05 m matches two of the sizes used in a previous study [1]. The average yields obtained by the ASSP in the present study are 0.148 and 0.100 compared to 0.194 (1 test) and 0.087 (3 tests) obtained in the previous study [1] for the 3.05 m and 1 m pan size, respectively. Our present experiments confirm the trend of increasing smoke yield with increasing pan size though the magnitude of the increase, about 50%, is less than the more limited results of the previous study [1].

The results for 2 m pan size for two different studies involving 2 burns each [1, 5] fall between the current results for the 1 m and 3.05 m pan size. The data at the smaller pan sizes of 0.085 m and 0.6 m indicate a further reduction of yield with decreasing pan size [1, 8] down to a value of about 0.055 for the 0.085 m pan diameter.

The data from 2 m to 15 m based on 5 studies [1, 7, 8, 9 and the present study) with 5 types of crude oils (murban, Arabian light, Louisiana crude, murban-Arabian light mixture, and Newfoundland crude) appear to be independent of size; with one exception the data fall in the range 0.13 to 0.16. For the pan sizes 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 at 17.2 m are significantly lower than the results from 2 m to 15 m. The results from one series [9] range from 0.101 to 0.111 with a mean of 0.107 while the other was a single test with a value of 0.127 [8]. The cause for an apparent decrease is not known.

Fig. 2 also contains the results obtained from sampling smoke produced by individual oil well fires in Kuwait [10, 11]. The University of Washington's Convair C-131A research aircraft was used for sampling in the plume for one study [10] and a Royal Saudi Air Force UH1N helicopter fitted with a NASA smoke sampling package was used in the other [11].

We believe their values significantly underestimate the true value for two reasons. First, the total particle yield is about twice the smoke yield. 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.

Secondly, the sampling methods could affect the results. In an oil burn test in Canada [12], both the ASSP and aircraft sampling were used on the same test with the ASSP giving an average yield of 0.151 compared to the aircraft value 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 identical to the one used in Kuwait.

Primary Sphere Size

Our observation that the volume mean diameter of the primary sphere increases by more than 80% (58 nm vs. 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 aerodynamic properties, since for a 106 nm sphere the optical size parameter, $\pi D/\lambda=0.7$ for wavelength $\lambda = 0.5 \mu\text{m}$, and Knudsen number, 1.2, are both approaching the value 1, which marks a change from Rayleigh to Mie scattering and free molecular to continuum dynamics.

How do these sizes compare with other fuels studied? The geometric mean sphere diameter and geometric standard deviation were measured for the smoke produced by burning seven fuels as buoyant turbulent diffusion flames with a burner diameter of 5 to 25 cm [2]. The volume mean diameter derived from these measurements extends from 33 nm to 56 nm for fuels ranging from the least sooting, isopropanol, to the most sooting, toluene. This result suggests that a large fire size is needed to obtain a large volume mean diameter for a buoyant diffusion flame at ambient conditions.

There are very limited data for large scale fires. Surprisingly there are no published data on the primary sphere size distribution for the smoke from the Kuwait fires. Our result for the volume mean diameter for a 12 m pool fire, 101 nm [8], is similar to the result for the 2.7 m \times 2.7 m pan fire, 106 nm. Radke *et al.* [13] 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."

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 m - 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 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 nm 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.

Acknowledgment

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

REFERENCES

1. Koseki, H., and Mulholland, G.W., *Fire Technology* 27:54-65 (1991).
2. Koylu, U.O., and Faeth, G.M., *Comb. Flame*, 89:140-156 (1992).
3. Koseki, H., Kokkala, M., and Mulholland, G.W., in *Proceedings of the Second Fire Safety Science International Symposium* (G. Cox and B. Langford, Eds), Elsevier, London, 1991, pp. 865-874.
4. Mulholland, G.W., Henzel, V., and Babrauskas, V., *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., N.Y., 1989, pp. 347-357.12. Ward, D.E., Nelson, R.M., and Adams, D.F., in *Proceedings of the Seventy-Seventh Annual Meeting of the Air pollution Control Association*, Air And Waste Management Assoc., Pittsburg,PA., 1979, Pap. 079-6.3.
5. Lawson, J.R., Mulholland, G.W., and Koseki, H., *Fire Technology*, 30: 155-173 (1994).
6. Benner, B.A., Bryner, N.P., Wise, S.A., Mulholland, G.W., Lao, R.C., and Fingas, M.F., *Envir. Sci. and Tech.*, 24: 1418-1427 (1990).
7. Walton, W., Twilley, W., McElroy, J., and Evans, D., in *Proceedings of the Seventeenth Arctic and Marine Oil Spill Program Technical Seminar*, Ministry of Supply and Services Canada, 1994, Vol.2, pp. 1083-1098.
8. 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., in *Proceedings of the Fifteenth Arctic and Marine Oil Spill Program Technical Seminar*, Ministry of Supply and Services Canada, Cat. # En 40-11/5-1992), 1992, pp. 593-657.
9. Walton, W., Evans, D., McGratten, K., Baum, H., Twilley, W., Madrzykowski, D., Putorti, A., Rehm, R., Koseki, H., and Tennyson, E., in *Proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar*, Ministry of Supply and Services Canada, 1993, pp. 679-734.
10. Laursen, K.K., Ferek, R.J., Hobbs, P.V., and Rasmussen, R.A., *J. Geophys. Res.*, 97: 14,491-14,497 (1992).

11. 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).
12. Ferek, R.J., Ross, J.L., and Hobbs, P.V., Final Report from University of Washington to Environment Canada entitled "Airborne Sampling of Smoke Emissions from the Controlled Burn of 20,000 Gallons of Crude Oil During Open Ocean Conditions Off Newfoundland," 1995.
13. Radke, L.F., Lyons, J.H., Hobbs, P.V., and Weiss, R.E., *J. Geophys. Res.*, 95: 14,071-14,076 (1990).

Table 1. Results for Smoke Yield and Primary Sphere Size

PAN SIZE	ϵ (ASSP)	ϵ (continuous sampling)	Volume Avg. Primary Sphere Diameter
1 meter diameter	0.090		
"	0.109	0.065	58 nm
"	0.097	0.057	
"	0.103		
Avg \pm sigma	0.100 \pm 0.008	0.061	
2.7 meter square	0.148	0.133	
"	0.160	0.153	106 nm
"	0.137	0.162	
Avg \pm sigma	0.148 \pm 0.012	0.149 \pm 0.015	

200 nm

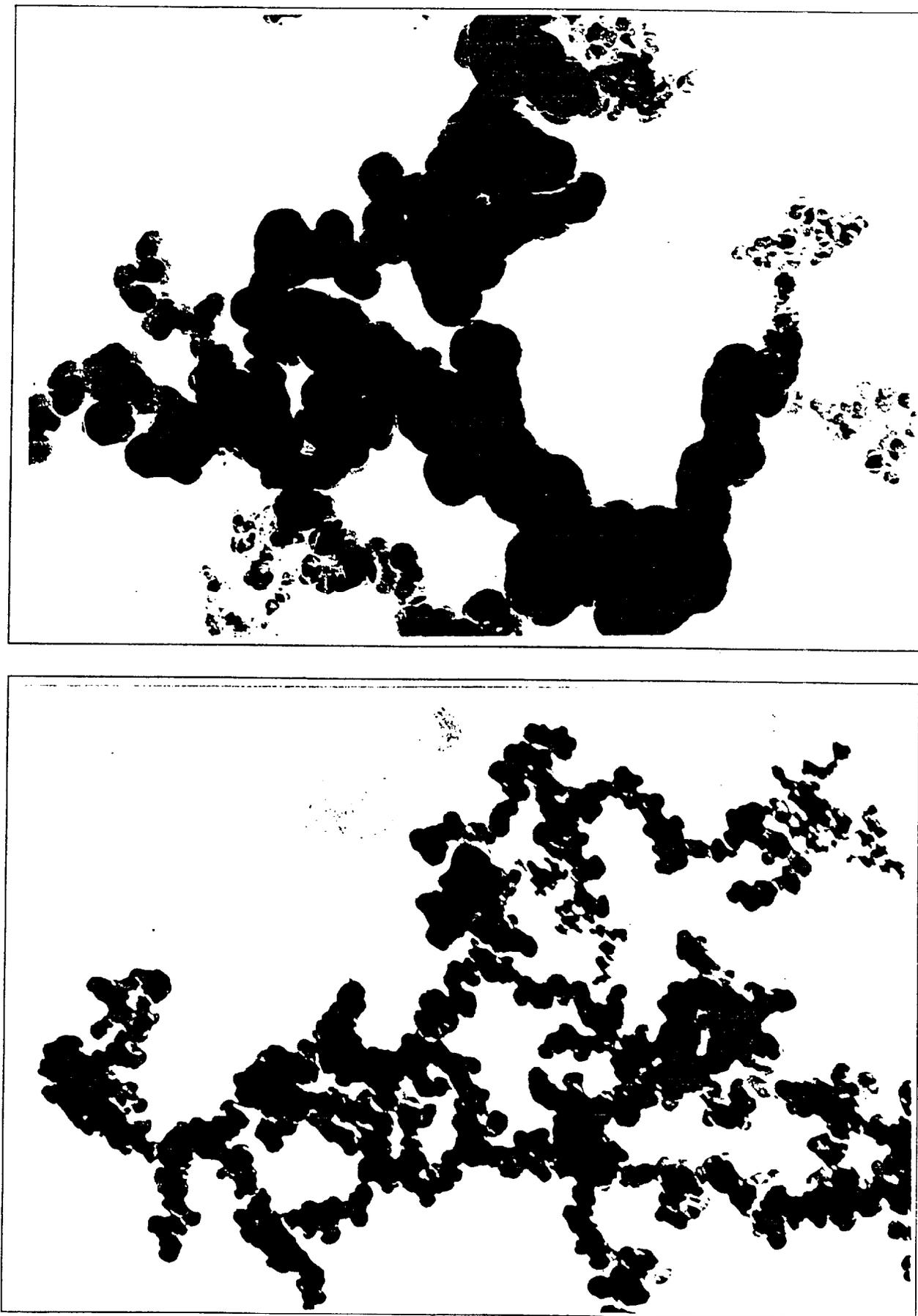


Fig. 1 TEM photographs of smoke collected from crude oil fires for 1 m diameter pan (left) and 2.7 x 2.7 m (right) pan.

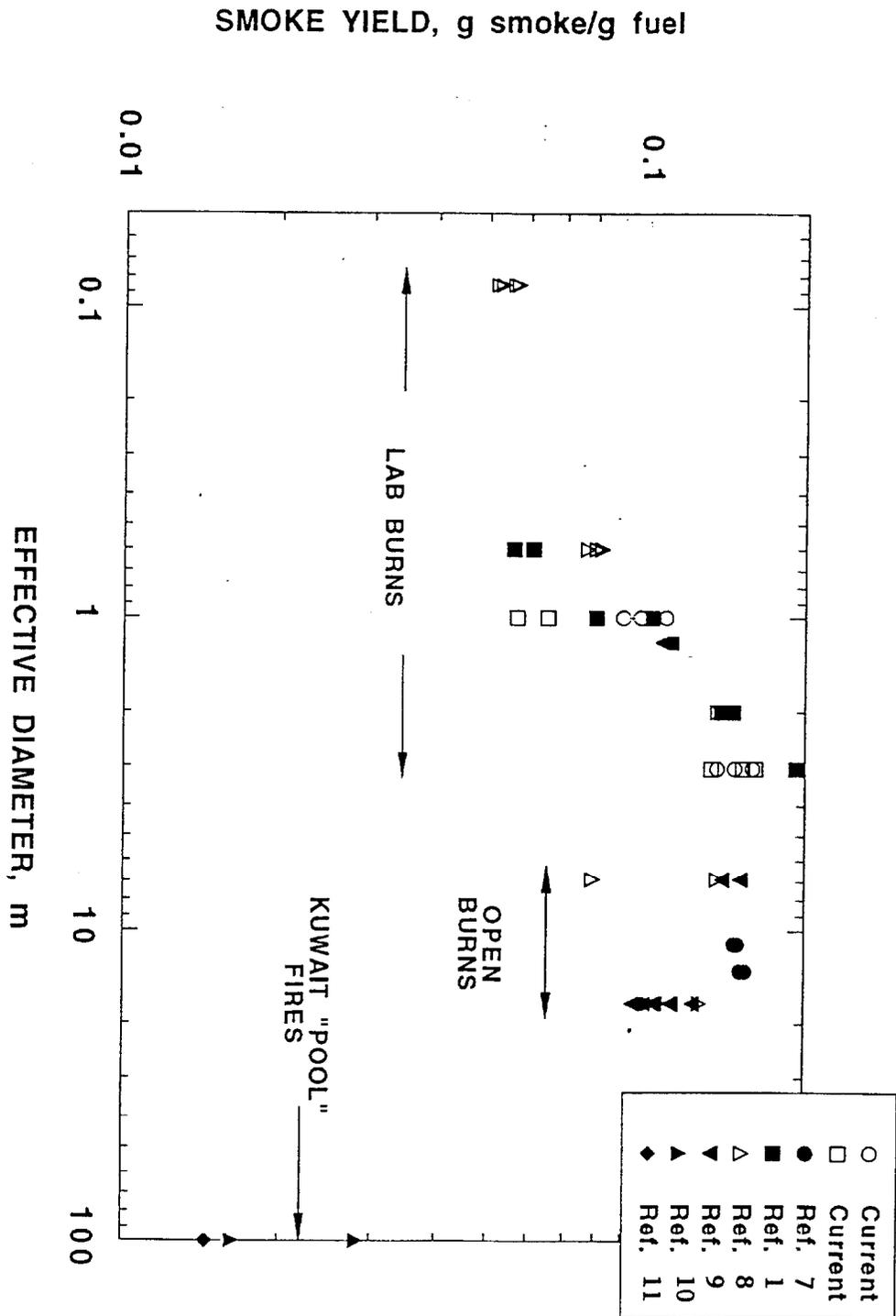


Fig. 2 The effect of pan diameter on the smoke yield of burning crude oil

Discussion

Edward Zukoski: If you go back in the literature on small diffusion flames, there seems to be a time history of the particles. They are big and wet to start with, and they get dried out and they get smaller as they go up. Have you tried to take that sort of time scaling into account in what you've done here?

George Mulholland: My chemist's view of the controlling factors of the particle growth consists of basically two things; one is the time and the other is the temperature. When you look in the carbon black industry, you find that they are very clever in controlling the size. If they want their particles bigger, they lower the temperature, and if they want them smaller, they increase the temperature. So I thought that might be an important parameter along with the time. The problem is that the data do not seem to indicate that the bigger flames have a lower temperature. But when I use a correlation similar to yours, the time scale goes from something like 0.7 s for the total residence time in the flame to something like 1.1 s as you go from the 1 to 3 pool.

Edward Zukoski: It goes in the wrong direction.

George Mulholland: No that's going in the right direction, but I'm skeptical that the time by itself would account for it.

John Rockett: It seems to me that I've seen data for smoky fires: the larger the fire, the higher the core temperature because of the radiation blanketing. The outer surface of the flame can radiate, but the interior radiation is trapped inside. Would that have a bearing on the particle size seeming to go in the wrong direction?

George Mulholland: I agree with that assessment. It's an expected effect that the bigger fire with the radiation trapped would have a higher temperature, at least high up. I think much of the formation of the primary size soot occurs very close to the surface, so I thought that maybe the temperature is lower there, but Hiroshi's data suggests that there's really not much difference if you scale your heights. So, we've looked but it's not obvious.

Howard Baum: I think that there are two factors that are possibly different as you go up in this size. The first, which you've already mentioned, is the residence time of these particles. I suspect that the ratio is much larger than simply even a ratio of D or of D^* . The larger fires with a larger dynamic range of active scale are probably going to have a much more meandering path for the soot particles. So I would expect the age to be much higher for the larger fires than a simple relationship might indicate. The second, a kind of fractal surface volume effect would not be on the particles but on the apparent surface of the smoke exposure to the oxygen. In other words, it might be much harder to see oxygen or spend a smaller fraction of it's time in regions that did have oxygen with the larger fire.

George Mulholland: Howard makes good points. The correlation that I used was actually from Gerry Faeth's paper. But when I look at the non-dimensional expression, it is very similar to the kind of scaling used by Ed Zukoski, as well as Howard Baum and Bernie McCaffrey, in terms of

Discussion cont.

a velocity and height vs. velocity to integrate to get a time. I basically used the expression Faeth developed, but it is based on a scaling approach and may not be realistic for an actual trajectory in any one place within the flame. I think from Howard's comment about the oxygen, one might suspect two populations of particles, if one can envision some reason why the flame structure would be two different, distinct regions that lead to different populations of particles. If something occurs in the vortex on the outside and something else occurs higher up, it requires a chemist's level of understanding.