

³⁴ Bellman, R. E. and Kulaba, R. E., *Quasilinearization and Nonlinear Boundary-Value Problems*, American Elsevier, New York, 1965.

³⁵ Richtmyer, R. D., *Difference Methods of Initial-Value Problems*, Interscience, New York, 1957, pp. 101-104.

³⁶ Godunov, S. K. and Ryabenki, V. S., *Theory of Difference*

Schemes, North-Holland, Amsterdam, 1964.

³⁷ Ames, W. F., *Nonlinear Partial Differential Equations in Engineering*, Academic Press, New York, 1965.

³⁸ Fay, J. A. and Riddell, F. R., "Theory of Stagnation Point Heat Transfer in Dissociated Air," *Journal of the Aeronautical Sciences*, Vol. 25, No. 2, Feb. 1958, pp. 73-85.

DECEMBER 1969

AIAA JOURNAL

VOL. 7, NO. 12

An Experimental Study of Fuel Droplet Ignition

BERNARD J. WOOD* AND WILLIS A. ROSSER JR.†
Stanford Research Institute, Menlo Park, Calif.

By means of photographic techniques, the size histories, ignition lags, and loci of ignition of small (from 100 to 300 μ in diameter), single, freely falling fuel droplets suddenly exposed to a hot, oxidizing atmosphere in a furnace were determined as a function of initial droplet size, oxidizer temperature, fuel composition, and droplet spacing. The results show that ignition lag depends significantly on the temperature of the atmosphere, on the droplet-droplet spacing, and on the chemical nature of the fuel, but it appears to be only weakly affected by the oxygen concentration in the oxidizer. The ignition lag seems to be independent of the initial droplet size if the droplets are large enough to ignite. This characteristic insures that droplets with initial diameters smaller than a characteristic value will not ignite during their lifetimes. In spite of the complexity of the ignition process, the experimental results give qualitative support to theoretical models representing approximations to the physical situation of a spontaneously igniting fuel droplet.

I. Introduction

EXTENSIVE studies^{1,2} of the combustion characteristic of single droplets have contributed to a satisfactory analytical theory of steady-state droplet burning. The ignition process, a transition from a state in which the rate of chemical reaction is small to one in which the rate is large and is associated with a visible flame, is considerably more complex. Recently, the results of theoretical studies of droplet ignition and extinction, based on the model of a spherical droplet in a hot, gaseous environment, have been published.³⁻⁵ Experimental studies, however, are essential as a firm empirical basis for the development and refinement of a satisfactory analytical theory of droplet ignition. The work described in this paper was undertaken with this specific objective in mind.

II. Experimental Studies

A. Approach

To understand the process of droplet ignition, certain parameters and their mutual dependence must be determined quantitatively. For a specific fuel of known thermodynamic and transport properties and a specific oxidizer temperature, we must know the rate of vaporization preceding ignition, the size of the droplet at ignition, and the duration of the ignition lag. Experiments on these variables have been carried out by many investigators using a variety of techniques.¹ In general, however, those who were able to observe the ignition behavior of individual droplets employed large

drops [diameter (D) > 1000 μ] suspended on fibers; those who employed small, unsupported droplets depended on average mass or diameter changes and time extrapolations to obtain vaporization rates and ignition lags.

Our approach was to attempt direct and simultaneous measurement of the rate of vaporization, the diameter, and the ignition lag of small ($D \sim 100 \mu$), freely falling droplets suddenly exposed to a hot oxidizing atmosphere, and to determine the effect on these parameters of droplet initial diameter and oxidizer composition and temperature.

B. Techniques

1. Measurement of preignition and postignition droplet vaporization rates

A photographic technique employing dark-field illumination was adapted to follow a liquid-fuel droplet along a free-fall trajectory in a heated furnace. The device, shown schematically in Fig. 1, consisted essentially of a camera, with a sufficiently long bellows to give 10 \times magnification, looking through a furnace equipped with quartz windows into a dark-field condenser. The condenser collected light from a Strobotac† and focused it in a hollow cone at a point near the vertical axis of the furnace. Light diverging from this focal point fell outside the aperture of the camera lens, unless a spherical transparent droplet was situated in the cone. In that case, the droplet acted as a secondary lens that focused an image of the condenser into the field of view of the camera. The film recorded a bright ring with a diameter proportional to the focal length (and therefore the diameter) of the droplet. The constant of proportionality was determined empirically using glass spheres of known size fused on the ends of fine fibers in addition to freely falling liquid droplets sized by a standard replication technique.⁶

A monodisperse stream of droplets was produced by means of a resonant reed atomizer⁷ driven at 60 cps. This device

Received November 15, 1968; revision received June 23, 1969. Work supported by U.S. Army Edgewood Arsenal under Contract DA-18-035-AMC-122(A). Much of the experimental work in this study was carried out by R. C. Smith.

* Chemist, Surface Physics and Chemistry Program. Associate Fellow AIAA.

† Senior Chemist, Surface Physics and Chemistry Program; now Principal Research Scientist, Avco Everett Research Laboratory, Everett, Mass.

‡ Model 1531-A, General Radio Corp., Cambridge, Mass.

was equipped with a rotating sector wheel that could interrupt the droplet stream. Thus, either a steady stream of droplets following each other at a rate of 60 droplets/sec, groups of a few droplets spaced at about 1-sec intervals, or a succession of separated single droplets could be obtained from the atomizer. In every case the droplets fell through a water-cooled tube extending into the center of the furnace along its axis. When the droplets emerged from this tube, they were suddenly exposed to a high-temperature environment. Air was forced through the water-cooled tube and the furnace from top to bottom at a total volumetric flow rate of 10 liters/min. This resulted in a high linear air velocity in the droplet protection tube which diminished to about 5 cm/sec in the body of the furnace, thus permitting a reasonably uniform ($\pm 5\%$) axial temperature profile to be maintained.

The field of view of the camera encompassed a length of 1.2 cm; hence, in many cases, only a fraction of the lifetime trajectory of a droplet could be recorded on one photograph. Fractional trajectories of various droplets were obtained by raising or lowering the furnace with respect to the camera. Droplet diameters down to 50μ were easily resolved on Polaroid Land 57 (3000-speed) film, using a simple optical comparator to make the measurement.

The Strobotac was ordinarily set to flash at a rate of 400 sec^{-1} . With such illumination, each droplet falling through the field of view of the camera would be recorded on the film as a series of images separated in time by 2.5 msec. Hence, the rate of change of diameter of the droplet with time (and thus its rate of vaporization) could be derived directly from the photograph. Light emitted by burning droplets was too dim to record on the photographs. Whether ignition occurred was determined from visual inspection of the droplet stream in the furnace.

2. Direct measurement of ignition lag

To measure directly the time interval between the arrival of the droplet in the hot furnace and the appearance of a flame, i.e., the ignition lag, a modified dark-field optical system was devised. The droplet stream was illuminated obliquely from the rear by the collimated light beam of the Strobotac. The light was directed at an angle in such a way that the primary beam was outside the field of view of the camera. With this arrangement, light scattered by the droplets in addition to light emitted by flames was recorded by the camera. The images on the film indicated the time-position history of the falling droplet but not the time-diameter history. Hence, in conjunction with these measurements, the initial diameters of the droplet were determined by a standard replication technique.⁶ Since the appearance of the flame could be seen in the photograph, the ignition lag could be measured directly.

C. Results

1. Vaporization rates

Spherical liquid drops have been observed¹ to vaporize in accordance with a diameter-squared law

$$D^2 = D_0^2 - \epsilon t \quad (1)$$

where D_0 is the initial drop diameter, and the slope of the plot of diameter squared D^2 against time t is termed the evaporation constant ϵ . Our results, exemplified in Fig. 2, indicate that this law is followed by hexadecane droplets in the size range and under the conditions employed in our experiments. Our results for hexadecane droplets are summarized in Table 1.

Less extensive measurements of the vaporization rates of aniline droplets were also carried out. At an air temperature of 600°C , droplets of this fuel exhibited an evaporation constant $\epsilon = 4 \pm 1 \times 10^{-3} \text{ cm}^2/\text{sec}$. This is somewhat lower

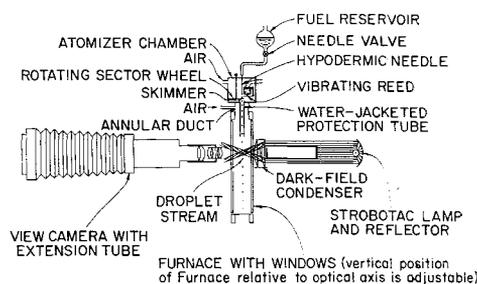


Fig. 1 Schematic diagram of apparatus with dark-field photo-optical accessory.

than the value obtained for hexadecane under similar conditions (Table 1), as one would expect from consideration of the stationary state conductive heat-transfer model of a vaporizing droplet.⁸

2. Characteristic initial droplet diameter for ignition

The results of earlier experiments,⁹ in which 60 droplets/sec streams of fuel oil were directed into a hot oxidizing atmosphere, indicated that a characteristic minimum size for ignition existed at each temperature and oxidizer composition. Droplets initially smaller than this size vaporized completely without the appearance of a flame, while those of larger size ignited and burned with a visible flame. This characteristic diameter decreased with increasing oxidizer temperature. Similar experiments with hexadecane demonstrated similar results, but when the droplet frequency in the stream was reduced first to groups of 3 or 4 drops at approximately 1-sec intervals and finally to isolated single droplets, significantly different results were obtained. The data for single droplets are shown in Fig. 3 and the effect of droplet-droplet proximity is illustrated in Fig. 4.

3. Ignition lag

A substantial number of direct measurements of ignition lag were made on groups of 3-5 hexadecane droplets with initial diameters from 120 to 170μ in the temperature range 590° to 750°C . The data indicate a small dependence on temperature but show no systematic dependence on initial diameter (open symbols in Fig. 5). Based on the observed logarithmic variation of ignition lag τ with temperature T ,

$$\tau = \tau_0 e^{+E/RT} \quad (2)$$

the droplets exhibit an apparent activation energy E for ignition of 13 kcal/mole.

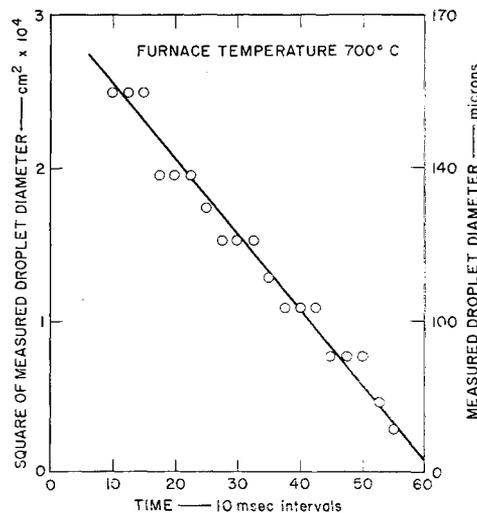


Fig. 2 Typical experimental time-diameter history of vaporizing hexadecane droplet.

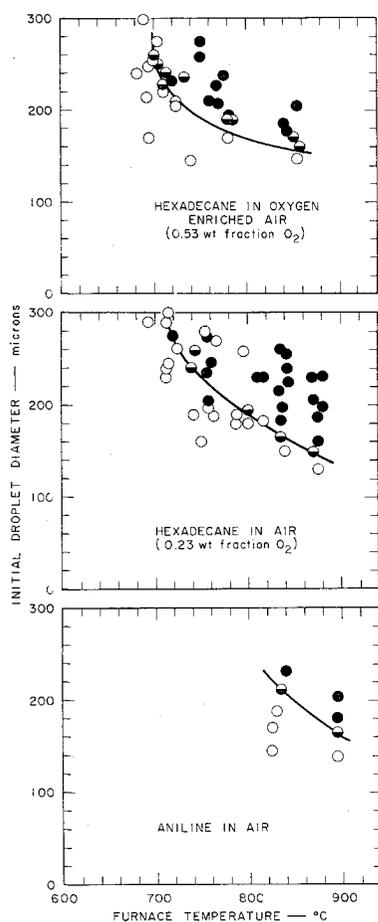


Fig. 3 Characteristic ignition curves showing relationship between initial droplet diameter, oxidizer temperature, and ignitability. Droplet velocity (relative to air) is 60 cm/sec. Solid symbols: droplets ignite; open symbols: droplets do not ignite.

Ignition lag can also be determined indirectly from the measured characteristic diameters for ignition (Figs. 3 and 4) and the measured preignition evaporation constants (Table 1). When a droplet ignites that has an initial diameter equal to the characteristic diameter, it does so in a flash. In this case the initial mass of liquid fuel has virtually completely vaporized before the critical condition for ignition is attained, and when ignition does occur at this moment, the liquid fuel that remains is sufficient to sustain only a brief flash of blue flame. The ignition lag τ is thus the time interval required for the droplet of this characteristic initial size D_0 to be completely vaporized. In such a case, the droplet diameter at ignition D may be considered to be zero, and Eq. (1) becomes $D_0^2 = \epsilon\tau$. Thus, the ignition lag τ can be computed from the measured initial size of the droplet and its rate of evaporation (Table 1). On the basis of the measured characteristic diameters for ignition (Figs. 3 and 4) and the average vaporization rate (Table 1), the values of ignition lag for those droplets that exhibit ignition just before completely evaporat-

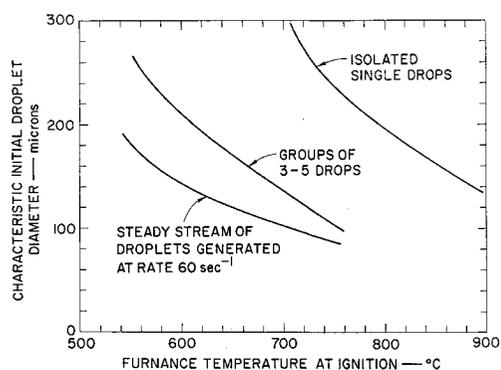


Fig. 4 Characteristic ignition curves for hexadecane droplets in air.

Table 1 Measured evaporation constants of hexadecane droplets (based on droplet diameter)

Atmo- sphere	Furnace Temp., °C	Droplet stream, droplet/sec	Evaporation constant ϵ , (cm ² /sec) $\times 10^3$		Initial droplet diameter, μ
			Before ignition	During burning	
Air	830	3		9.5	173
		60		15.0	158
Air	750	3		6.3	173
N ₂	720		5.3		189
Air	750	60		11.7	196
Air	700	3	6.2	6.3	193
Air	690	3	6.2		196
N ₂	680		6.3		196

ing were calculated and plotted with the direct ignition lag data (solid symbols in Fig. 5). Both sets of data are in agreement. Similar data for isolated single droplets and 60 droplet/sec streams are also shown in Fig. 5.

Ignition lags for single aniline droplets at two temperatures, 835° and 895°C, were also computed from the characteristic diameter for ignition (Fig. 3), and found to be 113 and 68 msec, respectively.

4. Locus of ignition

By using a high-speed motion picture camera, it was possible to follow the disposition of a single droplet over a portion of its trajectory in the furnace. The camera was located so that the region where the droplet ignited was near the center of the field of view. A large number of droplets of hexadecane were photographed in this way. As with the still photographs of the freely falling droplets, neither a contact surface nor a flame boundary could be discerned on the films. However, a yellow region in the wake of a droplet showed up vividly. The appearance of such yellow flames seemed to be associated with the trajectories of two or more droplets traveling close together. The motion pictures showed that the yellow incandescence invariably commenced in the wake of the droplets and pursued them. This suggests that ignition commences in the wake of the droplet with the formation of a flame that propagates in the same direction as the droplet's motion, and possibly eventually envelopes the droplet.

III. Discussion

A. Droplet Vaporization Rates

At furnace temperatures of 750°C and less, the observed rates of vaporization of single hexadecane droplets appear to be identical before and after ignition of the droplet (Table 1). Yet, under identical conditions of oxidizer and temperature, droplets burning in a steady stream of 60 droplets/sec exhibit evaporation constants longer by about a factor of 2 than those observed for nonburning droplets. These latter results agree with earlier work,^{2,9} and with the theoretical model⁸ of droplet combustion in which conductive heat transfer from the flame to the droplet governs the rate of vaporization of the liquid.

We conclude that in experiments in which the evaporation constant ϵ of a single droplet does not increase after ignition the flame is not thermally coupled to the evaporating droplet and does not supply the energy required for continued evaporation of the drop. Rather, the hot furnace atmosphere supplies the evaporation energy and the heat released by combustion is dissipated. It seems likely that such an "uncoupled flame" is a flame in the wake of and at some distance from the droplet. Such wake flames which have been observed in extinction studies with large, stationary-state drops, have been interpreted in a similar way.¹⁰

In the case of a stream of droplets, combustion may begin in the wake of a single droplet, but the resulting flame must

Table 2 Thermodynamic properties of fuels

Fuel	Boiling point, °C	L/Q^a	i^b
Aniline	183	0.021	7.8
Diethylene glycol	245	0.051	5.0
Hexadecane	288	0.021	24.5

^a L = heat of vaporization; Q = heat of combustion.
^b i = stoichiometric oxygen/fuel ratio, moles/moles.

then propagate throughout the "column" of vapor surrounding the stream of droplets and establish a localized high-temperature region into which succeeding droplets fall and are ignited. Under these circumstances the droplet flame must enclose the droplet rather than be restricted to the wake region. It seems likely that convective effects may be important here. However, no experimental indications could be obtained of the effect on ignition of droplet velocity relative to the oxidizer.

B. Ignition Lag and Associated Effects

Previous studies^{1,9,11-14} of droplet ignition do not in themselves give the principal features of even a qualitative model for the process. They do suggest that the total ignition lag represents the time required to reach a critical state or size, that internal heating of the droplet is an important feature of the problem, and that not all droplets will reach the critical state during their evaporation lifetime. It is important to point out that measured values of ignition lag may be dependent in part on the geometric and thermal factors characteristic of the particular experiment. Hence, one must be cautious in attempting to make a quantitative correlation between experimental results and a theoretical analysis of droplet ignition.

One approach⁵ to an analytical model for an igniting droplet considers the energetic conditions which permit a steady-state temperature distribution within a spherical shell of reactive vapor with unequal boundary temperatures. As the temperature of the outer boundary of such a system is raised, a critical condition will be approached in which the rate of heat loss from the reactive region is balanced by the rate of heat generation due to exothermic chemical reaction. This is a metastable situation, however, and a slight increase in temperature will produce thermal runaway (explosion or ignition).

Because of the mathematical complexity, the model deals only with the steady-state energetics of the situation, so it is capable of exhibiting the effects of reaction rate constants and activation energies on ignition, but it does not explicitly include the possibly important roles of fuel-oxidizer stoichiometry, ambient oxygen concentration, and the time required for a super-critical system to ignite. The model does, however, relate the critical initial diameter to the energy of activation and suggests that in practical cases droplet ignitability is insensitive to ambient oxygen concentration, in agreement with our experimental results (Fig. 5).

Recently, Peskin et al.^{3,4} reported another theoretical approach to droplet ignition in which the effects of fuel-oxidizer stoichiometry and oxygen concentration in addition to reaction kinetics have been incorporated. Like the theory of Rosser and Rajapakse⁵ (discussed previously), this model is based on a spherically symmetric droplet-oxidizer system. It successfully accounts for the observed behavior of droplets in the evaporation limit (reaction rate $\rightarrow 0$) and in the steady-state combustion limit (reaction rate $\rightarrow \infty$) where heat- and mass-transfer processes govern the rate of vaporization of a droplet. Furthermore, the model predicts that in going from evaporation to combustion, the system will pass through a characteristic value of reaction rate at which heat is no longer required from the environment but rather is supplied to it. This corresponds to a transition from a

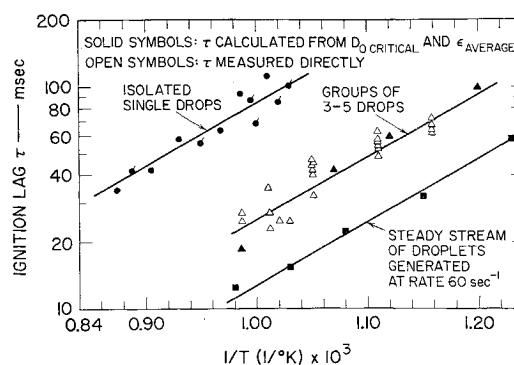


Fig. 5 Ignition lag of hexadecane droplets as a function of oxidizer temperature and droplet-droplet proximity. Oxidizer: air, except ●: 0.53 wt fraction oxygen.

kinetics-controlled regime to a diffusion-limited regime. It is concluded that ignition is associated with such a transition.

Numerical solutions obtained from the model require the insertion of specific values of a multiplicity of independent physical parameters. Such solutions are of doubtful value as a comparison with appropriate experimental measurements. However, a comparison of the functional relationships among the experimental data with those predicted by theory is significant. Thus, a logarithmic dependency of the square of the characteristic droplet diameter on the reciprocal of the ignition temperature predicted by this theory is demonstrated by the experimental data in Fig. 6. The slope of the curves suggests that hexadecane droplets exhibit an effective activation energy for ignition of 14 kcal/mole, independent of their state of aggregation.

The data (Fig. 6) indicate that a given diameter droplet of aniline requires a higher ignition temperature than a like-sized droplet of hexadecane. Based on an examination of the thermodynamic properties of these fuels (Table 2), it seems possible that this may be attributable to their substantially different stoichiometric ratios i . The theory is in qualitative agreement here, also, for it predicts a decrease in ignition temperature when the value i is raised, other parameters being held constant.

In its original form^{3,4} the theory predicts that ignitability increases with decreasing oxidizer concentration. Later calculations¹⁵ not involving a "modified flame surface" invalidated this conclusion and indicated that ignition temperature decreases with increasing oxidizer concentration, but so slowly that the variation would probably not be observable experimentally. Under other conditions, viz., at very low oxidizer concentrations or with fuels exhibiting different com-

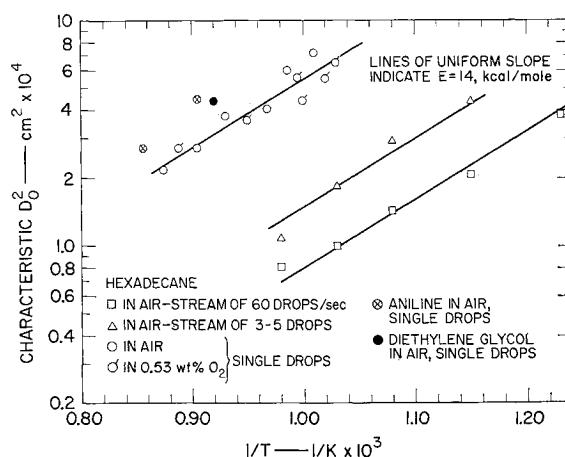


Fig. 6 Relationship of characteristic diameter for ignition and oxidizer temperature for igniting droplets (no wake flames).

bustion kinetics, the theory¹⁵ predicts that oxidizer concentration effects would be more pronounced.

C. Wake Ignition and Burning

The appearance of a luminous zone in the wake of a falling droplet suggests that ignition occurs in this region. Such ignition behavior has been demonstrated¹⁶ for droplets of organic liquids falling through an oxidizing atmosphere containing white fuming nitric acid. Our movies indicate that in many cases the luminous region follow the droplet in its trajectory but never overtakes and envelops it. It seems likely, therefore, that in some instances the "burning" droplets observed in our experiments may have been in fact vaporizing droplets with luminous flames consuming the vapors in their wakes. As mentioned earlier, this notion is consistent with the measured evaporation constants under certain conditions. It is evident from the observed variation in characteristic diameter for ignition with droplet spacing (stream frequency, Fig. 4) that such wake flames are reliable ignition sources for droplets that encounter them.

References

- ¹ Wise, H. and Agoston, G. A., "Burning of a Liquid Droplet," *Advances in Chemistry*, Ser. 20, 1958, pp. 116-135.
- ² Wood, B. J., Rosser, W. A., and Wise, H., "Combustion of Fuel Droplets," *AIAA Journal*, Vol. 1, No. 5, May 1963, pp. 1076-1081.
- ³ Peskin, R. L. and Wise, H., "Ignition and Deflagration of Fuel Drops," *AIAA Journal*, Vol. 4, No. 9, Sept. 1966, pp. 1646-1650.
- ⁴ Peskin, R. L., Polymeropoulos, C. E., and Yeh, P. S., "Results from a Theoretical Study of Fuel Drop Ignition and Extinction," *AIAA Journal*, Vol. 5, No. 12, Dec. 1967, pp. 2173-2178.
- ⁵ Rosser, W. A. and Rajapakse, Y., "Thermal Stability of a Reactive Spherical Shell," *Combustion and Flame*, Vol. 13, 1969, pp. 311-317.
- ⁶ May, K. R., "The Measurement of Airborne Droplets by the Magnesium Oxide Method," *Journal of Scientific Instruments*, Vol. 27, 1950, pp. 128-130.
- ⁷ Rayner, A. C. and Hurtig, H., "Apparatus for Producing Drops of Uniform Size," *Science*, Vol. 120, 1954, p. 672.
- ⁸ Wise, H., Lorell, J., and Wood, B. J., "The Effects of Chemical and Physical Parameters on the Burning Rate of a Liquid Droplet," *Fifth Symposium (International) on Combustion*, Reinhold, New York, 1955, pp. 132-141.
- ⁹ Wood, B. J., Rosser, W. A., and Wise, H., "A Study of Ignition and Combustion of Fuel Droplets," Publication 1722, American Petroleum Institute, Div. of Marketing, New York, 1963, pp. 19-21.
- ¹⁰ Agoston, G. A., Wise, H., and Rosser, W. A., "Dynamic Factors Affecting the Combustion of Liquid Spheres," *Sixth Symposium (International) on Combustion*, Reinhold, New York, 1957, pp. 708-717.
- ¹¹ Kobayasi, K., "An Experimental Study on the Combustion of a Fuel Droplet," *Fifth Symposium (International) on Combustion*, Reinhold, New York, 1955, pp. 141-148.
- ¹² Nihiwaki, N., "Kinetics of Liquid Combustion Processes: Evaporation and Ignition Lag of Fuel Droplets," *Fifth Symposium (International) on Combustion*, Reinhold, New York, 1955, pp. 148-156.
- ¹³ Masdin, E. G. and Thring, M. W., "Combustion of Single Droplets of Liquid Fuel," *Journal of the Institute of Fuel*, Vol. 35, 1962, pp. 251-257.
- ¹⁴ El Wakil, M. M. and Abdou, M. I., "Ignition Delay Analyzed from Self-Ignition of Fuel Drops," *SAE Journal*, Vol. 71, May 1963, pp. 42-45.
- ¹⁵ Polymeropoulos, C. E. and Peskin, R. L., "Ignition and Extinction of Liquid Fuel Drops—Numerical Computations," *Combustion and Flame*, Vol. 13, 1969, pp. 166-172.
- ¹⁶ Wood, H. L. and Charvonia, D. A., "The Ignition of Fuel Droplets Descending Through an Oxidizing Atmosphere," *Jet Propulsion*, Vol. 24, 1954, pp. 162-65.