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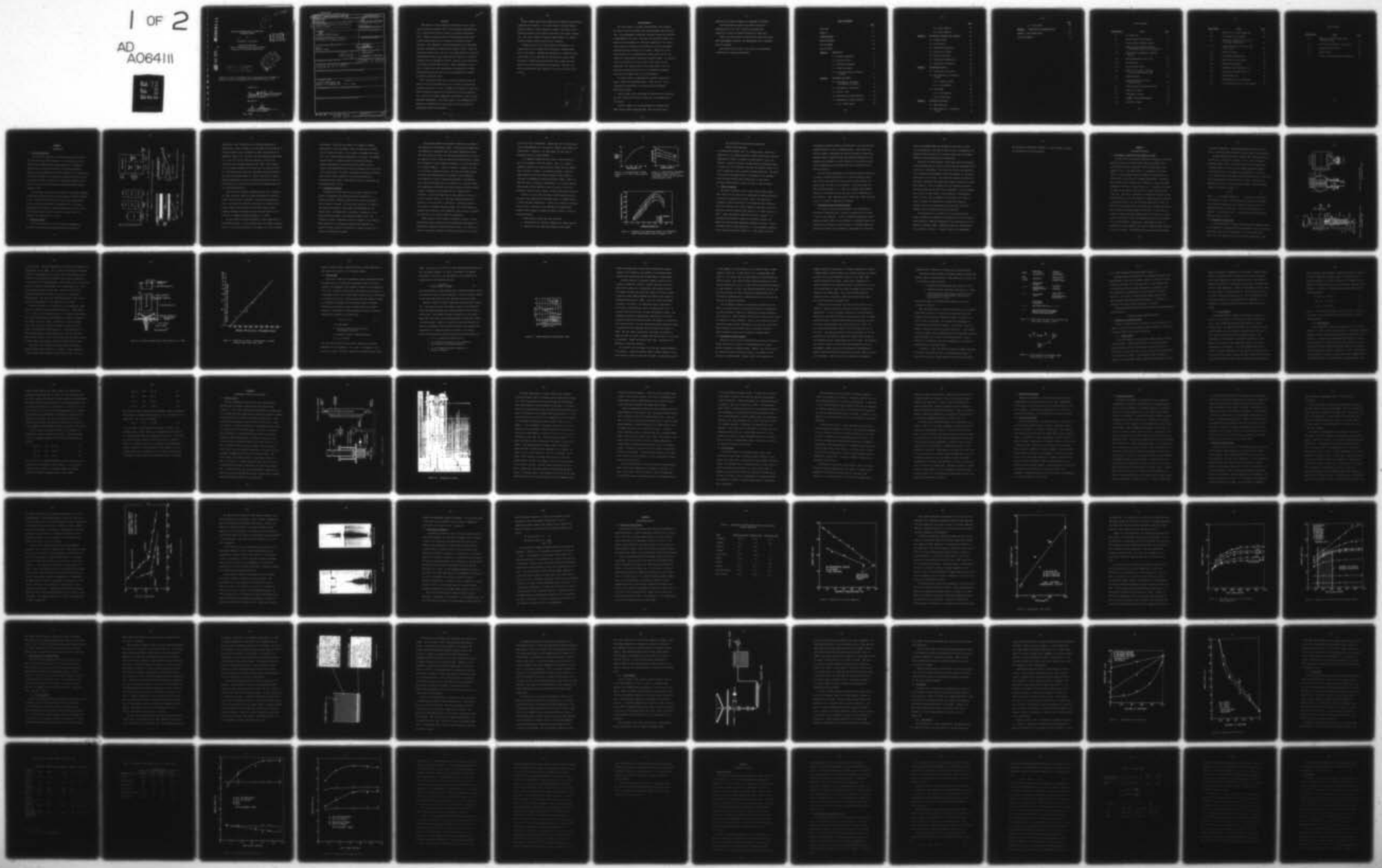

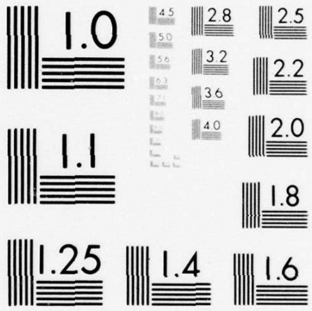
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SOOTING CHARACTERISTICS OF LIQUID POOL DIFFUSION FLAMES

by

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Princeton University
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Submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering from Princeton University, 1978.

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ABSTRACT

With regard to a more economic and efficient use of our natural petroleum and coal resources there is the inevitable trend toward the use of higher boiling fractions as well as alternative hydrocarbon fuels. However, increasing content of high molecular weight hydrocarbons results generally in an increase of particulate and soot formation. This represents a serious disadvantage and is undesirable from both environmental, operational, and economic reasons. Smoke and particulate emission play a key role in the smog formation in industrial and metropolitan areas, while carbon and soot deposits in a combustor increases the heat exchange too severely, leading to local overheating, and eventually causing engine failure. Recent experiments in these areas are aimed at not only understanding the mechanisms of forming condense-phase nuclei but also at ways of supressing soot formation by additives inside the flame.

This investigation deals with a liquid fuel diffusion flame and examines the use of the smoke point test as a means of qualitatively measuring the ability of a fuel to produce soot relative to other fuels. Results indicate the necessity of controlling the initial conditions (i.e. initial fuel (burner) temperature and airflow) in order to obtain meaningful measurements. This thesis reports a new technique for the smoke point determination that has proved to be more accurate and reproduceable than previous methods.

Recent studies indicate water addition in a premixed flame chemically suppresses soot formation. As a result, addition of water inside a diffusion flame is a likely direction to pursue. Both water in fuel emulsions and direct steam injection were used in the present investigation. The results indicate a dominant thermal effect and a possible secondary chemical effect of water on soot formation.

Blending of various fuel types reveals the domination of an aromatic fuel over an aliphatic when determining a combined smoke point of the mixture. Applying this information to alternative hydrocarbon fuels, the oil shale and coal derived fuels, having a higher percentage of aromatics than conventional fuels, produce soot more readily than their petroleum derived counterparts. Testing of oil shale and conventional fuels supplied by the Air Force verifies this result.

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This thesis carries T-1393 in the records of the Department of Mechanical and Aerospace Engineering.

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CHAPTER 1

INTRODUCTION

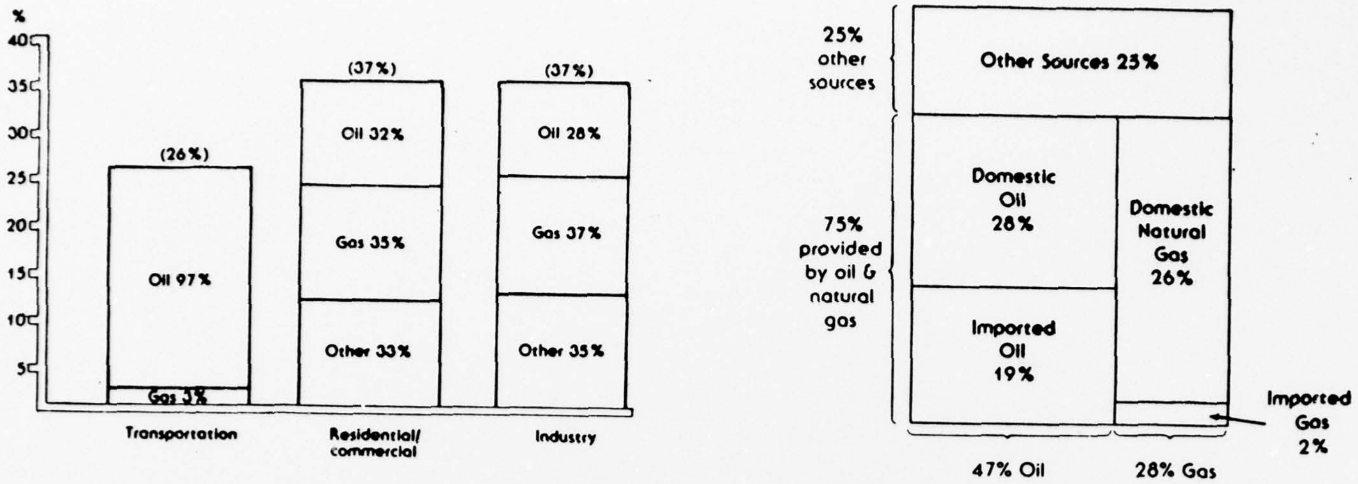
1.1 Petroleum Dependence

Over 75% of all energy used in the United States comes from oil (47%) and natural gas (28%) (Figure 1.1). At the present time one thinks of the automobile, power generating plants, and industrial manufacturing as the major contributors to pollutant generation; however, with the projection of aircraft using 30% of the transportation fuel by the year 2000, not to mention the numerous applications of the gas turbine in industry, examination of future fuel supplies from the point of view of the aviation industry becomes increasingly important (Longwell, 1976).

The first major realization of the extent of the present dependence on petroleum and hydrocarbon fuels occurred during the OPEC oil embargo of 1973. Since that time the price of oil has risen from $4.65 per barrel to about $14.00 per barrel in September 1977. As a direct consequence of this increase, the price per gallon of JP-4 to the Air Force increased from 11 cents in June 1973 to about 43 cents in September 1977 (Mikolowsky et al. 1977).

1.2 Alternative Fuels

Such price increases in oil begin to make the production of alternative fuels from non-petroleum resources both viable and



A) Where U.S. Energy Went in 1976

B) 1976 Total U.S. Energy Demand

Figure 1.1 U. S. Energy Use (after Legassie et al.,1977)

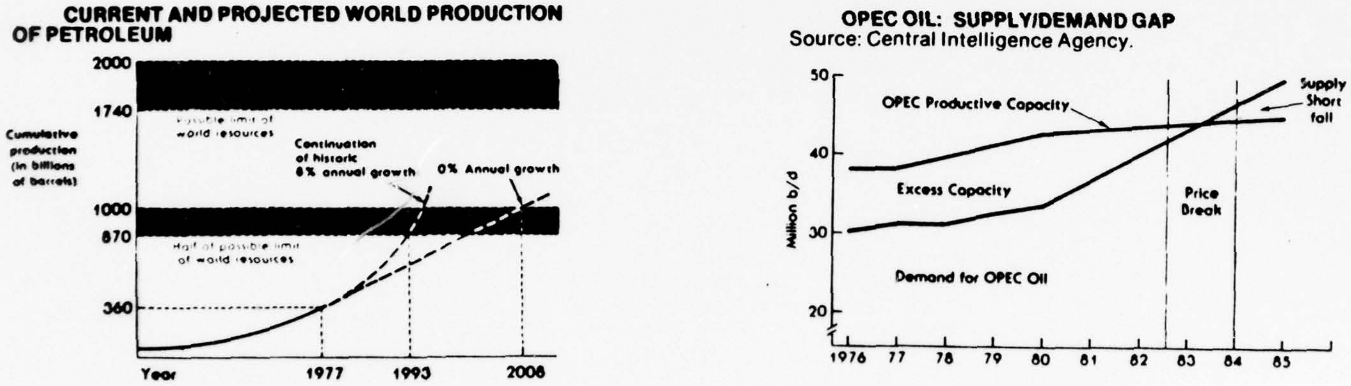


Figure 1.2 Petroleum Demand and Production (after Legassie et al., 1977)

competitive. With the prediction that worldwide production of petroleum will reach a maximum in the late 1980's while the demand for energy continues to grow, development of other energy resources is imperative (Figure 1.2). Studies by the Rand Corporation (Mikolowsky et al. 1977) for the Air Force show synthetic JP fuel the best alternative fuel projected through the year 2000. Since synthetic JP can be readily produced from coal and since coal makes up 90% of U.S. conventional energy reserves, indications would seem synthetic fuel from coal derived sources is a logical alternative to explore. Projected production costs show the average delivered unit fuel cost for synthetic JP is about 39 cents per gallon, extremely competitive with petroleum based fuels.

While the use of synthetic hydrocarbon fuels, such as synthetic JP, seems attractive, there are serious differences with respect to natural fuels that must be realized. Variations from conventional fuel in such aspects as volatility, viscosity, and concentrations of olefins, sulfur, and trace metals will no doubt occur; however, changes in hydrogen and nitrogen content are characteristics which will cause the biggest problems (Blazowski et al. 1976).

The most important parameter expected to change significantly is fuel hydrogen content. As will be shown later, the carbon to hydrogen ratio is a very strong indication of the tendency of a fuel to produce particulates. (A low C/H ratio means a low tendency to produce particulates.) Due to the higher content of aromatics (50 to 80%), raw coal liquids are known to have a carbon to hydrogen ratio around .80 to .65. From experimental experience it is evident a low hydrogen content results in a larger quantity of particulate formation. Industrial hydrogenation of alternative fuel, however, leads to "cleaner" fuel specifications but obviously increases the cost of such a fuel significantly. The serious consequence of burning coal derived fuels without further treatment is the increased formation of particulate wastes, which is objectionable from both a combustion and environmental point of view.

1.3 Particulate Formation

Extended use of lower grade fuels is strongly connected to the problem of suppressing and reducing particulate formation in a combustion process. Essentially there are two types of particulate matter formed in an engine. The first type, called soot or smoke, is the particulates formed in the gas phase and discharged with the exhaust gases. The second type, called coke or cenospheres, is the particulates which adhere to the combustion chamber walls. The formation of either is undesirable from the viewpoint of any combustor. Smoke formation is an environmental nuisance and especially in a military tactical situation the presence of a smoke trail may aid in aircraft identification in combat.

A more serious problem in particulate formation is the effect of coke formation on the combustor itself. The particulates formed from the combustion of hydrocarbon fuels are mainly comprised of carbon. This solid carbon can effect the radiative characteristics of a flame or combustion process. While the radiation and increased heat transfer may be beneficial in some industrial processes, it is very detrimental in a turbojet combustor. A layer of carbon on a combustor wall acts as an insulator, inhibiting cooling. The lower the hydrogen content the higher the carbon deposition and combustor liner temperature. This condition can result in warping and cracking of the combustor not to mention increased stress on the engine (i.e. increased turbine inlet temperatures and possibly particles striking the turbine blades). A general consequence of coke deposition is a reduced overall efficiency. Severe coke deposition can cause combustor failure in as little as 30 hours (Wear et al. 1956) while reduced deposition can extend the life to the order of 1,000 hours. Increasing combustor life results in tremendous economic savings. With carbon deposition, combustor walls remain hot after combustion stops resulting in possible post-ignition of fuel, such as occurs in automobiles.

Studies show very little carbon is necessary to obtain a visibly dense exhaust plume, with particle size distribution being important in determining the degree of visibility (Faitani 1968). As a result, the effect of particulate formation on combustion efficiency is very small and in most cases is negligible. Studies show loss of heating value due to coke deposition is on the order of .004 per cent (Schalla and Hibbard 1957). Similarly, one would expect the same order of magnitude loss due to smoke formation.

It is generally agreed the major cause of carbon formation is due to the presence of fuel rich regions. Thus, in a turbojet combustor (generally an overall fuel lean system) fuel rich regions exist and carbon is formed. As combustors are made to operate at higher pressure ratios with better efficiency, carbon formation increases as experimentally verified by Faitani (1968). Figure 1.3 shows the effect of pressure on smoke density. As a first approach, burner design has been modified but one can only go so far until problems of flame stability, relight, and many others become important.

Figures 1.4 and 1.5 show the effect of fuel hydrogen content on combustor liner temperature and SAE smoke number (a standard measure of smoke formation) respectively. In each case a decrease in hydrogen content means an increase in liner temperature and smoke number. Longwell (1976) suggests a maximum 20% aromatic content to avoid the following problems:

1. Smoke formation under high power conditions.
2. Overheating of the combustion chamber due to flame radiation.
3. Formation of solid carbonaceous deposits which caused

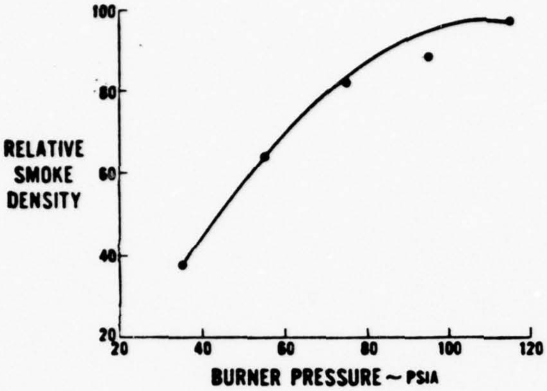


Figure 1.3 Pressure Effect on Smoke Emission: F/A = 0.0176 (after Faitani, 1968)

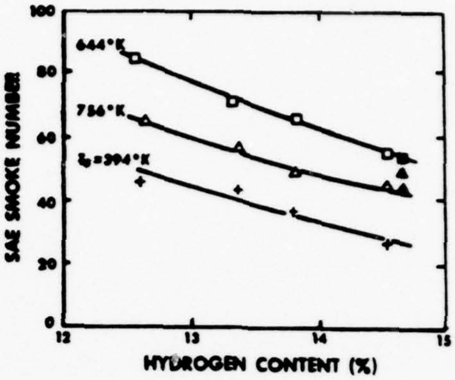


Figure 1.4 Smoke Emission Dependence on Hydrogen Content (shaded data correspond to shale oil JP-4 results) (after Blazowski, 1976)

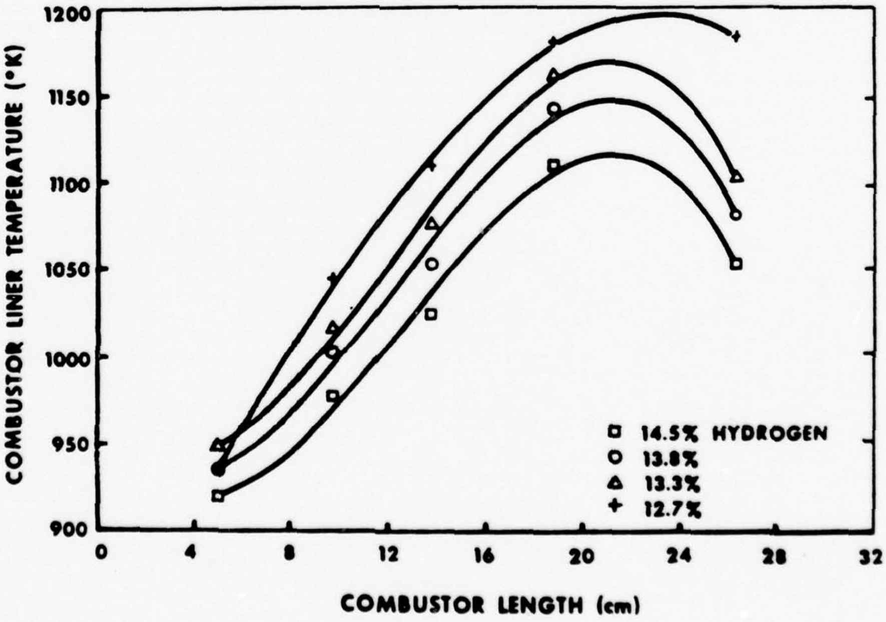


Figure 1.5 Combustor Liner Temperature Results at Low-Pressure Ratio Cruise Condition (after Blazowski, 1976)

fuel spray distortion and turbine damage when deposits became detached.

In transportation systems, such as a turbojet engine, the need for compactness of the combustor results in rapid cooling rates, eventually decreasing the ability to oxidize the carbon before it leaves the combustor. Current aviation gas turbines quench the combustion gases so rapidly that it is difficult, even when the aromatic content of the fuel is restricted to 20%, to achieve low smoke combustion. The effect of alternative hydrocarbon fuels on the combustor can be imagined. Using low grade alternate fuels would result in large carbon formation unless appropriate steps are taken to stop the process.

1.4 Trends in Research

The overall conclusion one must come to when studying smoke or coke formation is the great need to understand the problem and process of particulate formation more clearly. Work in the past mainly attempted to explain the physical or environmental factors effecting particulate formation with a lesser emphasis on proposing theories of particulate formation (Minchin 1931, Schalla et al. 1954, Clarke et al. 1946). Gaydon and Wolfhard (1953) were the first to present in an organized manner different theories of particulate formation and comment on them based upon experimental evidence of the day. Schalla and Hibbard (1957) in NACA 1300 report in a concise manner the physical factors effecting particulate formation. In 1965 Palmer and Cullis developed an extensive review of the literature to this date and also presented theories in view of experimental data. Recent years have seen the attempt to understand and isolate the process of particulate formation mainly in premixed flames with different mechanisms on soot formation being proposed. As work continues it is realized that more than one mechanism may be involved, which will be explained in more detail in Chapter 2.

Practical work in suppressing soot formation using metal additives in flames is reported from Cotton et al. (1971) and Feugier (1975). Their results show addition of certain metals (mainly alkaline earth metals) cause a decrease in soot formation. Still more recent work done by Müller-Dethlefs et al. (1976) on a premixed flame shows the addition of H_2O inside the flame also plays a role in decreasing the soot formation. Thus, additives inside a flame seem a likely direction to go in an attempt to suppress soot formation.

1.5 Investigation Areas and Thesis Outline

As a result of work currently underway in the Fuels Research Laboratory on emulsified fuels, interest was generated on the effect of water on soot formation. In view of published experimental results showing a chemical effect of water addition in a premixed flame, it was postulated water addition on the fuel side of a diffusion flame would substantially inhibit soot development by forming OH in the fuel-rich side of the diffusion flame. The OH radical is then able to attack the soot precursors. The chemical effect of water on suppressing soot formation should be greater in a diffusion flame, thus this proposal formed the main motivation for the investigation.

Basically, the work performed in this thesis deals with diffusion flames resulting from the burning of liquid fuels and encompasses three main areas of investigation. The first area involves the examination of the wickless burner proposed by Clarke and stresses the testing and modification of this burner. The second area involves the addition of H_2O inside a diffusion flame using either emulsion structures or direct steam addition. Lastly an examination of new synthetic fuels made available through the Air Force will be presented. A two step approach will be taken in these studies. First, mixtures of some different classes of fuels, such as aliphatic with aromatic, will be made in order to determine the dominant soot formation fuel component. Secondly, tests will be conducted on some alternative fuels which represent viable alternative fuels for Air Force use.

The organization of this thesis is in the following manner. Chapter 2 examines the background of the smoke point test and theory of carbon formation, laying the groundwork for the investigation of water addition in diffusion flames. Experimental apparatus and techniques are the subject of Chapter 3. Chapter 4 looks at the experimental results which are discussed in Chapter 5. Lastly, Chapter 6 contains the conclusions of this investigation.

CHAPTER 2

BACKGROUND AND THEORY

2.1 Development of Smoke Point and Tendency to Smoke

As early as 1927 investigators endeavored to determine the sooting qualities of fuels in diffusion flames (Kewley and Jackson 1927). Correlations were made by comparing either the smoke height or the tendency to soot. The smoke height is a consequence of the flame itself. A small diffusion flame will exhibit a characteristic blue color overall, very similar to a premixed bunsen flame. Increasing the fuel flow causes a luminous tip to develop at a particular height (dependent on fuel type, testing device, etc.). In reality, the luminous zone does not appear at the tip, but at a point within the blue flame area. This onset of luminosity is reproducible; however, because this point occurs at very low heights in a diffusion flame its accuracy is very much in doubt. For this reason the smoke point is used. As fuel flow is increased further, the luminous zone extends itself higher until it finally protrudes through the blue zone. At this point the flame has a long red streak extending from the tip and soot is visibly emitted. The height at which this phenomenon occurs is often referred to as the smoke height or smoke point. Smoke emission occurs at a height that is large compared to the onset of luminosity and, therefore, is easier to measure. Reproducibility and accuracy are also improved by using the smoke point. When comparing different fuels using this test, a lower flame height indicates a greater amount of soot formation.

Another parameter often used to describe soot forming qualities of various fuels is called the "tendency to soot." First introduced by Kewley and Jackson (1927), this correlation consists of subtracting the smoke height of each fuel from the maximum measurable height in a particular device. A low number then corresponds to a less sooty fuel. Minchin (1934) later modified this correlation since, he criticizes, the previous definition specifies any fuel capable of reaching the maximum scale height as having no sooting tendency. Minchin therefore defined the "tendency to smoke" as

$$S_t = \frac{K}{h} \qquad (1)$$

where S_t is the smoking tendency, K is, a constant on the same order of magnitude as h, and h is the flame height just short of smoking. (With h given in millimeters, K was originally chosen as 320 to be consistant with data for kerosene. That value of 320 persists as a standard.) This definition for S_t proves valuable when correlating different classes of fuels.

2.2 Development of Smoke Lamps

As early experimentors learned, flame shape and size depends strongly on the geometry of the apparatus used in measurements. One of the earliest lamps used for measuring the smoke point is the Davis factor lamp (Fig. 2.1a). The lamp was first used in 1926 and incorporates a wick

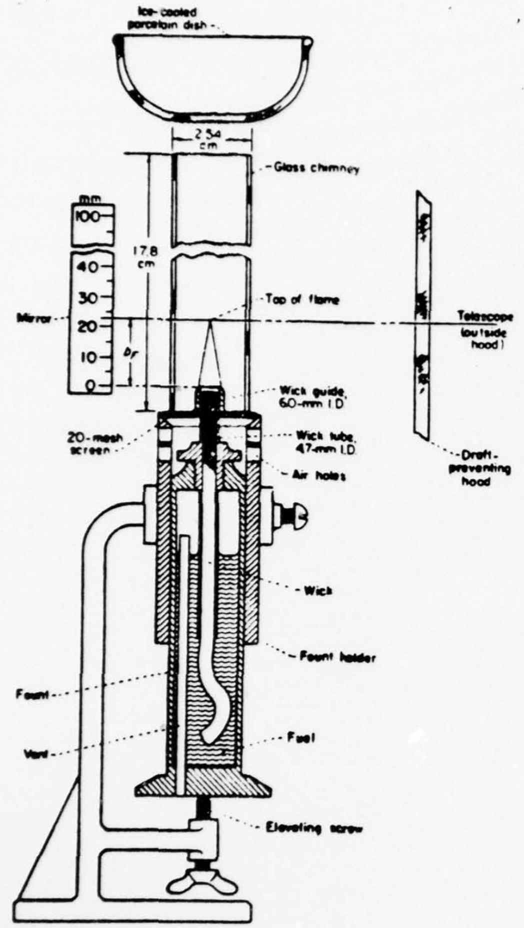


Figure 2.1a NACA Modified Davis Factor Lamp (NACA 1300)

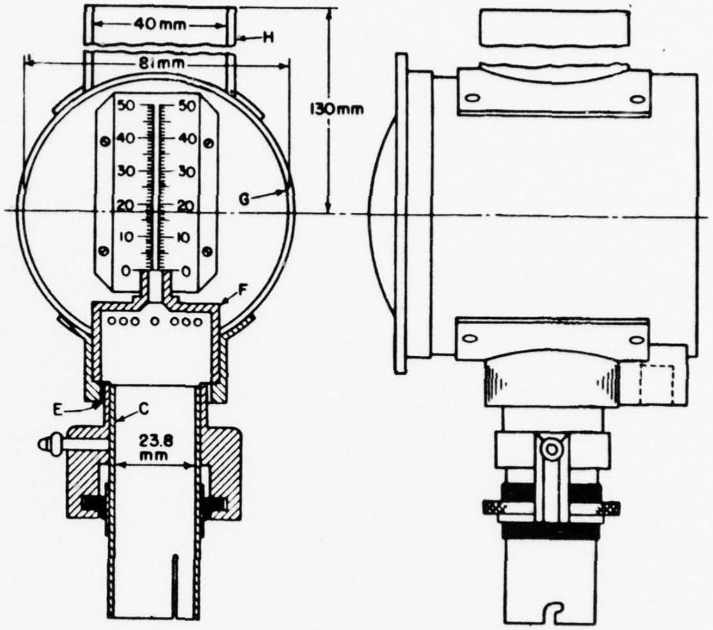


Figure 2.1b IPT Smoke Lamp (Inst. Petrol. Tech.)

to burn the fuel. The main disadvantage of this lamp is its limitation to flame heights of only 102mm. Later, in 1935, the Institute of Petroleum attempted to standardize the use of such a wick burning lamp by setting criterion for the apparatus and technique when testing for smoke point of a particular fuel (namely kerosene). The IP lamp is also a wick burning type and is limited to flame heights of only 50mm (Figure 2.1b). Even today testing procedures use this lamp. The first test, IP 57/55, evaluates a kerosene with respect to its ability to burn without producing smoke. The second test, ASTM method DI322-75, uses the same lamp for the determination of the smoke point of jet fuels.

Another lamp found in the literature for use in determining smoke point is the wickless burner proposed by Clarke et al. (1946) (Figure 2.1c). Basically, this apparatus consists of a wickless, conical burner. This lamp accurately measures flame heights up to 450mm; a significant improvement over previous lamps. Work done by the Sun Oil Company (Jezel 1950) shows that a definite correlation exists between the wickless and wick-burning lamp (Figure 2.2). Each lamp displays the proper trends; however, findings indicate the wick type lamp gives more consistent results. Only in the case when the flame height exceeds IP lamp's range, Jezel suggests, should the wickless burner be used.

Also found in the literature are various devices for burning gaseous diffusion flames (Schalla et al. 1954). A visual observation is used to detect the first smoke issuing from the flame. The rate in

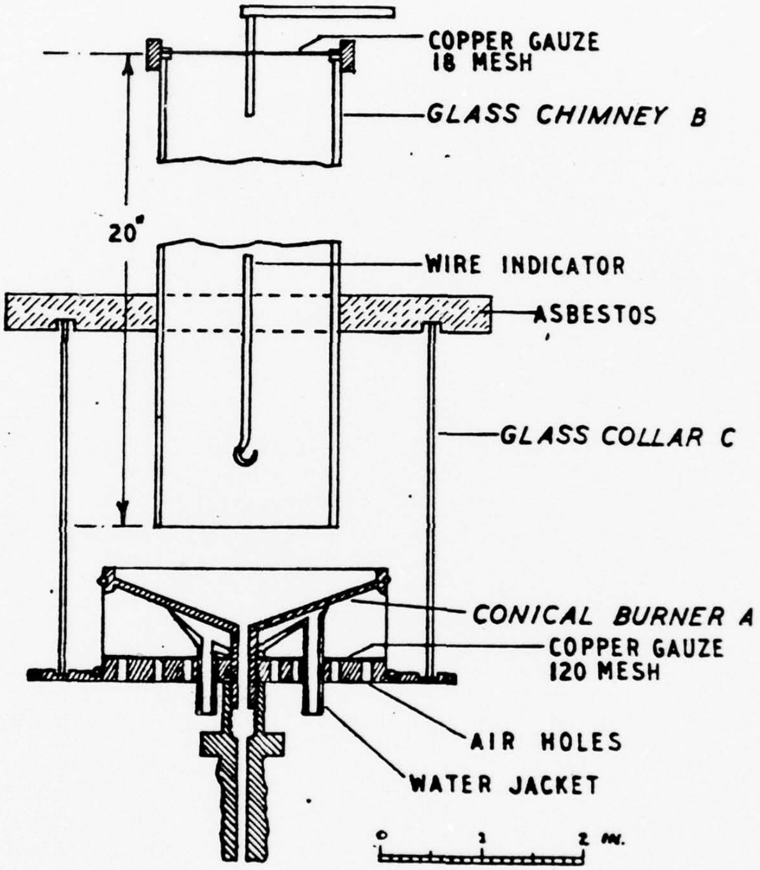


Figure 2.1c Clarke Wickless Burner (after Clarke et al., 1946)

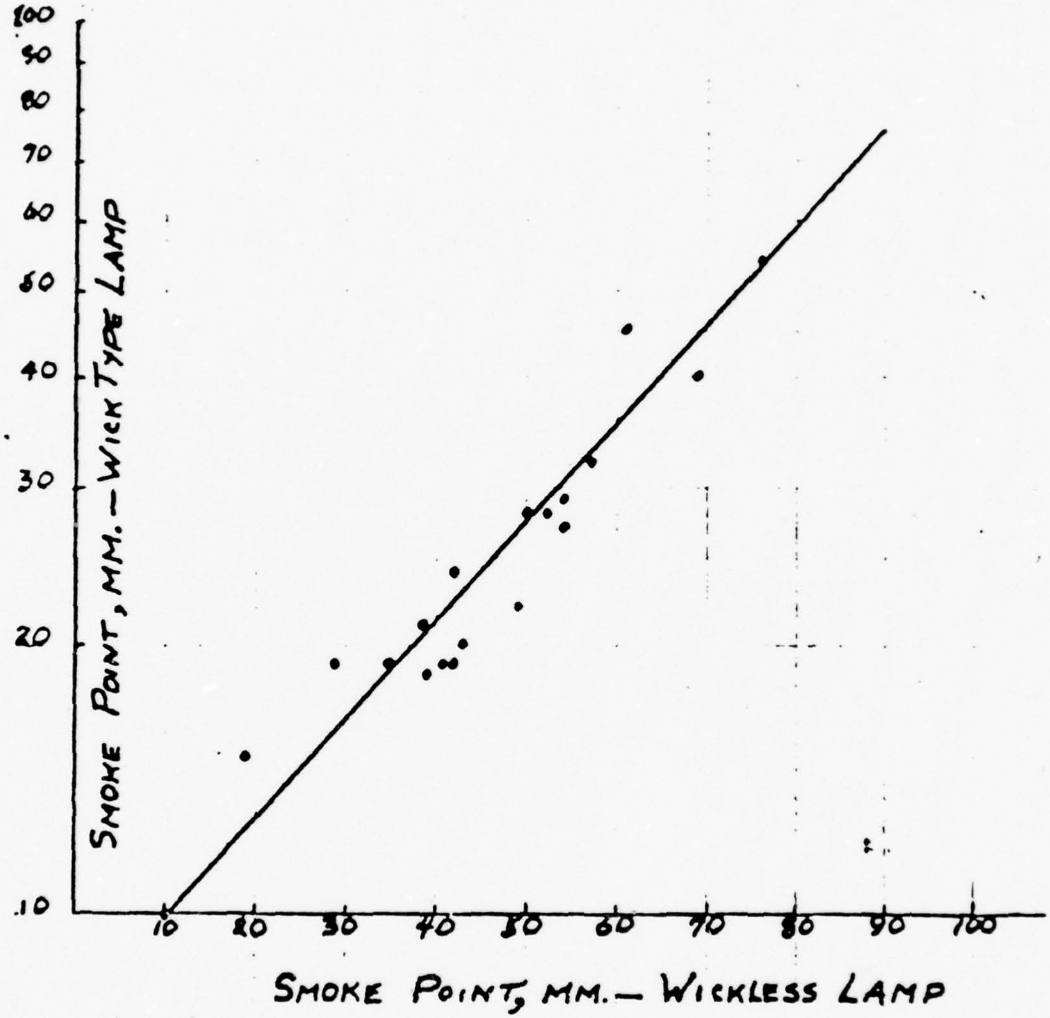


Figure 2.2 Smoke Point of Fuels: IPT Wick Lamp vs. Clarke Wickless Lamp (after Jezel, 1950)

grams per second at which a hydrocarbon could be burned smoke free is then used as the criterion for its smoking tendency.

2.3 Previous Work

Early work in smoke point determination mainly considered kerosenes. The objective was to evaluate the testing method and try to obtain insight on the dependence of the tendency to smoke with the composition of the fuel. The direct application of such tests was the selection of an appropriate fuel to burn in wick lamps, the main source of illumination in the world at that time. Minchin reasoned that the tendency to smoke of a substance is determined by the molecular volume of combusted products and the molecular volume of oxygen required for complete combustion. He proposed the following empirical formula to correlate individual fuel properties and flame height:

$$\frac{1}{V} = K_1 \, y/x + K_2 \tag{2}$$

V = flame volume

y = molecular volume of oxygen required for complete combustion

x = molecular volume of combusted products

K_1, K_2 = constants

Since the flame he used was conical with a constant base, Minchin concluded $1/V = 1/h$ x constant. If x and y are known, h can be found if K_1 and K_2 are known. Minchin then proceeded to test various fuels. A plot of y/x vs. 1/V for all fuels tested was made and from this plot the general constants K_1 and K_2 were found (to be applied universally to all fuels). He then obtained a final expression for height based on these constants given by:

$$h = \frac{(x + 3)^2}{36.1\,xy + 54.9 - 26.65x^2} \qquad (3)$$

This relationship, he stated, applied only to complete combustion and was not accurate for highly volatile substances. Volatile substances tended to have large flame radii and, thus, departed from the cone shape.

Equation 3 predicts trends in hydrocarbon groups accurately (Figure 2.3). The results show that the tendency to smoke of the hydrocarbon series investigated decreases with increased number of carbon atoms or boiling point. The paraffins represent an exception to this general scheme since they show a weak increased tendency to smoke with increase in molecular weight. Addition of paraffinic side chains explains the trend for the different series (except paraffins) since increasing the paraffinicity of a molecule decreases the effect of the nucleus. General conclusions made by Minchin concerning the smoke tendency are:

1. It is a valuable and informative test.
2. It is directly proportional to the complexity and composition of petroleum mixtures.
3. It is a fundamental property dependent on molecular structure.

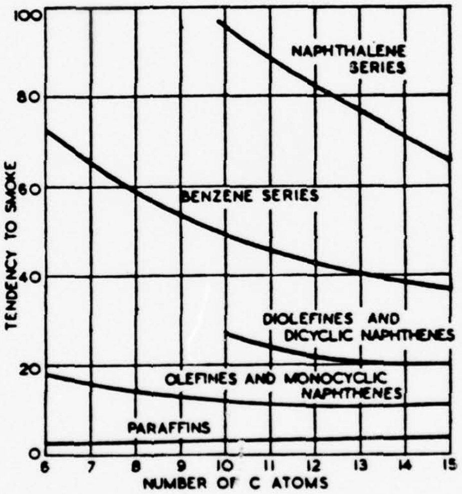


Figure 2.3 Smoke Tendencies (after Minchin, 1931)

Minchin's findings seem to behave quite satisfactorily; however, inherent in his findings is the inability to distinguish between branched chain molecules having the same number of carbon atoms.

In 1946, Clarke et al. proposed a method to account for the variation in molecular structure. Clarke's work had a practical application in mind, that of developing a new incendiary material (for bombs) that would not obscure the target with clouds of smoke. To begin his work, Clarke developed the wickless burner capable of measuring flame heights to 450mm. In all, he tested 115 different substances in the burner. For hydrocarbon fuels, Clarke found a correlation by considering the carbon to hydrogen ratio (C/H). He found the lower the C/H ratio, the lower the tendency to smoke. This technique was useful for comparing most substances but it did not adequately explain the difference between, for example, an iso-paraffin and a normal paraffin. For this inconsistency Clarke thought the degree of compactness of the hydrocarbon molecule effected the tendency to smoke. The more compact the molecule, the greater the tendency to smoke even when the carbon to hydrogen ratio was the same for two different molecules. Further work done by Hunt (1953) substantiates the dependence on molecular structure.

In the 1950's, with the advent of the jet age, interest renewed in soot formation. Gaydon and Wolfhard (1953) included a chapter on solid carbon formed in flames in their book on flames. Of particular interest is their summary of various theories on soot formation which includes comments on each one. In 1954, Schalla et al. published NACA 1186, which is a very concise report on smoke formation in both premixed and diffusion flames. This report includes detailed descriptions of their physical observations as well as a small section on postulated mechanisms of smoke formation. In 1955 a very detailed experimental work was done by Street and Thomas on carbon formation in premixed flames while in 1957 Schalla and Hibbard wrote a comprehensive review of smoke and coke formation including 45 references.

With the emphasis shifting to environmental considerations, the 1960's saw renewed interest in explaining the kinetics and mechanisms of carbon formation, in addition to explaining the physical effects on carbon formation. Palmer and Cullis (1965) wrote a review article listing 197 references on carbon formation. They list seven theories on carbon formation and explore recent developments up to that time. Since 1965, Homan and Wagner have contributed much to furthering the ideas of carbon formation but their work is confined to premixed flames.

2.4 Mechanisms of Carbon Formation

Because the focus of this investigation deals mainly with diffusion flames, concern will be limited to proposed mechanisms of carbon formation operative in diffusion flames. However, since little testing has actually been done on diffusion flames it is necessary to draw from work on premixed flames. Bancroft (1927) first observed that a luminous flame can be considered as a colloidal suspension of carbon in a gaseous medium. Minchin suggests that through coagulation the charged particles vary in size depending on position in the flame; large particles being near the bottom. Clarke further supposes that in certain instances in the coagulation process, the particles at the tip of the flame become so large they cannot be consumed in the existing temperature and oxygen supply. Thus, soot formation depends on competitive rates of reactions forming and reactions which oxidize soot and soot precursors (Glassman 1977).

Basically, one can consider that there are four phases to soot formation: precursor formation, nucleation, surface reactions, and agglomeration. Of the four phases, nucleation is the more important. Nucleation is the process in which gas phase reactions lead to condense-phase solid nuclei. Weinberg (1962) showed carbon particles will form on positive ions introduced into the reaction zone of a flame. He also showed carbon particles acquire a positive charge when they are very small. The nucleation process involves the pyrolysis of the fuel molecules into lower molecular weight fuel fragments which polymerize and dehydrogenate until condense-phase nuclei are formed. The polymerization process is known to require unsaturated compounds and there is experimental evidence that even in the presence of large amounts of oxygen, aliphatic hydrocarbons break down into olefins, thus, fulfilling this requirement. Radical molecule type reactions are considered

(Glassman 1977) to account for the high rate of carbon formation.

Work done by Homan and Wagner on premixed flames of acetylene and benzene indicate three main groups or hydrocarbons play an active role in the process of carbon formation:

1. Acetylene and polyacetylenes (mass range 26 to 146).
2. Polycyclic aromatic hydrocarbon (mass range 79 to 300).
3. Reactive polycyclic hydrocarbons, probably with side chains which contain more hydrogen than aromatics (mass range 150 to $>$ 550).

Relative quantities of each group differ depending on fuel type (aliphatic or aromatic).

Homan and Wagner propose a carbon formation route in an acetylene flame shown in Figure 2.4. Basically, the route could start with aliphatic fuels converted to acetylene (as shown by Glassman et al. (1975) in fuel rich systems). The acetylene then polymerizes to polyacetylene and polyacetylene radicals. As the chain length increases, cyclization increases and becomes important. If the molecule retains its radical nature, polymerization with polyacetylene continues. Homan and Wagner point out that any resulting polycyclic aromatic molecules are by-products rather than intermediates in the process of carbon formation in acetylene flames.

In contrast to this, high amounts of polycyclic aromatic molecules are formed in the oxidation zone of a premixed aromatic flame. To explain the high rate of carbon formation from aromatic fuels Gordon

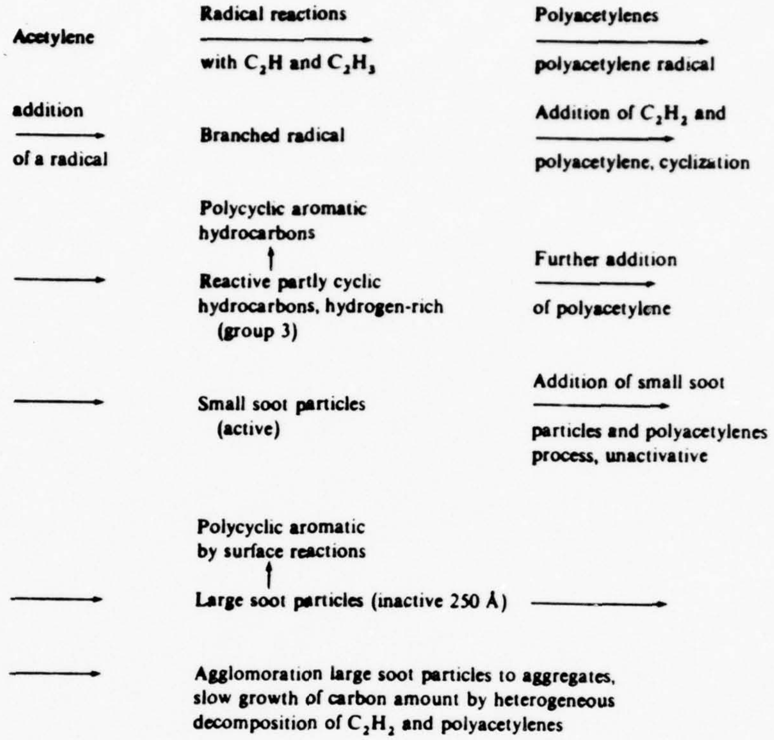


Figure 2.4 Carbon Formation Route from Acetylene Flame (after Homan and Wagner, 1976)

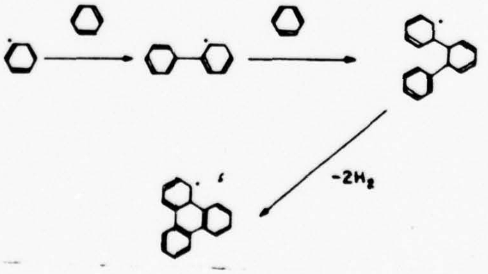


Figure 2.5 Carbon Formation from Benzene Flames (after Gordon et al., 1959)

et al. (1959) proposed the mechanism shown in Figure 2.5.

Although the theories presented on soot formation deal mainly with premixed flames, these can be extended to diffusion flames if one keeps in mind the character of the diffusion flame. In the pyrolysis zone of the diffusion flame the oxygen concentration is negligible, thus, the condensation of intermediates is favored compared to oxidative depletion. As a result, a diffusion flame produces much more soot than a premixed flame under comparable conditions. In general, for a diffusion flame carbon formation decreases in the order

naphthalenes > benzenes > acetylenes > di-olefins > mono-olefins > paraffins

or more generally

aromatics > alkynes > alkenes > alkanes.

2.5 Suppression of Carbon Formation

As more is understood about the process of carbon formation, the emphasis is directed towards suppressing carbon formation by application of physical methods and/or chemical additives.

2.5.1 Burner Design

In turbojet combustion, improved burner design attempts to reduce carbon formation. Studies have been made on air flow distribution, premixed systems, and fuel injection but the overall focus of any study seems to be the elimination of fuel rich regions by better mixing of the fuel and air supply. The preliminary studies indicate this approach can be successful; however, additional problems must be solved before any significant advancement can be realized. Problems include stability and ignition (due to leaner mixture ratios in the ignition zone), carbon deposition on fuel injection nozzles (a small amount of carbon forms regardless of conditions), and durability (improved mixing increases flame temperature). Despite any improvement there will always be a small amount of carbon formation in a turbojet combustor due to its inherent operational characteristics. With the predictable trend toward lower grade fuels these problems will be compounded. As a consequence, alternative methods of inhibiting carbon formation are needed.

2.5.2 Metal Addition

One possible method to suppress carbon formation explored by Cotton et al. and Feugier is the addition of various metals inside a flame. Cotton studied the effects of forty metals in a propane diffusion flame. He examined the efficiency of soot removal for each metallic additive and also proposed a semiquantitative mechanism for soot removal involving mainly the alkaline earth metals. The significance of this work was its performance in diffusion flames. Addition of the metals, Cotton postulated, tended to increase the concentration of OH radicals. (It is well documented that the OH radical is primarily responsible for the oxidation of carbon particles and their precursors (Homan 1968, Milikan 1962, Fenimore and Jones 1967, and Flossdorf and Wagner 1967).) Thus, increasing the OH concentration tends to decrease carbon formation. Feugier also reports on addition of metallic additives to premixed flames. He found the lower the ionization potential of the metal, the greater the tendency to soot. Addition of alkaline-earth salts, on the other hand, decreased carbon formation. To explain the observed behavior Feugier postulated the following mechanism:

$$M + H_2O \longrightarrow MOH + H \qquad (4)$$

$$MOH + H_2O \longrightarrow M(OH)_2 + H \qquad (5)$$

$$H + H_2O \longrightarrow OH + H_2 \qquad (6)$$

where M is an alkaline-earth metal. Again, an overall increase in OH radicals occur and readily oxidize soot precursors to prevent carbon nucleation.

2.5.3 Water Addition

An idea drawing more attention in recent years is that of water addition to a flame to inhibit carbon formation. Preliminary experiments performed by Dryer (1976) using emulsified fuels indicated the use of emulsions in a diffusion flame decreases carbon formation. Studies on fuel injection in a diesel engine show water addition on the fuel side decreases carbon formation while water addition on the oxidizer side increases carbon formation (Greeves et al. 1976). More recently, studies examined the addition of water vapor inside a premixed bunsen flame (Müller-Dethlefs and Schlader 1976) and indicated water vapor inhibits carbon formation and yields a greater heat release than predicted if water acted only as an heat sink. The water vapor then must play a chemical role because the flame temperature (and consequently the burning velocity) does not decrease to the extent predicted if the water vapor acted solely as an inert diluent. The critical C/O ratio (the air-fuel ratio at which the yellow luminescence, due to condense-phase particles, just disappears) was significantly affected by the addition of water vapor. The C/O ratio increased linearly with increased water addition, indicating the water vapor was taking part in the combustion process probably through the formation of OH radicals.

Both the physical and chemical effects of water addition are discussed in a review article written by Dryer. The kinetic effect of water on combustion probably occurs along the following reaction sequence

$$H_2O + H \longrightarrow H_2 + OH \qquad (6)$$

$$H_2O + O \longrightarrow OH + OH \qquad (7)$$

$$H_2 + O \longrightarrow OH + H \qquad (8)$$

The net result is an increased production of the OH radical and thus, an increase in the oxidation of soot precursors. In the fuel-rich situation (such as present in a diffusion flame) the following reactions are generally negligible due to lack of oxygen.

$$H_2O + O \longrightarrow OH + OH \quad (7)$$

$$H_2 + O \longrightarrow OH + H \quad (8)$$

$$H + O_2 \longrightarrow OH + H \quad (9)$$

$$RH + O \longrightarrow R + OH \quad (10)$$

Thus, hydroxyl radical concentrations in diffusion flames are generally low resulting in increased carbon formation. The main reaction for the production of OH in this case becomes

$$H_2O + H \longrightarrow H_2 + OH \quad (6)$$

It can be argued in the premixed case that water is present at all positions inside a flame. However, in a premixed fuel-rich condition or a diffusion flame water is not formed until very late in the flame. For this reason water addition in the early stages of a fuel-rich flame can be expected to result in an increase in OH concentrations and thus a decrease in carbon formation. Water addition in a lean, premixed flame cannot be expected to have as large an effect because the presence of oxygen tends to form OH radicals early in the flame.

CHAPTER 3

EXPERIMENTAL APPARATUS AND TECHNIQUE

3.1 Wickless Burner

The basic experimental device used in this investigation is modeled after the original wickless burner developed by Clarke. Figures 3.1 and 3.2 show a schematic and photograph of the system used. It is evident from wick burning lamps an increase or decrease in exposed burning area causes an increase or decrease in flame height. Using this fact Clarke proposes a conical burner that could burn a liquid fuel directly. Filling the reservoir to a predetermined level results in a similar level in the conical burner. The level in the burner then corresponds to a certain exposed liquid surface area, which produces a specific flame height. Any change in elevation of the reservoir causes an equivalent change in the burner fuel level. In turn, the exposed liquid surface area changes, causing a change in flame height. Thus, an adjustable flame height is possible with this technique, dependent upon the angle of the conical burner. The conical burner in the present device is constructed of brass at an angle of 22 degrees. The inside diameter of the cone at the base is 2.5 inches and the location of the base is one inch from the burner base. A small brass tube, 1/4 inch outside diameter, connects to the apex of the cone and protrudes down through the burner base. Flexible tubing then links the reservoir to the brass tube.

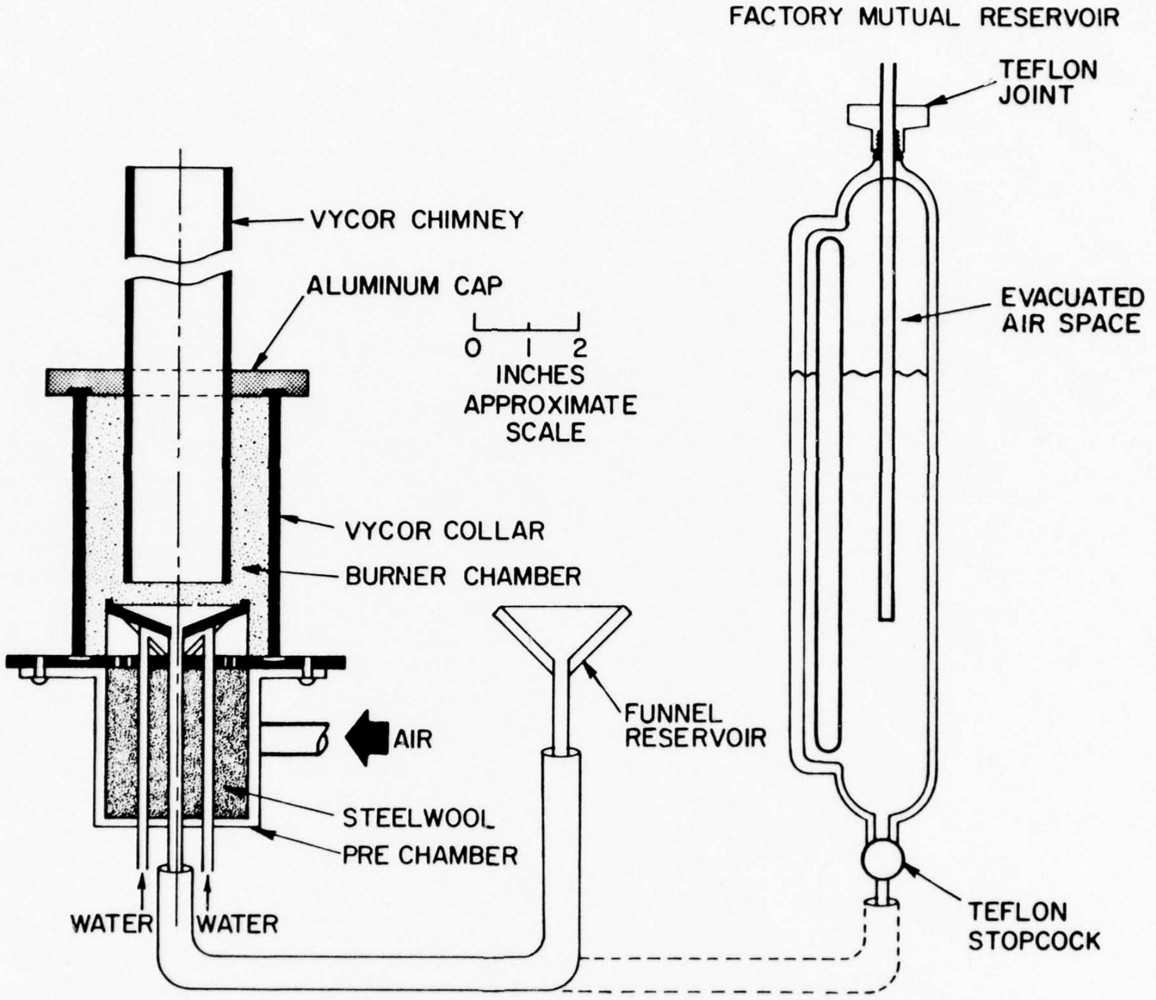


Figure 3.1 Schematic of System

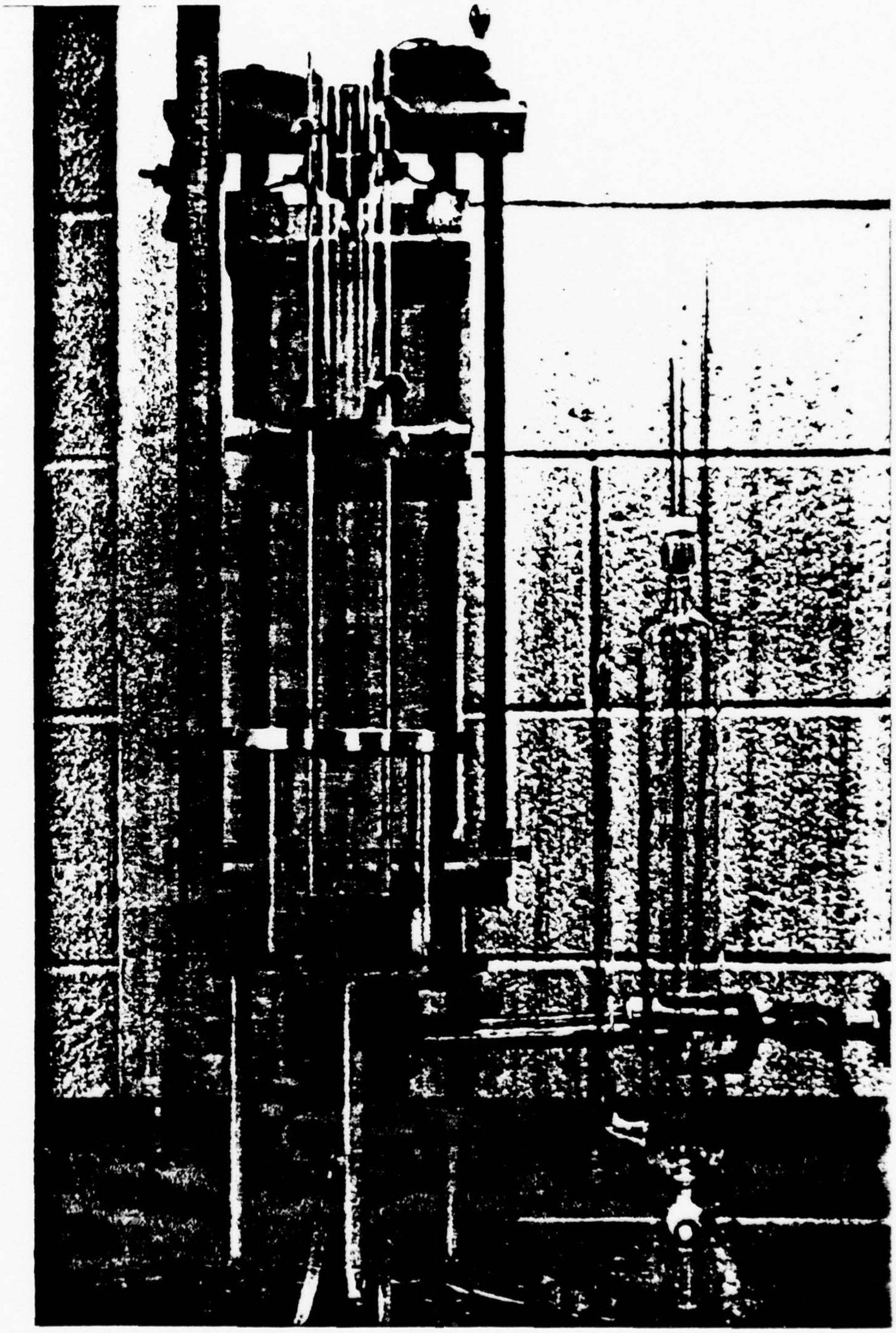


Figure 3.2 Photograph of System

To measure flame height, a steady, laminar flame is needed. Burning the wickless lamp in a quiescent room revealed severe flickering. Clarke then proposed to enclose the flame and use the draught from a glass chimney to provide oxidizer to the flame. The original device uses a glass chimney, while the present device substitutes vycor. Vycor is used because of its strength and thermal properties. A vycor tube (referred to as a collar) with the dimensions 3.55" ID, thickness .15", and height 5" encloses the conical burner, forming a burner chamber. A cap of aluminum 1/2 inch thick, placed over the collar, forms the top of this chamber. Both the cap and the burner base are fitted with a rubber gasket at the points of contact with the collar, allowing for an air tight seal. The cap contains an opening in the center sufficient to allow the passage of the chimney into the burner chamber. This opening between the chimney and the cap provides enough clearance to permit vertical adjustment of the chimney. The chimney is also a vycor tube with a 1.8" ID, .1" thickness, and 20" length. Holes drilled in the burner base allow air to enter the burner chamber. The holes are confined to the area of the projection of the burner on the base. 120 mesh copper screen then covers the holes. Another 120 mesh copper screen is fitted around the burner itself. The screens insure a uniform laminar flow of air to the flame. (Smoke visualization of the flow patterns for various chimney heights verified the flow was laminar.) Clarke also used an 18 mesh copper screen at the top of the chimney. This screen is discarded in the present device because carbon deposition on the screen restricts airflow and hence influences flame height while testing.

Original specifications indicate the conical burner should be of larger diameter than the chimney; also, the chimney should be adjustable to maintain air flow in the laminar flame region. Tests show there is a definite upper and lower chimney height at which the flame becomes unsteady. No strong influence on the flame height is found for chimney positions in the laminar flame region. In order to conduct experiments under a controlled condition, a standard chimney height of 3.5cm above the burner base is used. This provides a satisfactory flame for all fuels of interest. Chimney adjustment is accomplished by a mechanical gearing system to which the chimney is clamped. The flame is very sensitive to the symmetric (concentric) alignment of the chimney. A plexiglas plug inserted into the burner and a vertical level are sufficient to insure the chimney is always concentric with the burner.

Clarke found substances with high boiling points produce laminar flames only when the temperature of the burner is very high. As a result, brass, with a low heat capacity, is used in construction. The problem then occurs that substances with low boiling points tend to boil and produce an irregular flame. To remedy this situation a water jacket is fitted to the burner and used when burning highly volatile substances. A Neslabs Instruments Inc. RTE-8 provides water circulation. This unit is capable of a -30°C to 70°C temperature range ± .05°C. Preliminary experiments (to be discussed in Chapter 4) show a dependence of the smoke point on burner temperature; thus, a fixed burner temperature is another desired control for comparison of different fuels. Most experiments use a burner temperature of 40°C as a standard reference. If different, the temperature will be indicated. Legs 8 inches high are fastened to the burner base (6.5" diameter) and the entire unit is then bolted securely to a table. Because of the amount of carbon occasionally present in the exhaust gases, the device is mounted under a hood. The hood has no effect on the draught and hence the flame height.

3.2 Fuel Reservoir

The inherent design of the wickless burner yields a large sensitivity of flame height to reservoir height, especially in the region of the smoke point. An adjustable reservoir height is desirable; however, the adjustment must be sufficiently fine so close control of the flame height can be maintained. At first a small funnel (2" diameter) was used as the reservoir but, because of the small volume of fuel in the funnel, constant readjustment of the reservoir height was necessary to maintain a stationary flame height for measurement due to consumption.

The next logical reservoir was one of increased volume but similar in principle to the funnel. A rectangular tank 12" x 12" x 2" was constructed; however, its use was not satisfactory. It maintained a fairly constant height for short periods of time but, any adjustment or vibration caused waves to occur in the reservoir which oscillated the flame and required several minutes to subside. In addition, large amounts of fuel were required for such a large reservoir, which proved impractical.

A third reservoir used is a device developed by Factory Mutual Research Corporation (Figures 3.1 and 3.2). This device was developed to keep a constant fuel level in an open cup burner and at the same time give an indication of the mass burning rate of the fuel. (An evaluation of mass burning rates using this reservoir is included in the appendix.) The device consists of a cylindrical glass vessel with a 40 mm ID and a 28 cm overall length. At the lower end is a Teflon stop cock and at the upper end, a 3 mm ID, 30 cm long pyrex capillary supported by a Teflon joint. A side arm is added to provide ease of measurement of fuel level.

The operation of the device is quite simple. With the stop cock closed, the device, connecting tube, and burner are filled with fuel. Adjustment of the reservoir is made until the lower end of the capillary is at the desired level. The stop cock then opens and the reservoir is fixed in this position. Burning of the fuel results in a lower fuel level in the burner. This, in turn, causes a drop in reservoir fuel level and, as a result, a drop in pressure in the evacuated space above. The drop in pressure causes air bubbles to enter the cylinder through the glass capillary. Thus, an equilibrium pressure (essentially atmospheric) is maintained at the lower end of the capillary, supposedly maintaining a constant fuel level.

The device has two main disadvantages for the application considered. First, it is not easily adjustable. Raising the capillary increases the flame height; however, to lower the flame height one needs to lower the reservoir and wait until the fuel level burns down to the capillary tip. This entire process takes several minutes and is not practical for quick adjustments. Secondly, there is always a fluctuation in the flame height, an inherent characteristic in the operation of the device. Flame height is very sensitive to fuel level in the conical burner, particularly around the smoke point. The drop in pressure necessary to cause air bubbles to enter the cylinder corresponds to a fuel level drop sufficient to change the flame height about 1 cm (more at the smoke point). The device is useful to observe a region of flame height if it can be adjusted to oscillate around a particular height (i.e. the smoke point or some height at which a mass burning rate measurement is desired).

3.3 Temperature Measurement

Temperature measurements in this investigation are made using thermocouples of the standard copper/constant type. Thermocouples are positioned at the inlet and exit of the water-cooling jacket and of the chimney. Temperatures are measured only in an attempt to provide more information for the explanation of phenomenon involved.

3.4 Controlled Air Supply

One major modification to the original device is the addition of a controlled air supply (Figures 3.1 and 3.2). Preliminary studies indicate an influence of air supply on smoke point. These findings seem consistent with data contained in NACA 1300 on gaseous diffusion flames. A laboratory air supply, maintaining a constant 50 psig, is directed through a Brooks model 1110 rotameter (accuracy 1% full scale). A needle valve then regulates the air flow into two 1/2 inch pipes which then enters a 3 1/8" OD, 2.5" high prechamber. Bolted to the base directly under the air holes, the prechamber is sealed, only allowing the air to exit the chamber through the air holes in the burner base. Steel wool packs the chamber to insure a uniform dispersal of air before it enters the burner chamber. In some instances, the controlled air system is not used and the air holes vent directly to the atmosphere. Conditions where the air holes are open to the atmosphere or to the controlled air will be noted.

3.5 Operation Procedure

The operation procedure of the wickless burner is relatively straightforward. Because of flame sensitivity to chimney alignment, the first step is alignment of the chimney and burner. A plexiglas plug with a diameter precisely that of the chimney inside diameter inserts into the burner. The chimney then lowers around the plug and alignment using a vertical level occurs. Completing the alignment, the chimney is firmly clamped to the mechanical device used to adjust chimney height. After alignment of the chimney, the next step is to raise the chimney and remove the collar and cap. The reservoir, fuel line, and conical burner are then cleaned and filled with fuel to the appropriate level. At this time, depending on the test to be performed, water circulation at a preset temperature begins. If it is desired to have no cooling then this step is omitted. Also, if controlled air is being used, airflow and fuel level must be adjusted to insure a non-sooting flame. The fuel is then ignited, the collar and cap replaced, and chimney adjusted to the proper height. Ignition of the fuel in most cases can be accomplished by the use of a match. In the case of higher boiling point fuels two methods can be used. First, a propane torch can heat the fuel (in the burner) to the point where it will ignite. The resulting flame is very irregular until the burner reaches sufficient temperature to preheat the fuel. Secondly, a small amount of a volatile fuel can be placed in the burner with the heavy fuel. This fuel then ignites and provides the heat necessary to ignite and sustain the flame until the temperature reaches the desired level. When the appropriate flame height is obtained, a five minute wait is necessary to allow for stabilization of conditions. Once conditions stabilize, the measurement of the flame height or smoke point can be taken. If another measurement point is desired the flame height can be readjusted and the measurement taken after conditions have again stabilized. Lowering the reservoir extinguishes the flame as does cutting off the air supply. With the flame extinguished the fuel is removed and the collar, chimney, burner, and reservoir are cleaned. The device is then ready for use with another fuel.

3.6 Smoke Point Determination

Difficulty arises in the actual determination of the smoke point. Clarke found that each flame forms a long red "tail" just before visibly smoking. Present experimentation reflects the flame to be very sensitive in this area of the smoke point. A small increase in reservoir height causes this red "tail" to appear very quickly; however, the distinction between the red "tail" and the flame is not very well pronounced. Thus, to accurately determine at what flame height the red portion of the flame disappears can be difficult. The lower the smoke point the easier it is to determine the disappearance of the red portion of the flame. For this reason it is supposed that Clarke gave an experimental error of ± 3% of the mean value taken.

Clarke's technique for measuring the smoke point incorporates a wire hook, which he lowers into the chimney. The wire tip marks the flame height that corresponds to the smoke point. The position of the wire is then projected on a meter stick to obtain the smoke point. The zero or reference position in this case is the lowest spot in the conical burner. Several measurements are taken in this way and a mean value recorded.

The present investigation uses three techniques for measuring smoke point. The first technique is very similar to the one used by Clarke. Instead of a wire hook, a non-intrusive cathetometer measures flame height. A cathetometer is a vertically adjusting telescope with a cross-hairs sight. The telescope mounts on a vertical pole which contains a built in scale. To make a measurement, the flame is adjusted to the smoke point (or a little above). Looking through the telescope, the vertical position of the telescope is adjusted until the cross-hairs match the smoke point. The position of the telescope then corresponds to a measurement on the scale. Subtracting a reference measurement from the flame height measurement produces the true height of the flame relative to a reference point. The reference point for this experiment is always the upper edge of the burner base.

(To compare with Clarke's data, subtract an additional 1.3 cm from recorded heights.) Several measurements are taken and a mean value is then the smoke point. Use of the cathetometer allows a magnification of the smoke point region and, thus, a reduction in error. However, when the flame adjustment is difficult, a marking pencil can be used to indicate the flame height on the chimney exterior which can be subsequently measured by the cathetometer. This technique is the quickest and easiest to use of all tested.

A more accurate technique involves the use of photographic equipment. First, the flame is adjusted until it just begins to smoke. The flame is then allowed to burn down through the smoke point until the red "tail" disappears. Using the small funnel as the reservoir causes the elapsed time of burning to be usually one to two minutes. Meanwhile, a time sequence of flame height is being taken by the camera. From the developed pictures or the negatives time and height can be related. Figure 3.3 plots log h versus time and reveals two distinct linear regions. Region A corresponds to the flame before the smoke point while region B corresponds to the growth of the red "tail" of the flame. The intersection of these regions is then defined as the smoke point. Comparison with the previous technique shows the height at this intersection point to be very close to the smoke point. The procedure described here is most time consuming but is highly reproducible.

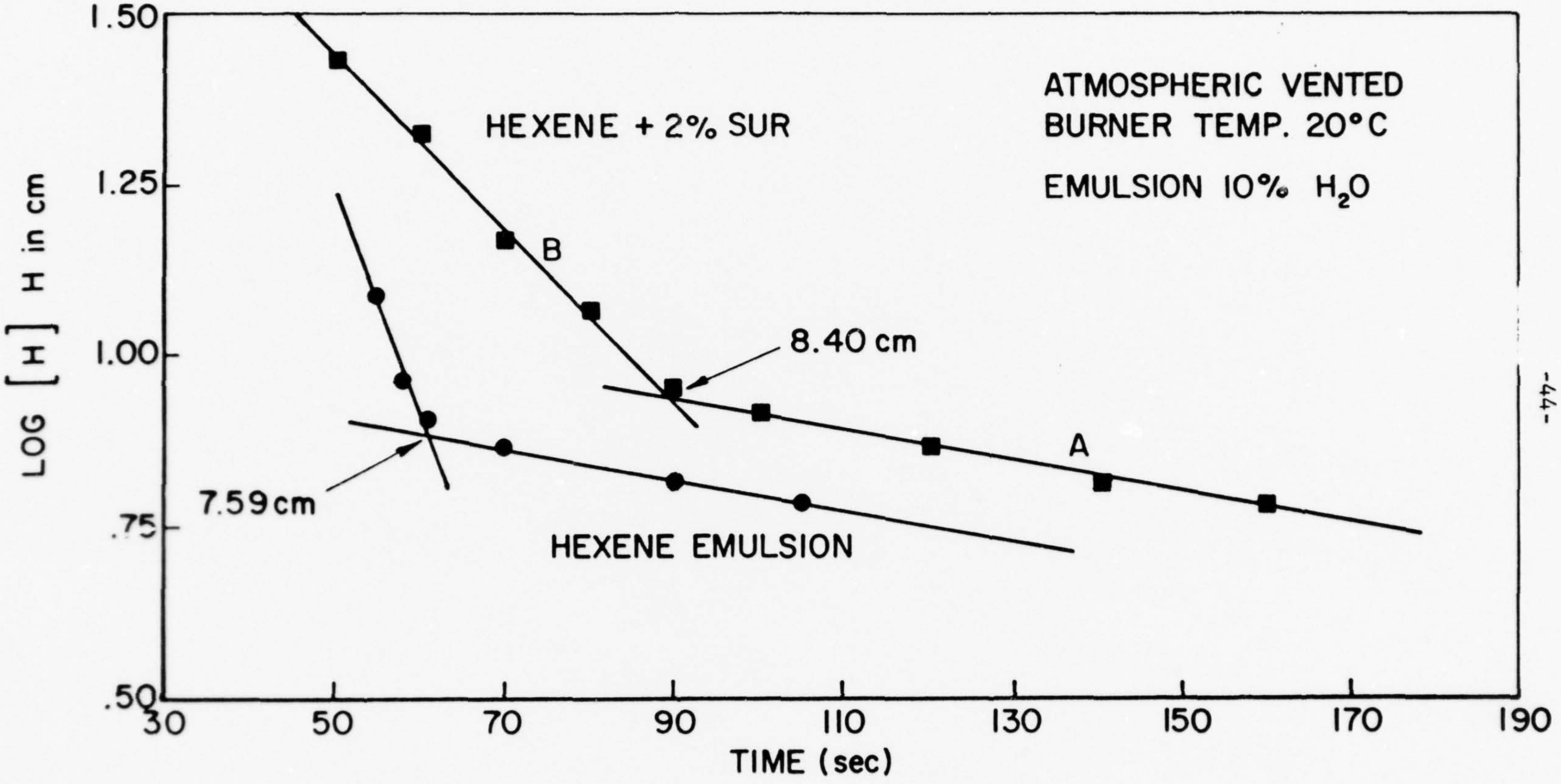
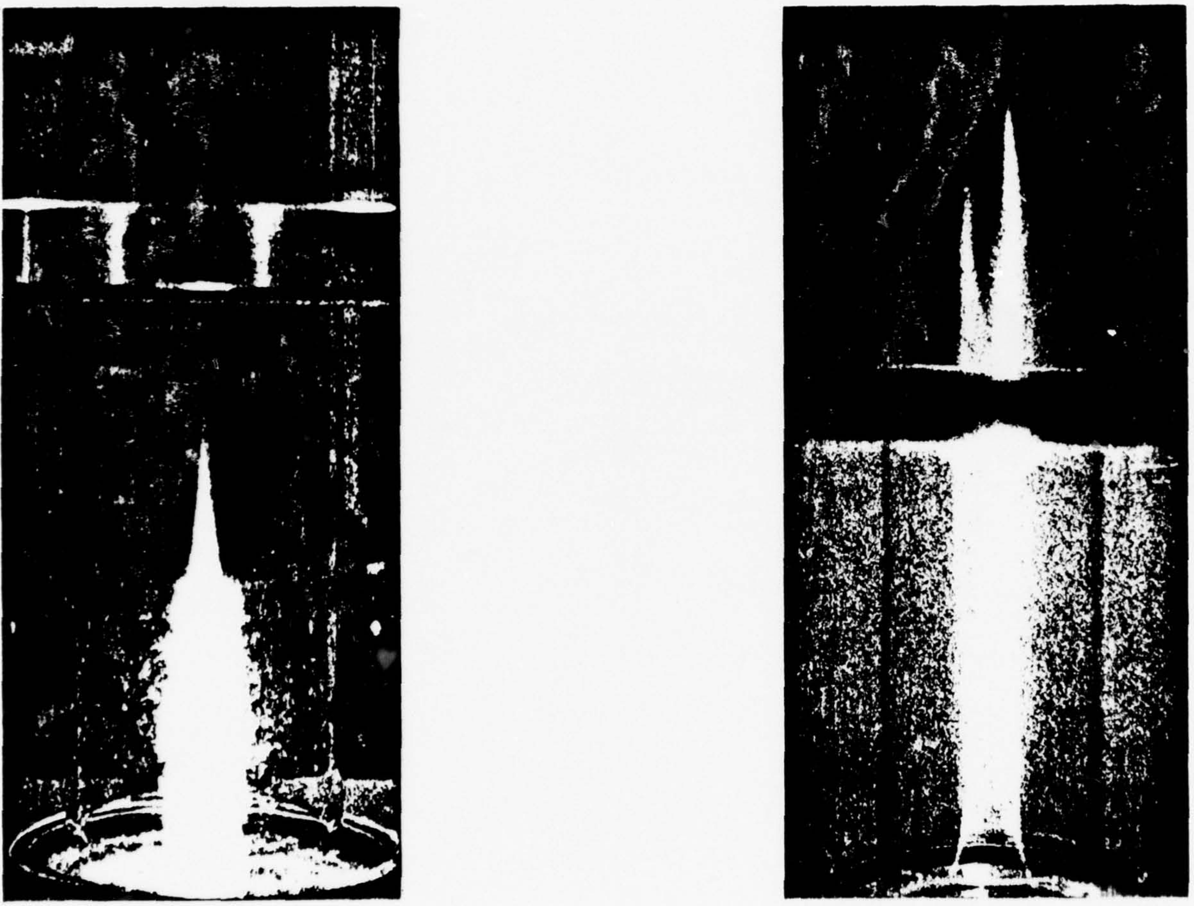


Figure 3.3 Log [H] vs. Time from Photographs

Any type of film will work with this technique; however, infra-red film produces the best results. Figure 3.4 shows a comparison of Kodak 2475 recording film and Kodak infra-red film. The 2475 film displays the flame but the grain of the film prohibits accurate definition of the flame height. In contrast, the infra-red film has a much cleaner image of the flame tip allowing more precise measurement of the flame height. Thus, when using this technique an infra-red film is suggested.

In the interest of time a third technique, very similar to the photographic technique is used. Instead of photographs, marks corresponding to height are made on the chimney in a time sequence as before. Plotting log h versus time gives the same two distinct regions, with the intersection corresponding to the smoke point. Comparison with the first technique again shows a correlation between the intersection point and the smoke point.

The photographic technique is presumably the best technique. It provides a permanent record and is the most accurate. The disadvantage is the time necessary to develop the film and the expense involved. In the interest of time, the last technique is better but not quite as accurate as the photographic method. The first technique still is the quickest and easiest and should be used where the difference when comparing two measurements is large (i.e. comparing a paraffin with an aromatic fuel). When higher accuracy is



Kodak 2475 Recording Film

Kodak Infra-Red Film

Figure 3.4 Pictures of Flames

needed, the photographic method is preferable. In any case the error of the device does not exceed ± 3% of the height as proposed by Clarke and in most cases the error is improved.

3.7 Preparation of Emulsions

To determine the effect of water on the soot formation process water must be added on the fuel side of a diffusion flame. Because of work in this laboratory using emulsified fuels water in fuel emulsions were considered as the prime method of water addition. In order to make an emulsion of water in fuel, selection of the appropriate surfactant is necessary. (A surfactant is a stabilizing additive that insures the emulsion is of the desired internal phase.) The method of selection used for this investigation is the HLB method developed by Griffin (1949) and detailed by the Atlas Chemical Industries, Inc. (1963). The HLB (Hydrophile-Lipophile Balance) is the balance of the size and strength of the hydrophilic (water-loving or polar) and lipophilic (oil-loving or non-polar) groups of emulsifier (surfactants). An emulsifier that is lipophilic in overall character is given a low HLB number (generally below 9.0) while a hydrophilic emulsifier has a high HLB number (generally above 11.0).

Using the Atlas HLB system of selecting chemical type of surfactant, a combination of Span 80 (HLB = 4.3) and Tween 80 (HLB = 15) was decided upon since blends, the method suggests, usually work best.

The Atlas system indicates for a water in oil emulsion (the type applicable in this investigation) an HLB range of 4 to 6 is appropriate; however, Rambeck (1977) showed values of HLB 5.0 and below are unstable. For that reason the following combination was chosen:

10% Tween 80 (HLB = 15)	1.5
90% Span 80 (HLB = 4.3)	3.8
HLB	5.37

The procedure for making the emulsion begins with selection of components. Usually 2% of the emulsion is surfactant and about 10% is water. At percentages of water greater than 20 difficulty in burning occurred due to the accumulation of a thick, white substance on the burner. Precise amounts of Span 80 and Tween 80 are measured. The Span 80 is then dissolved in the fuel and the Tween 80 with the water. The two solutions are poured into one beaker, immediately forming two distinct layers; the water layer on the bottom and the fuel layer on top. Dispersion of the water in the fuel is accomplished by using an ultrasonic vibrator developed by Crest Ultrasonics. The vibrator tip is immersed in the liquid and in the course of operation turns the mixture into a milky white emulsion. Examination under a microscope shows the dispersed water droplets to be very uniform on the order of one micron. Stability of emulsions made in such a way are typically two weeks or more at room temperature.

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Testing the Clarke Burner

The first area of investigation deals mainly with developing the Clarke type burner as a better reproducible qualitative test. Initial tests with no burner cooling, chimney height 3.5 cm above the base, and air holes open to the atmosphere are given in Table 4.1. The heights, when corrected for reference condition, are very similar to those obtained by Clarke. Thus, with the device constructed trends in fuel smoke points similar to those obtained by Clarke could be repeated.

Further testing revealed data that seemed inconsistent with the Clarke paper. Because initial tests showed that the chimney height does not influence flame height, the bottom edge of the chimney was fixed at 3.5 cm from the burner base. In the interest of control, a constant water circulation temperature maintained the burner temperature at a constant value. As a result of controlling burner temperature it was discovered that the smoke point exhibits a strong dependence on burner circulated water temperature (see Figure 4.1). With air holes vented to the atmosphere, heptane has a smoke point of 17 cm with no water circulation and a smoke point of almost 22 cm with water circulation at 20°C. The difference of 5 cm is much greater than the error associated with the flame height.

TABLE 4.1 COMPARISON OF PRESENT SMOKE POINTS WITH CLARKE DATA (SIMILAR CONDITIONS)

Fuel	Present Data (cm)	Corrected (cm)	Clarke Data (cm)
n-Pentane	17.50	16.2	15.5
n-Heptane	17.0	15.7	15.9
n-Octane	16.5	15.2	--
n-Decane	16	14.7	--
(ISO) Hexane	13.55	12.25	--
Hexene	6.6	5.3	5.1
Toluene	2.4	1.1	1.0
Acetone	25.3	24	26.3
Isopropyl Alcohol	18.5	17.2	17.9
Ethyl Alcohol	27.0	25.3	37.7

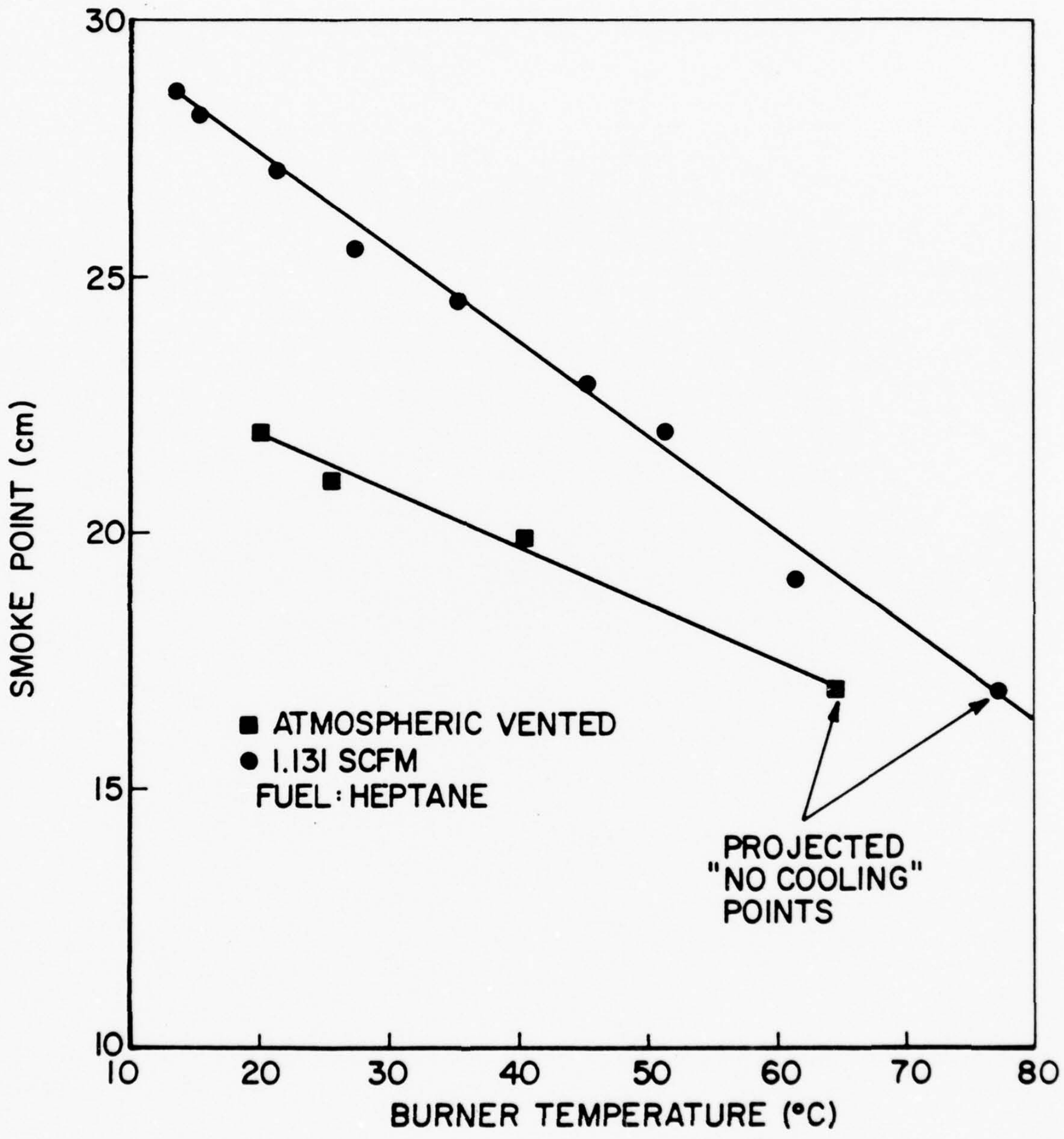


Figure 4.1 Smoke Point vs. Burner Temperature

Once reaching equilibrium, measurements of inlet and exit water temperature show a negligible temperature difference thus concluding the burner temperature is constant and close to the water temperature. Therefore, subsequent references in this thesis use water circulation and burner temperature interchangeably.

Measuring the temperature difference between the inlet and exit chimney air temperatures showed that as burner temperature increases, this change in chimney temperature at the smoke point decreases, as does smoke point. The initial chimney air temperature varies by only $30^{\circ}C$ for all burner condition cases between the case in which the burner temperature is at $25^{\circ}C$ and when the burner is not cooled; however, the exit temperature in the $25^{\circ}C$ case is $100^{\circ}C$ higher than the no cooling case for heptane. When flame heights are approximately the same it is noticed the change in chimney temperature is also similar. Figure 4.2 shows the change in chimney temperature correlation with flame height; thus, the increase in temperature for the $25^{\circ}C$ case is due to the increased flame height.

The original device, vented to the atmosphere, used a buoyant flow driven by the flame to provide the oxidizer. Because some discrepancy exists in the temperature difference across the chimney at the smoke point it was thought the variation in the burner temperature affects the mass flow of air to the system. Since the air contains the oxygen necessary for combustion, this change in mass flow could affect

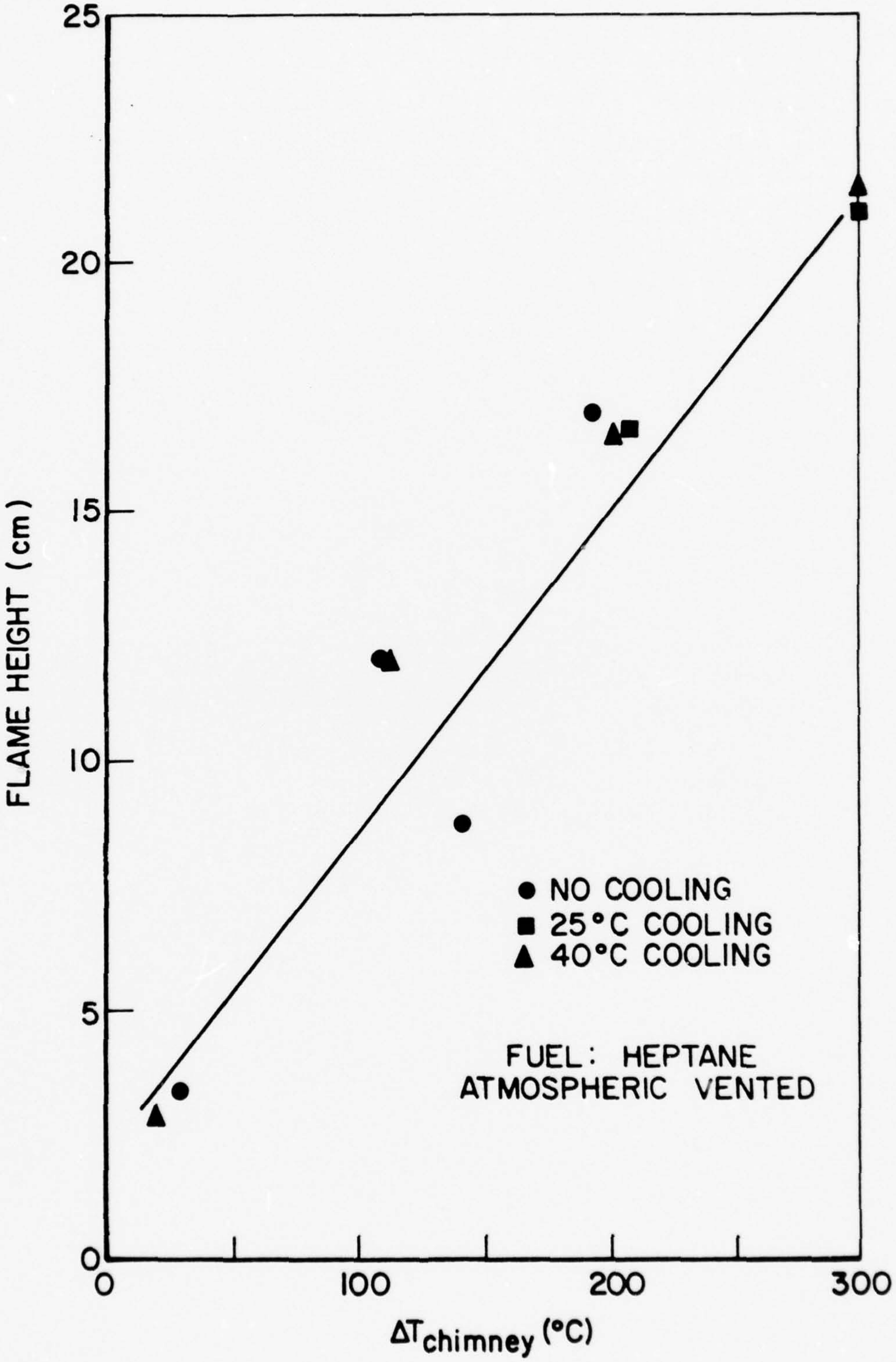


Figure 4.2 Flame Height vs. Δ T Chimney

the smoke point. For these reasons a controlled air system, previously described, was made and installed on the device. Subsequent experimentation showed even with the controlled air supply a variation of smoke point with burner temperature occurs (Figures 4.1 and 4.3).

Attempts to find an explanation for smoke point variations using mass burning rate measurements are detailed in the appendix. Up until the smoke point it would appear that each flame follows the same linear mass burning rate versus flame height relationship for a particular fuel, regardless of burner temperature. Thus, mass burning rate provides no further insight. As a result it is decided to use a fixed burner temperature compatible with fuels of interest for all tests.

An interesting result of adding a controlled air supply is that when one increases the air flow the smoke point of a given fuel increases until a limiting value is reached (Figure 4.4). Past this point, an increase in air flow does not affect flame height thus, the smoke point remains constant. The explanation of this phenomenon lies with the diffusional mechanism by which the oxidizer reaches the flame. Earlier studies confirmed this smoke point dependence on air flow (Schalla and Hibbard 1957, Schalla et al. 1954). Attempts to correlate the atmospheric vented case with the controlled air supply show the former was operating around .333 SCFM. Since different flame heights have different driving forces in the atmospheric vented case, a

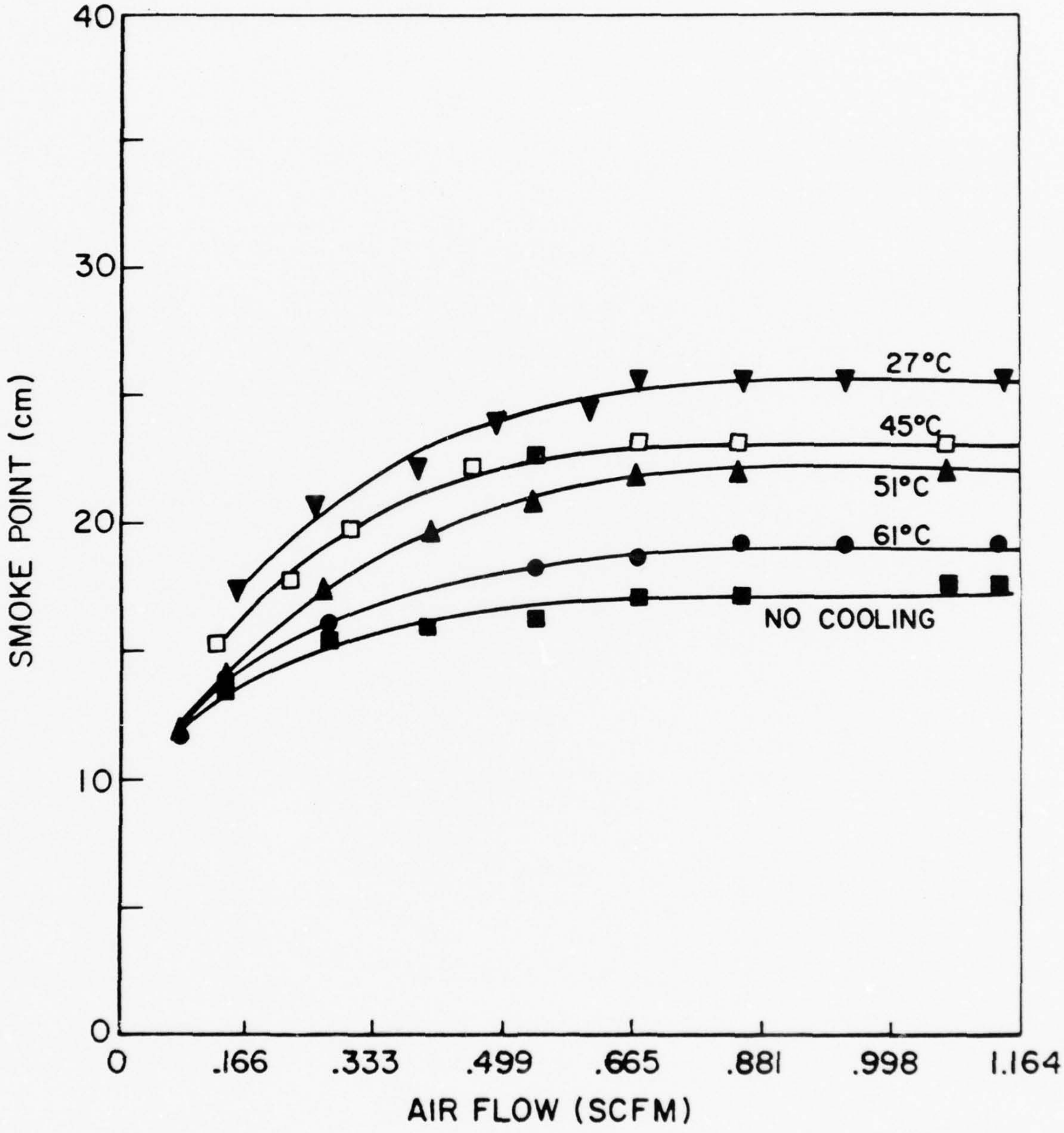


Figure 4.3 Smoke Point Variation with Air Flow and Burner Temperature

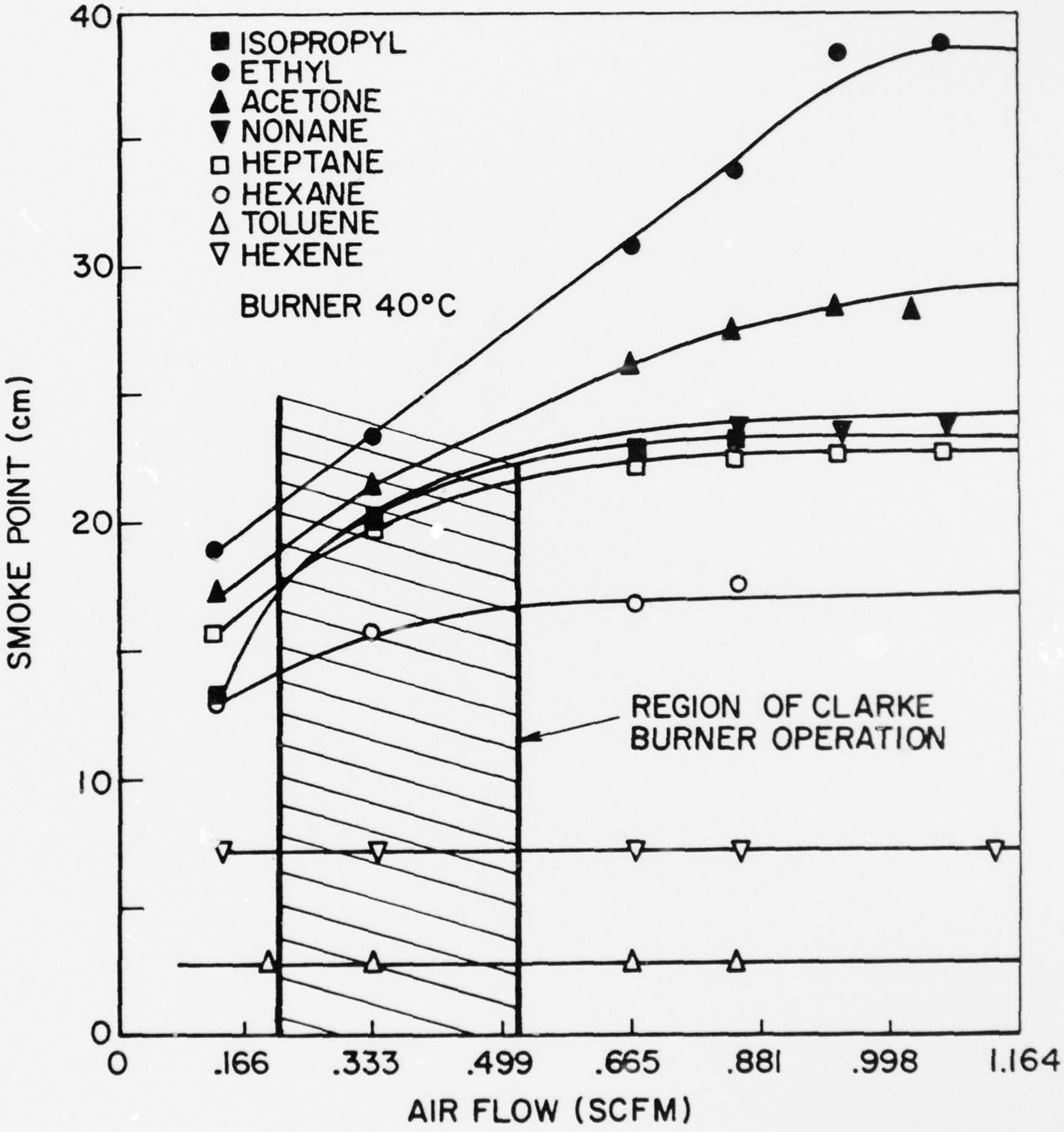


Figure 4.4 Smoke Point Variation with Fuel Type and Air Flow

broad region shown in Figure 4.4 indicates the range of operation. From Figure 4.4 it is apparently advantageous to operate at the higher values of air flow where the differences between fuels are more distinct. As a result, when using a controlled air supply care was taken to operate only in the region where the effect of air flow is eliminated.

4.2 Water Addition to a Diffusion Flame

Phase two of the investigation dealt with the aspect of water addition inside the diffusion flame. It had been postulated that water addition in the early stages of the flame would increase the concentration of OH radicals and consequently decrease the soot formation. The direct result of such a decrease would be an increase in the smoke point of a particular fuel. It is not known how much water would be necessary to see an effect or how large the effect would be. Two methods of water addition are studied: emulsions and direct injection of steam.

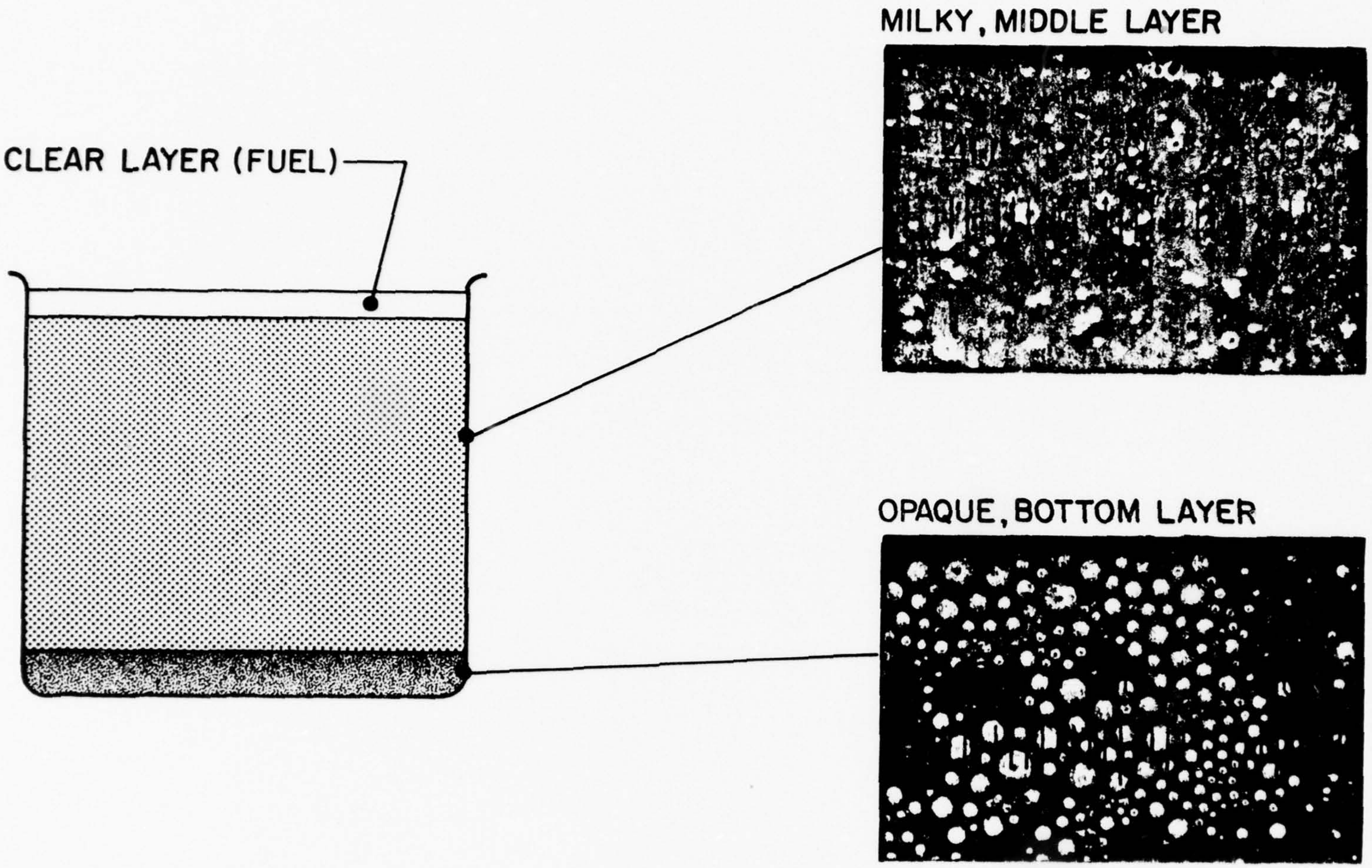
4.2.1 Emulsion Studies

Attempts at burning emulsions, made according to procedure outlined in Chapter 3, did not yield the expected results. When burning a heptane emulsion it is found that addition of 5% water does not extend the smoke point but if anything lowers the point approximately 1.5 cm. Similarly with a hexene emulsion (10% water) the smoke point is lowered about 1 cm from hexene without water (Figure 3.2). These observed differences between emulsion and pure fuel could be argued within experimental error but, in any event, the water addition did not behave as predicted.

This odd behavior prompted a series of studies aimed at determining the stability of an emulsion in a pool burning situation. It was hoped these studies would indicate how much water, if any, was entering the diffusion flame. The first such study involved the use of acetone. Acetone, when burned, produces a luminous diffusion flame of measurable smoke point. The important quality of acetone is its water solubility. Three different solutions of acetone and water were made and tested: 100% acetone, 75% acetone, and 50% acetone. The results indicate no strong influence of water on the acetone smoke point within experimental error. Observing the acetone/water flame with time gave an indication as to what was occurring in the pool. With time, it was observed, the flame height decreases and eventually quenches itself thus, indicating that water gradually separates out of the mixture and remains in the burner. A density determination of an acetone/water quantity before and after burning reveals about a 10% heavier solution after burning than should be expected, further verifying water separates out of the mixture. These observations lead to the conclusion that with the emulsion, some degree of separation may also occur.

The next test to determine stability of the emulsion involved mass burning rates. To determine effect of water addition on mass burning rates, pure heptane with 2% surfactant and a 10% water/heptane emulsion were burned in the device at two different flame heights. At 19 cm the emulsion burning rate (.488 ml/min) was 2.5% greater than the pure fuel with 2% surfactant burning rate (.476 ml/min). For 12.5 cm the difference was only .7% with the emulsion again having the faster burning rate (.360 ml/min vs. .3575 ml/min). With regard to the experimental error one could conclude that the mass burning rates in each instance are essentially the same. Two explanations could be offered to explain this phenomenon. First the emulsion could be cracking on the pool surface which would mean only fuel is being burned. Second, the water addition might actually be decreasing the pure fuel burning rate in the case of the emulsion.

These results prompted study on the surface stability of the emulsion. After an emulsion is made at room temperature, almost instantly a clear, top layer forms. At first it is only a very thin layer but with time the layer becomes thicker. The layer is clear and is comprised only of fuel. A definite interface exists between this layer and the one immediately below it. As the layer becomes thicker, a bottom layer forms and it, too, becomes thicker. Microscope studies show this layer to be mostly large water drops and small amounts of fuel and surfactant. Again, the interface between the bottom layer and the one just above is well defined. The middle layer is a very stable emulsion of uniform composition (Figure 4.5).



(1 division ≡ 3.4μ)

Figure 4.5 Emission Structure

The stability of the emulsion with temperature also proves interesting. In a water bath at 100°C, three different emulsions were studied. After heating the heptane emulsion for 15 minutes, the heptane (BP 98.57°C) completely vaporizes leaving only water and surfactant. Heating a tetradecane (BP 252.5°C) emulsion and a hexadecane (BP>252.5°C) emulsion for the same time period only serves to slightly increase the top and bottom layers. Addition of ethyleneglycol to the water bath enabled the temperature of the bath to increase to 120°C. At this temperature water vaporization occurs in the emulsion. Nucleation of water takes place on the container walls or the interface surfaces. After the process starts, the emulsion color gradually turns to clear, indicating that the concentration of water inside the emulsion is changing. The milky color of the emulsion slowly changes from the top to the bottom layer (which stays a dark, milky color throughout).

Because of these observations it was decided to burn an emulsion of tetradecane in the device. Since tetradecane has a high boiling point, no cooling could be used. Once such an emulsion is burning satisfactorily, large agitation is observed on the surface. The agitation is sufficiently violent to cause fuel to be expelled halfway up the chimney. This action causes the flame to become unstable and no measurements can be taken. With time, the pool of emulsion changes from the characteristic milky color to a clear consistency indicating the absence of water.

To examine more closely the stability of the heptane, a 25% water/heptane emulsion was made and burned under controlled conditions. Approximately 200 ml of the emulsion (140 ml heptane/10 ml surfactant/ 50 ml water) were burned in a metal beaker partially submerged in an ice bath (0°C). The emulsion was allowed to burn until it could no longer sustain itself. Of the 70 ml residue, about 10 ml were of a viscose yellowish, clear liquid (presumably the surfactant) and 60 ml were of a thick, white substance. The white substance resembled the bottom layer of a separated emulsion leading to the conclusion not much water vaporizes in this case. Burning the same emulsion with no cooling leaves very little residue indicating a larger amount of water vaporized. Tests done in the actual device also show a dependence on burner temperature, with less residue obtained for higher burner temperatures.

The results of all the studies would appear to indicate that despite the surface instability of the emulsion, water is entering the diffusion flame at sufficiently high burner temperatures. The difficulty with using emulsions are that the rate at which the water enters and the quantity of water entering the diffusion flame are never precisely known. However, the exact amount of water would not have been important if dramatic effects on sooting were observed. As the burner temperature increases more water enters the flame resulting in less residue. For a given burner temperature, though, one is never quite sure the rate of water addition is constant, since the emulsion composition is changing. In any case, the amount of water addition can never be greater than the total amount of water present. Since emulsions greater than 20% water usually produce unsteady flames, use of emulsions for water addition is limited to less than 20% water. At these low percentages the physical or chemical effect of water addition inside a diffusion flame does not exhibit a change in the sooting behavior that exceeds the experimental error.

4.2.2 Steam Addition

The next attempt at water addition inside a diffusion flame was to use direct injection of steam. In order to accomplish steam addition a minor modification was necessary to the fuel inlet to the burner. Figure 4.6 depicts this modification. Two concentric tubes allow for steam addition through the center tube and fuel through the outer. This arrangement enables the flame height to be adjustable as before. To eliminate condensation of steam in the tube, a heating tape at 100°C is wrapped around the steam tube. This limits operation to fuels with a boiling point greater than 100°C. Steam is generated in an evaporator with an escape valve to lower the pressure in the evaporator.

Using n-dodecane as the fuel, the burner was lit and allowed to reach an equilibrium. With the exhaust valve open, steam

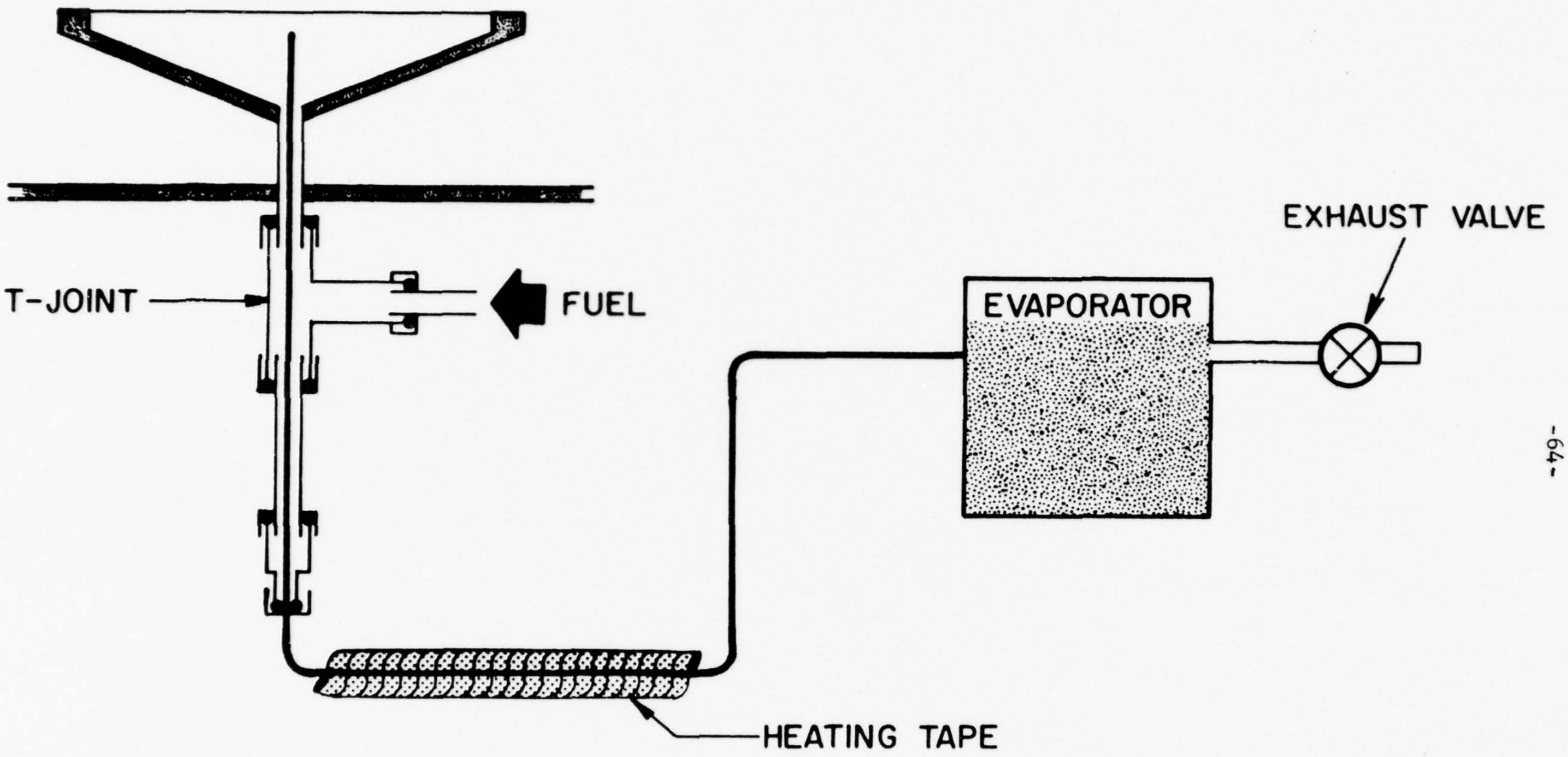


Figure 4.6 Steam Addition Modification

then is allowed to enter the interior of the flame. Immediately, the flame height decreases and the color changes more to a blue; much the same effect as if 0_2 were added making the flame premixed. There is some difficulty with the flame when the steam is added. With the exhaust valve closed, pressure in the evaporator is large enough to give the steam a very high velocity as it enters the flame. This causes the flame tip to become turbulent, increase mixing. Opening the exhaust valve lowers the steam velocity. Even with the valve open, if the steam tube is not aligned with the flame the steam flow causes a hole in the flame. The flame side near the hole is then blue and the opposite side not effected as much. Thus careful alignment of the chimney, flame, and tube was required for establishment of reproducible flame structures.

In order to determine whether the change in the flame structure was due to the chemical effect of the water addition, nitrogen was substituted for the steam. The same effect occurred leading to the conclusion that the observed effect is mainly a thermal one. The addition of inert substances with high heat capacities probably causes a lowering of the flame temperature. With less heat available in the flame, less heat diffuses to the pool of fuel, lowering the burning rate. Another possible explanation is the lower flame temperature changes the rate at which the precursors of carbon form.

As a result, the flame color became blue, indicating this fuel burns more efficiently.

Since the same effect was observed with both nitrogen and water, it was decided to saturate the N_2 with H_2O and then see if any difference occurs between this case and pure nitrogen. Results of this test are inconclusive because no observable difference in the two cases could be recorded.

Problems associated with not knowing flame or burner temperatures, steam flow or fuel mass burning rates, and not having a truly stable, adjustable flame resulted in no meaningful measurements being made for this water addition technique.

4.3 Fuel Blends

The third area of investigation was comprised of two main parts. First, mixtures of some different fuels under controlled conditions were tested to see effects of mixtures on a combined smoke point. These tests were done to determine dominant soot formation fuel components and provide information applicable to fuel blends. Secondly, some newer fuels, made available through the Air Force were tested to determine their sooting characteristics in relation to their composition.

4.3.1 Fuel Mixtures

Several mixtures, in varying volume percent, were made and tested for smoke point under controlled conditions. The smoke points were steady with time indicating the mixtures remained consistent throughout the tests. Results are given in Figure 4.7. Mixing heptane with (iso) hexane shows the resulting smoke points to be a linear combination of the pure fuel smoke points, dependent on the volume percents. Mixtures of heptane and hexene also exhibit the same results. Thus, in general, mixtures of aliphatic fuels have a combined linear smoke point dependent on their volume percent.

When mixing heptane and toluene, a very different type curve results. This curve shows the addition of only a small amount of toluene to heptane causes a substantial drop in smoke point hence a large increase in the soot formation character. A mixture of 80% heptane/20% toluene lowers the pure heptane smoke point 51%. Any increase in the amount of toluene past this point does not have as strong an influence. At the higher percentages of toluene, the mixture behaves very similar to the pure toluene. This behavior indicates a very strong influence on smoke point of an aromatic fuel over a paraffin. A few percent aromatic fuel mixed with a paraffin can greatly increase soot formation. Further data by Hunt suggests an even stronger influence on naphthalenes. Chapter 5 gives a detailed explanation of these results.

Mixtures of orth-, meta- and paraxylene with heptane were tested in an attempt to determine the influence of the methyl position on smoke point (Figure 4.8). Hunt suggests from data obtained in a Davis

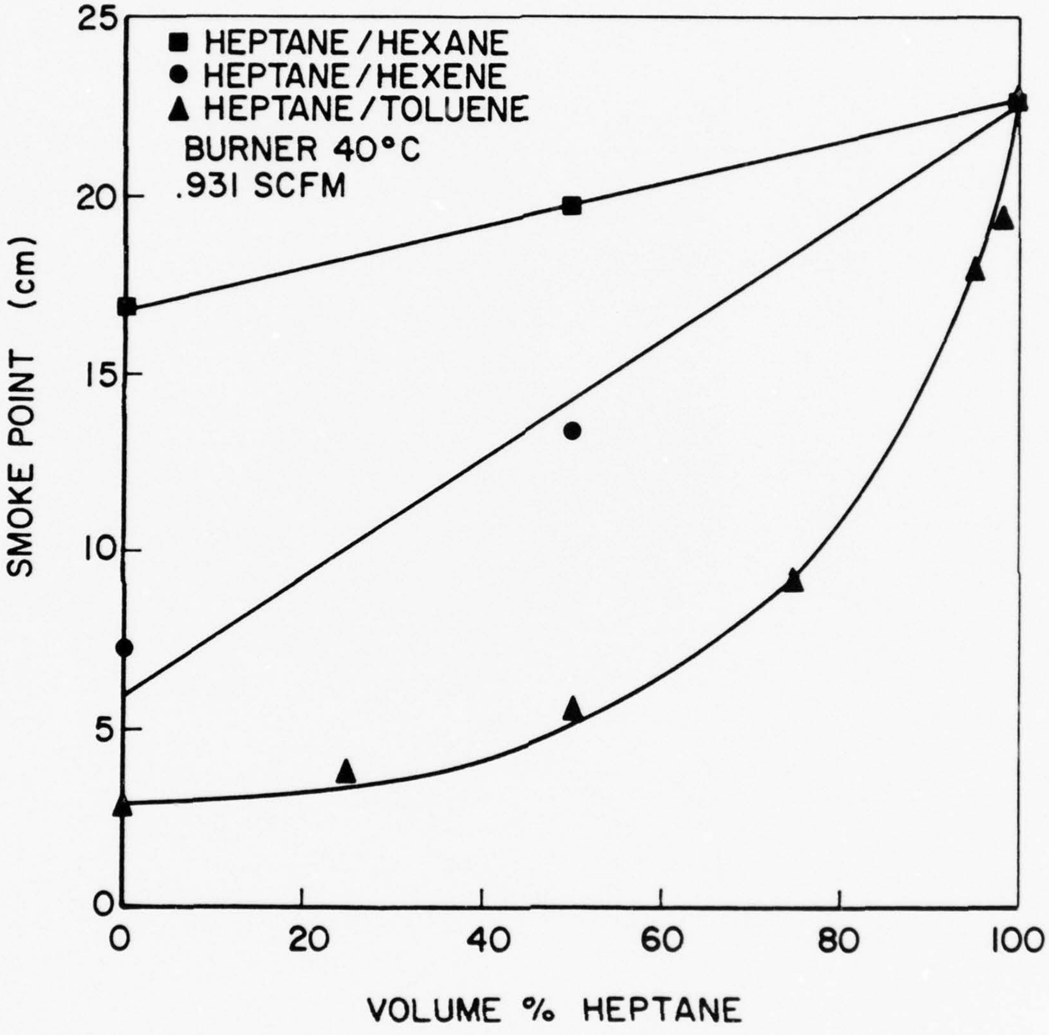


Figure 4.7 Smoke Points of Fuel Mixtures

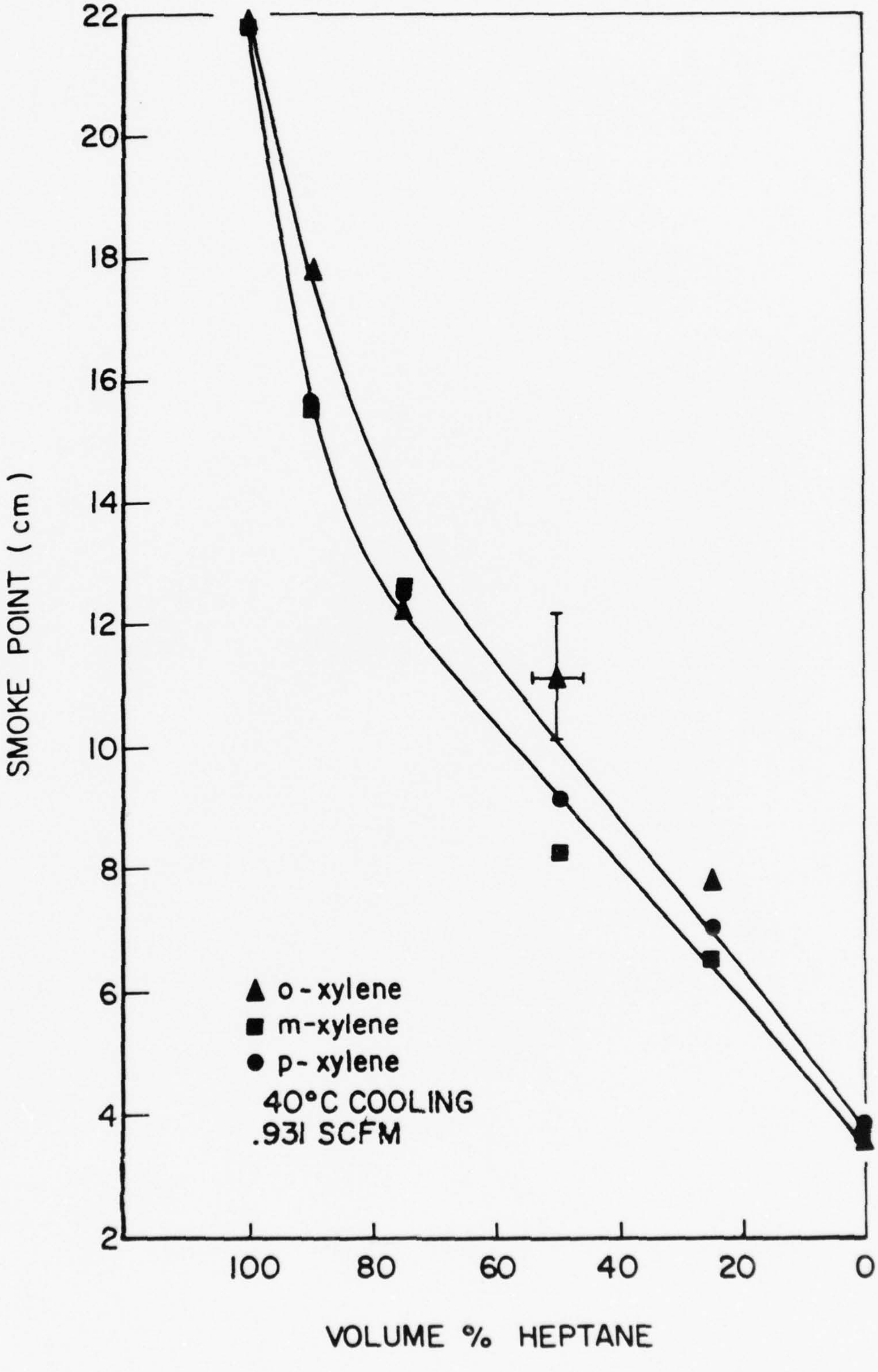


Figure 4.8 Heptane/Xylene Mixtures

factor lamp, that ortho-xylene has a slightly higher smoke point than the other two indicating meta- and para-xylene might be easier to polymerize and, thus, form soot more readily. Figure 4.8 shows the results of such mixing tests. The graph displays the basic aromatic/alkane trend; however, no strong conclusions can be made about the xylenes. Indications show that, indeed, orthoxylene has a slightly higher smoke point but because of the range of data this could be due to experimental error.

4.3.2 Future Fuels

Six fuels, provided by the Air Force, were tested for smoke point under controlled conditions. Table 4.2 and 4.3 provide available data on the fuels, which are JP-4 (oil shale and conventional), JP-5 (oil shale and conventional), JP-9 synthetic missile fuel, and JP-10 synthetic missile fuel. Gas cromatography performed by the Air Force indicates the oil shale fuels should have a higher normal alkane content and thus, should be cleaner burning fuels dependent on aromatic content. In direct conflict with this information is the hydrocarbon type analysis shown in Table 4.3. Discussion of these discrepancies follows shortly. The missile fuels are blends of conventional fuels to be used in future Air Force projects. Test results are given in Figures 4.9 and 4.10.

Comparison of the conventional fuels with the oil shale reveal some differences. The color of the fuels differs drastically. The

TABLE 4.2 DATA ON FUELS SUPPLIED BY THE AIR FORCE

	JP-4 Conv.	JP-4 Oil Shale	JP-5 Conv.	JP-5 Oil	JP-9	JP-10
% Hydrogen Content	14.59	14.52	13.96	13.72	11.76	11.85
Total Sulfur % Wt.	.01	.03	.05	--	.02	--
Gravity °A.P.I.	56.3	56.7	42.8	43.9	18.3	--
Heat of Combustion MJ/kg	43.67	43.42	43.39	43.14	--	--
Aromatic %	10.6	11.6	17.6	26.2	--	--
Olefins %	1.1	1.3	1.8	--	--	--
IP Smoke Point (mm)	35	40	26	23	15	18
Luminometer Number	83.0	66.0	60.0	42.0	30.2	32.2
Smoke Point Using ASTM Smoke Point Luminometer Relationship* (mm)	36.10	28.83	26.35	19.21	14.75	15.50

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*$SP = +\ 4.16 + 0.331\ LN + 0.000648 LN^2$

TABLE 4.3 HYDROCARBON TYPE ANALYSIS (Monsanto Research Corp.)

	Volume Percent			
Compound Type	Conventional JP-4	Shale JP-4	Conventional JP-5	Shale JP-5
Paraffins	67.6	67.9	47.2	62.0
Cycloparaffins	19.8	19.5	37.7	16.9
Dicycloparaffins	3.2	1.7	2.2	0.6
Alkylbenzenes	7.6	9.6	7.6	8.9
Indans and Tetralins	1.8	1.3	2.9	9.0
Naphthalenes	< 0.1	-	2.3	2.6

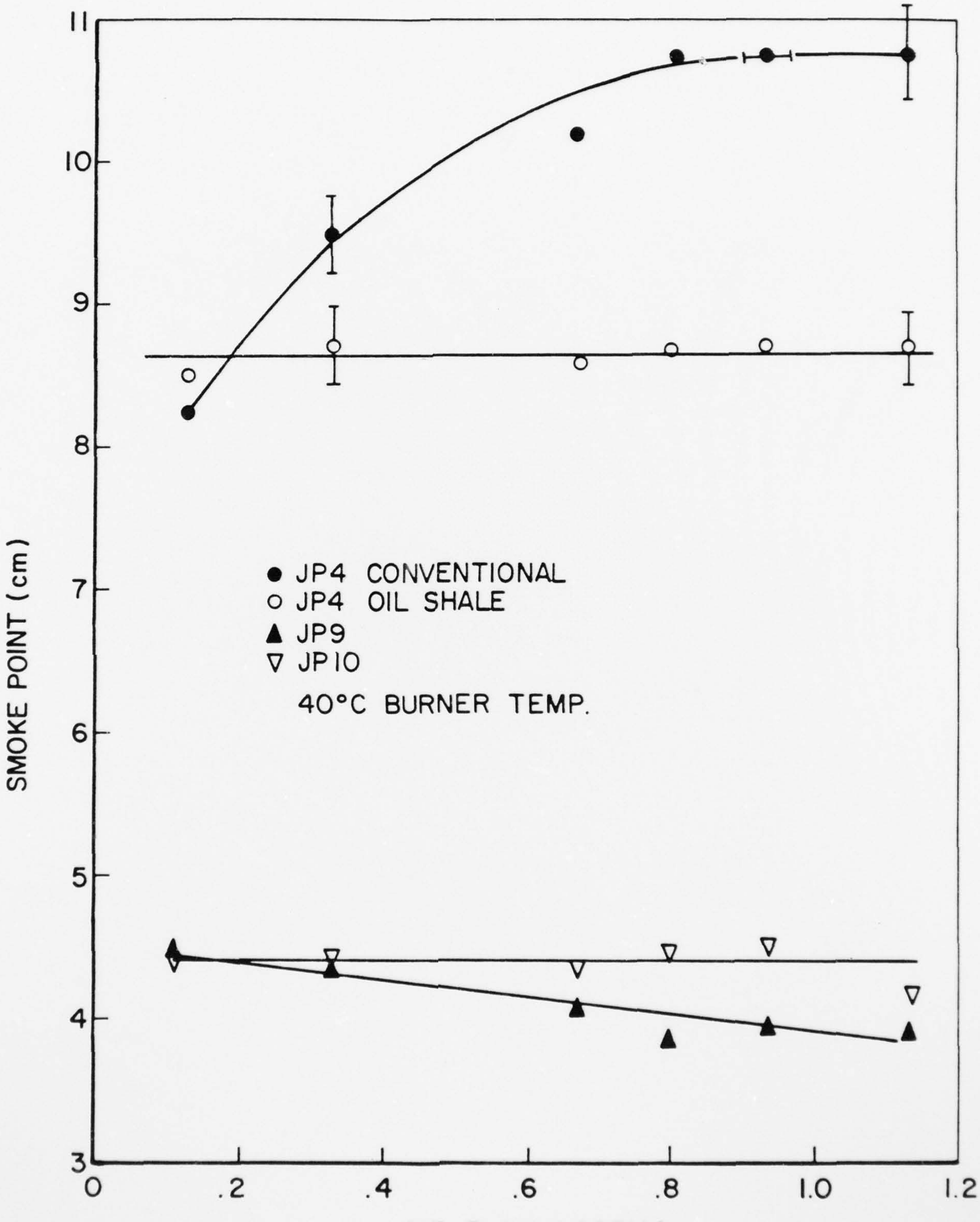

Figure 4.9 Alternative Fuel Smoke Points (1)

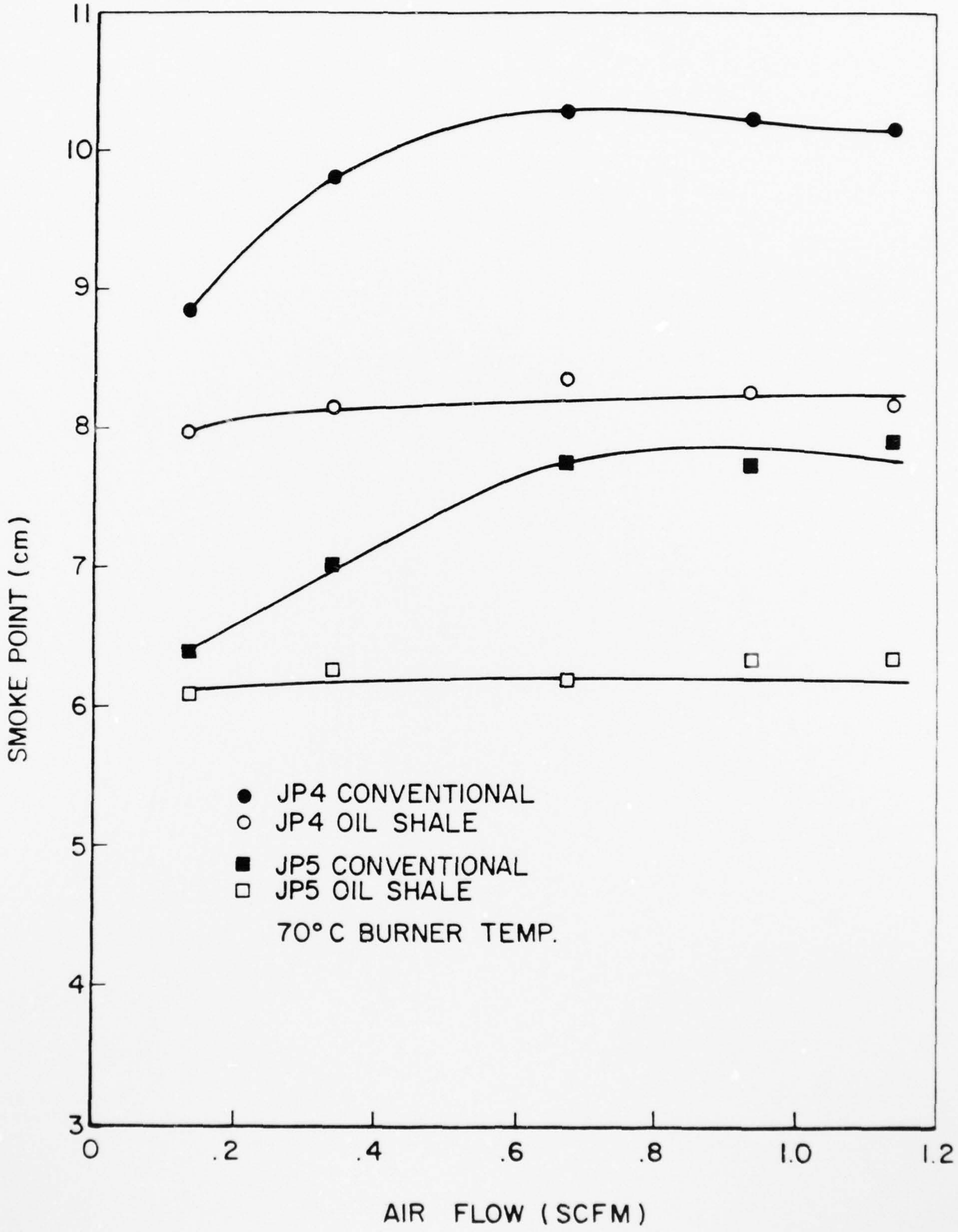

Figure 4.10 Alternative Fuel Smoke Points (2)

oil shale JP-4 is a rich, yellow color while the conventional fuel is clear. Again the oil shale JP-5 is a red, almost opaque color while the conventional fuel is a pale yellow. These differences indicate possible variation in composition and trace elements (impurities). When burning the fuels, the conventional JP-4 ignites easily. The oil shale JP-4 ignites, but will not sustain itself until heated. This difference indicates the oil shale has a smaller fraction of low temperature volatile compounds than the conventional fuel. Both JP-5 samples proved impossible to burn at 40°C burner temperature. Because of this fact, tests on JP-5 are run at 70°C burner temperature. At this elevated temperature the flame can sustain itself. Figure 4.10 shows these tests as well as JP-4 at this temperature for comparison.

The synthetic missile fuels are completely compatible with the 40°C burner temperature and results are shown in Figure 4.9.

Looking at the data presented in Figure 4.10 two characteristics are obvious when comparing the oil shale and conventional fuels. The percent hydrogen content correctly predicts the JP-4 fuels to have higher smoke points than the JP-5. However, in each case the oil shale has a lower smoke point than the conventional fuel. The explanation for such a phenomenon is not readily apparent from the information provided by the supplier. Gas cromatography supposedly revealed a higher percentage of normal paraffins in the shale fuels;

however, hydrocarbon type analysis does not totally verify this finding. Both JP-4 samples contain roughly the same amounts of normal paraffins while the JP-5 shale sample does have a higher amount of normal paraffins than its conventional counterpart. With the JP-5 samples the shale fuel definitely has a higher percentage of aromatic components and, thus, results in a higher sooting fuel and a smoke point lower than the conventional JP-5. For the JP-4 fuels the explanation is not as clear. The data provided indicate the conventional JP-4 to have about 1% less aromatic content than the shale JP-4. The smoke points provided by the Air Force for the JP-4 fuels show the shale fuel to soot less than the conventional. This is in direct conflict with the smoke points found by this investigation and the smoke point predicted by the aromatic content as shown in the heptane-toluene experiments. Looking at the curves for the JP-4 fuels found in Figure 4.10 reveals further interesting trends. The shale fuel shows no influence of the air flow and behaves largely as an aromatic while the conventional fuel shows an air flow dependence similar to a paraffin fuel. Thus smoke point dependence on air flow gives valuable information on fuel character and in this instance would indicate the data provided on the JP-4 fuels could possibly be in error. One would expect the shale fuel to have a substantially higher amount of aromatic components than the conventional fuel as reported in the JP-5 cases. Smoke points for the JP-4 fuels using the ASTM smoke point luminometer relation also contradicts the analysis data provided and confirms the findings of the investigation. As a result, the data supplied on the JP-4 fuels should be reviewed in light of the present findings.

The missile fuel smoke points also have interesting results. Both fuels have similar hydrogen content and, thus, similar smoke points. In addition the smoke points indicate these fuels have large potential to produce soot.

CHAPTER 5

DISCUSSION OF RESULTS

5.1 Smoke Point Test

The results of this investigation definitely establish the smoke point measurement as a valid test for qualitatively comparing the potential of a fuel to form soot. As an example, consider the results for toluene and heptane. Toluene has a smoke point of 3.5 cm as compared to 26 cm for heptane (at .931 SCFM, 40°C). Observing the two different tests, it is readily apparent that toluene forms soot much more readily than the heptane despite the fact that both have the same number of carbon atoms and a very similar molecular weight. The fuels we have tested follow in general the qualitative trends reported by Minchin, Clarke, and Hunt from detailed studies of various fuels (Figure 2.4). Qualitatively comparing the different pure fuels gives an indication of the dependence of the sooting tendency on molecular structure and properties of the fuel. Both Clarke and Hunt report some analysis on this subject, which is outside the scope of this investigation.

However, the important contribution of this investigation to the smoke point measurement of liquid fuels is the need for controlling both air flow and burner temperature. Figures 4.1 and 4.4 show that unless measurements are taken under similar conditions meaningful results will be lost. Figure 4.1 shows the smoke point variation with burner temperature to be linear indicating it may be possible to correct for unlike burner temperatures. If two different fuels are tested at unlike burner temperatures, the smoke points can be compared at a specified temperature if the smoke point dependency on the burner temperature for one or both of the fuels is known. The smoke point dependence on air flow is even more drastic (Figure 4.4). For comparison of different fuels it is always desirable to operate in the region where air flow does not influence smoke point. However, variation of the smoke point with air flow can give an indication of the sooting character or composition of a fuel (i.e. whether the fuel behaves as an aromatic or aliphatic). Following the two suggestions, fixed burner temperature and controlled air supply, meaningful smoke point measurements can be made.

5.2 Water Addition to a Diffusion Flame

From the tests performed by this investigation the role which water plays in the suppression of soot is very inconclusive. The emulsion experiments show the effect of water addition (at a constant burner temperature) is negligible or only serves to slightly lower the smoke point. Steam added inside the flame behaves essentially identical to nitrogen addition indicating a strong physical effect as opposed to a chemical one. These results necessitate further investigation of phenomenon involved with the intent of determining whether the effect of water addition to diffusion flame is mainly a chemical or a physical effect.

From a physical point of view water can be involved in different ways changing structure and properties of a laminar flame. Acting as a diluent, water contributes to a change of the heat capacity of the system. In this sense, water can be regarded as a heat sink, storing energy in its vibrational modes which otherwise would be available to decompose the fuel.

Furthermore, water can change the energy flux of the system due to its different thermoconductivity and thermodiffusivity when compared to the pure fuel. The evaluation of these processes requires a series of experiments involving different diluents, measurements of flame temperature and so on, which far extend the subject and purpose of this investigation.

Consideration of the chemical effect of water addition deals mainly with water being involved in the kinetics of the diffusion flame pyrolysis region. In a premixed flame or in the final stage of a diffusion flame water is apparent as a combustion product. Added water results only in a concentration increase which does not introduce new reaction channels or change the fundamental kinetic behavior.

The important chemical reaction in the pyrolysis region when considering the chemical effect of water addition on diffusion flames is:

$$H + H_2O \longrightarrow OH + H_2 \qquad (6)$$

This reaction increases the OH concentration and consequently could be responsible for the suppression of soot formation through OH attack on precursors. However, this reaction competes with the H attack on the fuel.

$$H + RH \longrightarrow R + H_2 \qquad (11)$$

Table 5.1 shows pertinent data on these reactions. Using ethane as a representative hydrocarbon fuel, the activation energy of reaction 6 is twice that of reaction 11, indicating 11 has the higher probability of occurring. Also since the pre-expotential factor of reaction 11 is greater than 6, there will be no temperature at which the rates become competitive. At 1000°K H radical attack on ethane is 3×10^2 faster than H radical attack on water. At 2000°K the ethane is still 20 times greater. In order to obtain competitive rates the water concentration has to be increased significantly. However, large concentrations of water inside the diffusion flame will probably cause a reduction in flame temperature due to the described physical effects and, thus, lower the reaction rates to where the reactions are no longer competitive. Most premixed studies have been conducted in this manner with a high concentration of water when compared to the fuel concentration. Turbulent flow reactor studies on water addition conducted by Young (1978) at 1100°K do not allow conclusions on the effect of soot suppression. Running in a fuel-rich situation Young added twice as much water as fuel to the system and saw no difference in the rates of

TABLE 5.1 REACTION RATES

		Log A	Ea(cal)
Baker, Baldwin and Walker (1970)	$C_2H_6 + H \rightarrow C_2H_5 + H_2$	14.121	9680
Baulch et al. (1972)	$H + H_2O \longrightarrow H_2 + OH$	13.968	20360

$$K_1 = 10^{14.121}\, e^{\frac{-9680}{RT}}$$

$$K_2 = 10^{13.968}\, e^{\frac{-20360}{RT}}$$

Temp ($^\circ K$)	K_1	K_2	K_1/K_2
100	9.197×10^{-8}	2.935×10^{-31}	3.134×10^{-23}
1000	1.012×10^{12}	3.296×10^{9}	3.071×10^{2}
2000	1.156×10^{13}	5.533×10^{11}	20.9

formation of species when compared to data without water at the same temperature. Due to the low temperature of the flow reactor study the chemical effect of water addition could be small. As a result, the chemical effect of water addition in a diffusion flame will possibly be small unless the temperature is high enough and the concentration of water large enough to make reactions 6 and 11 competitive. Computer simulation could attempt to explain the effect of water addition on a hydrocarbon oxidation system.

The possibility of a strong thermal effect on soot formation, as evidenced by the nitrogen addition to the diffusion flame, must be explored. The changing of the flame temperature will definitely effect the kinetics of the pyrolysis region in a flame and, thus, the rate of formation of the precursors of soot. The thermal effect could account for the variation in smoke point with burner temperature. Lowering the burner temperature is similar to lowering the initial temperature of the fuel. At low burner temperatures, the energy necessary to raise the fuel to the vaporization temperature is greater than half the heat of vaporization and, thus, the sensible enthalpy of the fuel becomes an important term. A simple energy balance calculation shows this term can reduce the flame temperature by 200°C, altering temperature gradients inside the flame and perhaps the rate of soot formation.

These ideas on water addition are only conjecture but indicate the need for more precise information to determine the effect of water addition in a diffusion flame.

5.3 Fuel Blends

The mixing of various fuel types shows the obvious domination of an aromatic structure over that of an aliphatic. A few percent of aromatic fuel mixed with a paraffin fuel tremendously increases the soot formation of the mixture. This behavior can possibly be explained by considering the type of precursors each fuel forms. With the aliphatic fuels, acetylene and polyacetylene are the primary precursors which then polymerize to form soot. The aromatic fuels, which already possess a high C/H ratio, are thought to produce polycyclic aromatic hydrocarbons as the precursors. If the two fuels are mixed together one can infer the aromatic fuel will dominate the process of soot formation. Polycyclic aromatic hydrocarbons can polymerize with a molecule of like structure or a polyacetylene and, thus, form condense-phase nuclei faster than the acetylene route alone.

Plotting the inverse smoke points versus percent heptane for the different mixtures reveals an interesting trend (Figure 5.1). Each of the mixtures plotted in this way prove to have a linear dependence of combined smoke point on volume percentages of components. With such a relationship it is possible to empirically predict the combined smoke point if the pure fuel smoke points and percentage of components are

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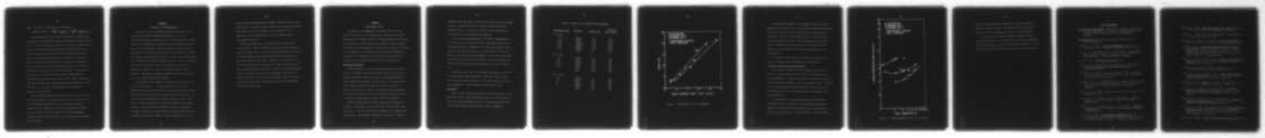

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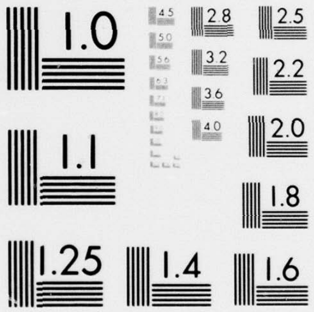

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known. The result is the empirical relationship:

$$1/\text{combined smoke pt.} = \frac{\text{Vol }\%A}{100}\ \frac{1}{\text{Smoke pt A}} + \frac{\text{Vol }\%B}{100}\ \frac{1}{\text{Smoke pt. B}}$$

A direct extension of the information obtained by blending fuels is possible when considering oil shale and conventional fuels (Table 4.2). Both oil shale JP-4 and conventional JP-4 have similar hydrogen content (14.52% and 14.59% respectively); however, analysis reveals the oil shale to contain 11.6% aromatics while the conventional fuel only 10.6%. In this range, an increase of as little as one percent of aromatic fuel can strongly influence soot formation as indicated by the toluene-heptane results lower smoke point (8.7 cm for the oil shale JP-4 and 10.75 cm for the conventional JP-4). Smoke point data supplied by the Air Force contradicts these findings (35mm for conventional JP-4 and 40mm for oil-shale JP-4). Further investigation using the ASTM smoke point luminometer relationship indicates the Air Force data to be incorrect and the present data to adequately represent the smoke points.

Similarly, when comparing the JP-5 fuels, the oil shale contains the higher percentage of aromatics (26.2% for the oil shale and 17.6% for the conventional) despite the fact the hydrogen content is roughly the same. Smoke point tests of this investigation display the same trends as both the Air Force data and ASTM luminometer correlation; thus, the oil shale has a lower smoke point and produces soot more readily.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The results of this investigation confirm the validity of the smoke point test under controlled conditions as a means of qualitatively comparing fuels for their ability for form soot. Tests also give an indication as to importance of fuel molecular structure relative to soot formation. However, in order to make meaningful contributions to the area of soot formation it is necessary to extend the technique to obtain more information. Sampling may provide information on precursors and important species involved. Also, a temperature profile of the flame may aid in rate determination and help to differentiate between the thermal and chemical effects of water addition. These types of extensions should provide further insights to the soot formation phenomenon involved.

The problem of water addition in a diffusion flame proves to be one of great complexity. A definite need exists to accurately determine the extent of the effect of water addition on soot formation. Because of the possibility of both chemical and thermal effects, carefully controlled experiments are needed to attempt to isolate these effects. Problems inherent in a liquid fuel diffusion flame suggest the use of a gaseous diffusion flame where flows can be precisely monitored. Presently, on-going research is exploring this possibility. In addition, flow reactor studies at elevated temperatures may also provide valuable information on the subject. Results of such a study could lead to an analytical model to explain the formation of condense-phase nuclei as well as the effects of water addition. The indications in this investigation are that the thermal effect of water addition dominates.

Mixed fuel studies show a strong influence of aromatic over aliphatic fuels. This is an important realization when considering alternative energy fuels. Oil shale and coal derived fuels originally have 50-80% aromatic content and extensive refining techniques are necessary to decrease this figure. However, it is not until there is less than approximately 20% that the soot formation character of the fuel has been significantly affected. Thus, if 20% or greater aromatic content is acceptable one need not be concerned as much with soot formation character as most fuels past this point behave very similar to the pure aromatic fuel. Such mixtures could lead to tremendous savings in refining costs.

APPENDIX

MASS BURNING RATES

The purpose of this appendix is to present some of the mass burning rate results of this investigation. The mass burning rate measurements were thought initially to provide information about smoke point dependence on burner temperature. However, within the experimental error of the measurements, no conclusion can be drawn. Included in this appendix are a description of the experimental procedure, a discussion of the results, and an evaluation of the Factory Mutual reservoir used in conjunction with the Clarke wickless burner.

Experimental Procedure

After preparing the Clarke wickless burner and Factory Mutual reservoir (procedure outlined in sections 3.5 and 3.2), the fuel is ignited and reservoir adjusted to obtain the desired flame height. Having adjusted the reservoir, the fuel level is then noted and the flame allowed to burn at this height for at least one hour. (At least an hour is needed to secure a reasonably accurate measurement. The lower the flame height, the lower the mass burning rate and, thus, the longer the time necessary to get an accurate measurement.)

While the flame burns, both flame height and pool diameter are measured. Flame height is taken as the point about which the flame oscillates, as this small oscillation is inherent in the operation of the reservoir. Pool diameter is measured in two ways. A number of concentric rings are lightly scribed in the conical burner at measured intervals. Counting the number of rings then indicates the pool diameter directly. As a check, a caliper is used to estimate pool diameter and the two measurements are compared.

After the designated time period, the flame is extinguished and final fuel level in the reservoir noted. The change between initial and final fuel level corresponds to a volume of fuel burned. When the volume of fuel burned is related to the time period of burning the result is a mass burning rate measurement at a particular flame height. Also known for the particular flame height is the pool diameter and surface area which enables the determination of the linear regression rate.

Measurements were taken in this manner using heptane as the fuel at three different burner conditions: 25°C, 40°C, and no cooling. In all cases the chimney height was 3.5 cm and the burner was vented to the atmosphere. Table A1 shows the results of the tests.

Discussion

Figure A1 shows the mass burning rates versus flame height at the temperature tested. Within experimental error, all cases follow the same linear relation indicating that for a given flame height there is a certain mass burning rate regardless of burner temperature.

TABLE A1 RESULTS OF MASS BURNING RATE MEASUREMENTS

Flame Height (cm)	$\dot{m}$ (g/sec)	Diameter (cm)	Regression Rate (mm/min)
No cooling			
3.35	.00106	1.13	.927
8.75	.00367	1.88	1.154
12.00	.005264	2.15	1.272
16.50	.006033	2.26	1.319
17.00	.006075	2.26	1.329
17.00	.006040	2.20	1.402
	.01375	3.4	1.329
40°C cooling			
2.8	.000949	1.27	.657
6.0	.00270	2.20	.623
12.0	.005199	2.83	.727
16.5	.00555	3.20	.665
19.5	.00743	3.40	.717
	.0117	4.33	.699
	.0331	6.22	.955
25°C cooling			
3.5	.001687	2.2	.390
9.0	.00456	3.4	.440
21	.00924	4.33	.550
21	.009743	4.33	.580
	.019806	5.65	.692
	.0253	6.22	.731

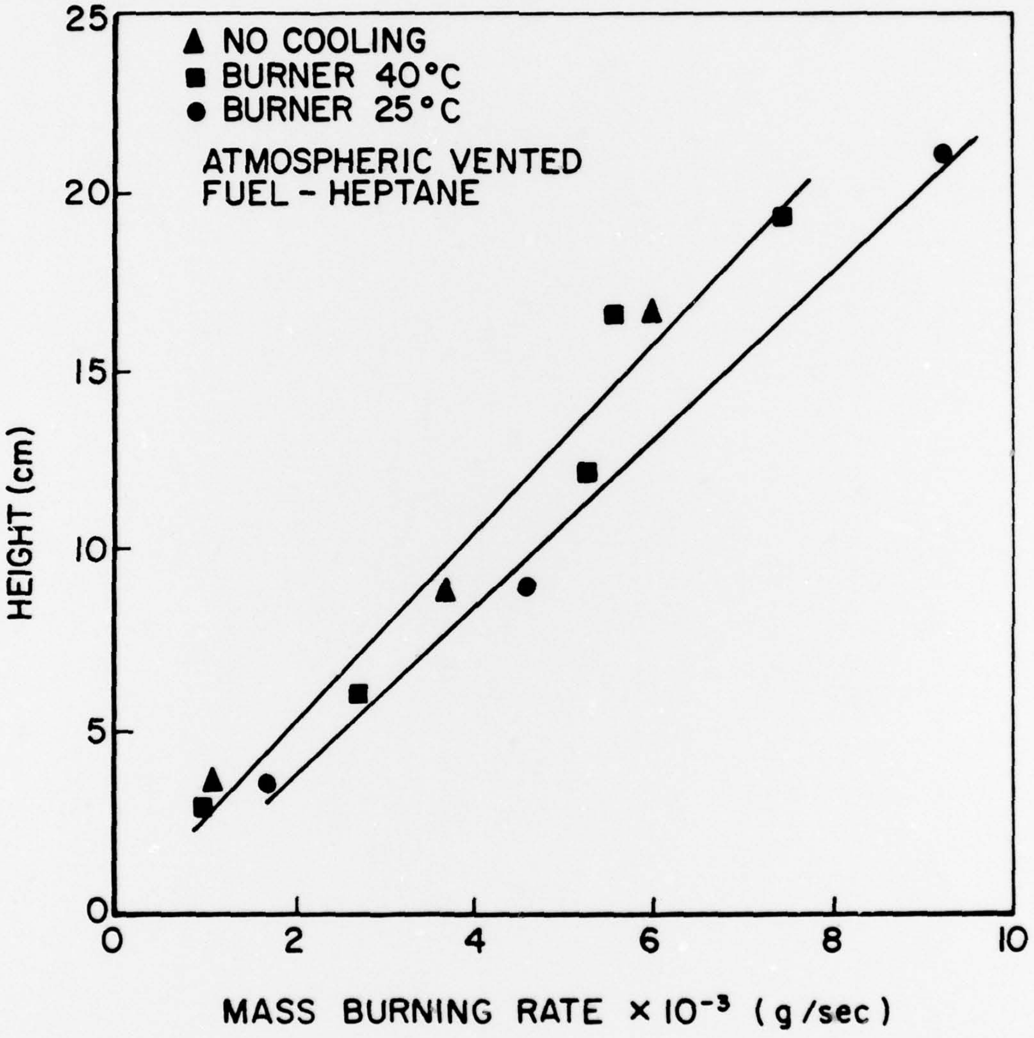

Figure A1 Mass Burning Rate vs. Flame Height

Plotting the more familiar linear regression rate versus pool diameter shows a distinct curve for each burner temperature (Figure A2). These curves, however, behave as predicted with the cooler burner temperatures having the lower regression rate at any pool diameter. The curve shapes do not behave as previous experimental data would indicate. Comparing the present results with Emmons (1961) shows there may be an influence of burner geometry and position on the regression rate.

From the mass burning rate data no conclusion could be drawn about the effect of burner temperature on the smoke point.

Evaluation of Mass Burning Rate Technique

The technique to measure the actual volume of fuel burned is as precise as the measurement of the fuel level. This change in fuel level corresponds to a volume of fuel, which is taken from the actual internal volume of the reservoir and is very precisely known. Dividing the mass of fuel burned (obtained by multiplying the volume of fuel by the density) by the time of burning gives the mass burning rate rather accurately.

The introduction of the error occurs with the pool diameter measurement and the flame height. The pool diameter measurement appears as a squared term in the regression rate; thus, the error increases as the square also. Since the flame is not always exactly

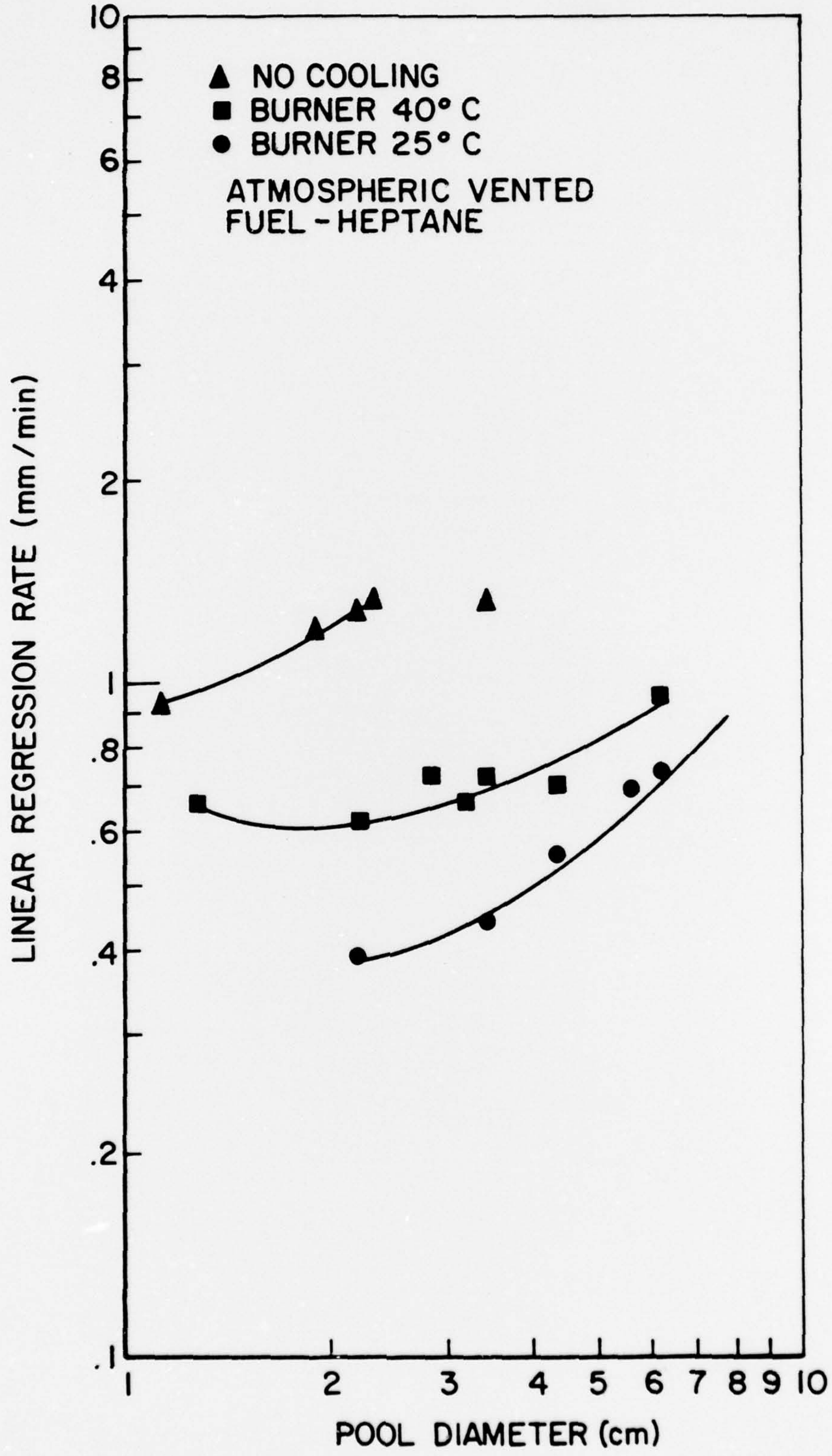

Figure A2 Linear Regression Rate vs. Pool Diameter concentric with the burner, determination of the pool diameter is subject to a degree of error. The flame height, which oscillates about a point, also introduces some error into the measurements.

The final results of these measurements, however, do predict valid trends in the data. Figure A1 has the same linear relationship as would be expected. In Figure A2 each temperature displays the same basic trends and the position of each curve is as would be expected.

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