Sooting Behavior in Temperature-Controlled Laminar Diffusion Flames

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The sooting tendency of gaseous and liquid hydrocarbon fuels has been determined systematically in an axisymmetric laminar diffusion flame whose temperature was controlled by nitrogen dilution. Sooting tendency was measured by the minimum mass flow rate of fuel (FFM) at the smoke height. Results, plotted as log 1/FFM versus 1/T, where T is a calculated adiabatic flame temperature, show that fuel structure plays a significant role in diffusion flames. Comparison of these flame results with basic pyrolysis studies in the literature supports the concept that pyrolysis of the fuel molecule is a controlling factor in determining the overall tendency to soot, even though such tendency results from the competition of pyrolysis of the fuel and heterogeneous oxidation of the soot particles. The pyrolysis characteristics affecting the sooting process are rate, sequence and nature of products, and pyrolysis mode (pure or oxidative). The aromatics show a temperature sensitivity with respect to sooting tendency significantly lower than the other fuels. Conjugation of the initial fuel molecule and pyrolysis intermediates enhances sooting propensity.

INTRODUCTION

The formation of soot during combustion is a very complex phenomenon that is detrimental to the efficiency and maintenance of combustion devices and, more important, causes environmental concerns [1]. Many of the extensive soot investigations with diffusion flames over the past 50 years were confined to the observation of overall effects, such as the flame height [2–4]. Later, as chemical analytical equipment and laser diagnostics developed, the basic literature has evolved into an attempt to understand the detailed steps of the sooting process [5–7]. However, the original qualitative flame height approach has been found justifiable when seeking controlling mechanisms which, when understood, could predict quantitative yields of soot and give some insights into the relative tendency of various fuels to soot in a well characterized combustion environment. Furthermore, such experiments provide guidelines for subsequent more detailed investigations.

Previous work on sooting tendency in flames and some work on the pyrolysis and oxidation of hydrocarbons [8–11] have suggested that under premixed conditions the rate of soot formation is controlled by the competitive effects of the rate of fuel pyrolysis during the combustion and the rate of oxidative attack on the soot precursors which form as a result of fuel pyrolysis. Since the rate of oxidative attack increases faster with temperature than the rate of fuel pyrolysis, for a given fuel, the higher the temperature the lower the tendency to soot. In diffusion flames, soot is formed on the fuel side [6] where there is essentially no oxygen present. Hence, there is no competitive mechanism to the pyrolysis of fuel leading to the formation of precursors, which is the main controlling factor. Consequently, the higher the temperature, the greater the tendency to soot. Oxidative attack in diffusion controlled processes still takes place, but at
a later stage, as heterogeneous oxidation of the soot particle.

One of the drawbacks of the earlier experimentation was that no attempt was made to separate the temperature effect from that of the fuel structure; this approach resulted in misleading conclusions about the factors controlling the soot process. Therefore, a systematic investigation on the sooting behavior of numerous fuels in both diffusion flames and premixed flames systems was initiated at Princeton; in both cases the temperature was controlled by nitrogen dilution of the fuel. This study is an extension of the initial effort on diffusion flames \[12\] to higher boiling point hydrocarbons. Nitrogen was added to the fuel in a coaxial laminar diffusion flame; flame height and mass flow rates were measured just before the flame broke open near its apex and emitted a streak of soot.

By controlling the flame temperature, a verification of the fundamental role of pyrolysis in the sooting tendency of diffusion flames was attempted and efforts were made to interpret sooting trends on the basis of pyrolysis kinetics results. The main focus of this paper is to relate the flame measurements made in this study to results of basic kinetic studies of hydrocarbon pyrolysis in a systematic investigation of the effects of fuel structure on sooting.

**EXPERIMENTAL ARRANGEMENT**

The apparatus used is depicted schematically in Fig. 1. The burner consisted of two concentric tubes. Fuel and diluent flowed through the inner one, a stainless steel tube measuring 10 mm i.d. and long enough to ensure a fully developed laminar flow profile. Air was forced through the
outer annulus whose confining brass tube measured 100 mm i.d. The air passage was filled with 3.0 mm glass beads; the final section of this passage consisted of a stainless steel honeycomb that ensured streamlines parallel to those of the flow from the inner tube. A 450 mm long pyrex cylinder was used as a chimney to shield the flame from air draughts. Gaseous flow rates were monitored by means of rotometers and eventually measured by a soap film flowmeter. Liquid fuels were vaporized using two different techniques. For most of the aromatics, a heated bomb was used to vaporize the fuel in a thermostatic bath of silicon oil, operated at temperatures 30–50K higher than the B.P. of the fuel tested. The fuel flow rate was controlled by a needle valve and eventually mixed with heated N₂ diluent, well upstream of the burner lip. Metering was achieved by clocking the liquid meniscus regression in the burettes used as fuel reservoir. Given the typical flow rates of 1 cm³/h, a second system was designed to speed up the measurement, and allow the testing of fuels of boiling points eventually higher than that of silicon oil (230°C). Fuel stored in a stainless steel reservoir was pressurized by regulated nitrogen and forced through a 300 mm long, 150 μm i.d., stainless steel capillary tube into the evaporator. The evaporator consisted of a 10 cm long stainless steel porous cylinder encapsulated in a ~13 mm i.d. stainless steel tube wound with heating wire; the high porosity of the cylinder enhanced the contact of liquid and hot surface, and minimized the line volume; this design thus ensured good controllability and response of the system. A preheated stream of nitrogen swept the hydrocarbon vapor into the burner. Fuel flow rates were controlled by varying the stagnation pressure in the fuel reservoir. At the small liquid flow rates of operation Hagen–Poiseille flow was established in the capillary, so that the volumetric flow rate was directly proportional to the pressure drop across the capillary. Since essentially all the pressure drop in the line was determined by the capillary, it was sufficient to measure the stagnation pressure in the fuel tank by a mercury manometer and later, off line, obtain volumetric flow rates by calibration of the system, using glass microburettes. During operation with these condensible mixtures all lines were heated to approximately 40K above the fuel boiling point. Thermocouples measured all appropriate temperatures necessary to determine standard volumetric and mass flow rates. All flame heights were measured at atmospheric pressure, with the air supply run in a highly overventilated mode to eliminate any effect of air flow rate on sooting tendency [2]. Flame heights were measured by a cathetometer.

The fuels tested were benzene, toluene, ethylbenzene, the xylenes, α-methyl naphthalene, tetralin, decalin, 1,3- and 1,4-cyclohexadienes, 1,5- and 2,4-hexadienes, butadiene, C₃, C₄, and C₆ cycloalkanes, C₅ and C₆ cycloolefins, isooc-tane, n-octane, and isobutane. The purity of the chemicals was better than 99 mol %. The experimental method has been previously described [12]. Briefly, the sooting tendency was classified by the minimum height (sooting or smoke height) at which smoke just broke through the flame. The greater the height or the fuel mass flow rate required to achieve these conditions, the less is the tendency to soot. As the amount of nitrogen added to the fuel is changed, the fuel flow rate has to be modified accordingly, in order to restore the incipient sooting condition. Consequently, for a given fuel, different sooting heights are obtained as functions of nitrogen dilution and, therefore, flame temperature.

**INTERPRETATION OF THE Sooting HEIGHT**

In a previous study [12] it was assumed that the diffusion flame, defined as the surface where fuel and oxidizer meet in stoichiometric proportions, ends at the same point as the luminous flame, even though it was recognized that some carbon monoxide and soot could be further oxidized outside the luminous zone. The original interpretation of the sooting height has now been significantly modified on the basis of a careful review of the recent literature and some preliminary experiments performed in this laboratory.
Indeed, the results available in the literature are apparently contradictory. Spengler [5], investigating the chemical structure of an axisymmetric sooting n-hexane diffusion flame in air, found that the true diffusion flame height was only 60% of the luminous one. Furthermore, the reported soot volume fraction peaks also at the same height, and indicates that some destructive process of soot was taking place beyond this point. It was concluded that beyond this height, but still inside the luminous flame envelope, oxidation of CO and soot takes place in a kinetically controlled regime. Roper et al. [13] came to the same conclusion by determining the true diffusion flame height from the measurements of CO concentration and soot volume fraction in the diffusion flames of several hydrocarbons in air. Boedeker and Dobbs [14] measured the temperature by CARS thermometry in a laminar ethene diffusion flame. They found that the peak temperature is reached well before the luminous flame height. Since all the heat should be released at the diffusion flame surface, their findings would still support the concept of a true diffusion flame height significantly smaller than the luminous one. In contrast, Mitchell et al. [15] and Saito [16] measured concentration and temperature profiles in a methane diffusion flame and suggested that the reaction zone, visibly identified by the blue hue associated with the burnout of CO, may envelop the luminous sooting region.

Some hints of reconciliation of the two seemingly conflicting pictures presented may come from the visual observation of a diffusion flame as the fuel flow rate is increased. As Palmer and Cullis [17] stated, "The luminous region first appears not at the tip but at a point within the otherwise blue flame area. As the fuel flow is further increased, the luminous point gets larger until it extends beyond the boundary of the blue flame surface and the luminous greybody radiation. Therefore, for the typical conditions at which measurements were carried out, there would appear to be a crossover between the diffusion flame surface and the luminous greybody radiating region. The soot particles generated in the soot forming region on the fuel side of the diffusion flame may not be completely oxidized at the diffusion flame surface. They would therefore survive beyond such a surface in a high temperature oxidizing environment where they would continue to emit the characteristic continuum greybody radiation. On the other hand, there would be no crossover of these two zones for very low fuel flow rates or for fuels having a low tendency to soot, such as methane.

The fundamental question remains as to why diffusion flames smoke as the fuel flow rate is increased beyond the sooting condition and how the unifying picture proposed affects the interpretation of such phenomena. Schug et al. [18] and Roper et al. [13], respectively, showed that the luminous flame height and the true diffusion flame height are directly proportional to the fuel volumetric flow rate. As the fuel flow rate is increased, the ratio of the luminous flame height to the true diffusion flame height increases. Consequently, the height of the oxidation region increases more than the height of the soot forming region, coincident with the true diffusion flame height. However, this fact does not necessarily imply an analogous behavior in the residence times in the two regions, because the velocity field is not uniform. Therefore, a conclusive answer demands detailed velocity measurements in order to establish the effect of the increase of the fuel flow rate on such residence times. Furthermore, residence times do not necessarily tell the whole story since, considering the competing nature of soot formation and oxidation, different effectiveness of the two processes may also play a role in the determination of the overall soot loading of the flame.

Initially Glassman and Yaccarino [12] suggested another possible explanation for soot breakthrough. They proposed that oxygen diffused from the air to the fuel side at the very base of the flame and acted as a catalyst for the fuel pyrolysis. As the fuel flow rate is increased, the flame lifts off the burner and more and more O₂ penetrates the fuel, and thus enhances the fuel pyrolysis and the formation of soot. The addition of small amounts of oxygen to the fuel side of an ethylene diffusion flame [18] confirmed the feasibility of such a hypothesis.

In conclusion, it appears that the smoke height of the diffusion flame represents an integrated
measurement of the tendency of fuels to soot, and results from the balance of soot forming processes and heterogeneous particle oxidation; particle oxidation is in general believed to begin inside the luminous flame zone.

Concerning the effects of nitrogen dilution, Schug et al. [18] showed that dilution had essentially no effect on the luminous flame height, which was found to be a function only of the fuel flow rate. In order to ascertain the effects of nitrogen dilution on the true diffusion flame height, experiments were performed on two nonsooting fuels, CO and methanol, for which there could have been no masking effects from the luminous region of the flame. The fuel flow rates were kept constant while nitrogen was progressively added to the fuel side of the diffusion flames. The flame height in both cases increased as the nitrogen flow rate was increased. This behavior can be explained by a phenomenological analysis (see Appendix). Reconsidering then the results of Schug et al. [18], it would appear that in a sooting flame nitrogen dilution does not affect the visible (luminous) flame height but should increase the true diffusion flame height and, therefore, the height of the soot forming region. Furthermore, temperature measurements [14] reveal that the N₂ dilution decreases the temperature in the pyrolysis region but subsequently it increases the temperature in the soot oxidation region. The proposed explanation is that the cooling of the pyrolysis region of the flame decreases the rate of particle formation and therefore the radiative loss from soot. Consequently, higher temperatures in the upper part of the flame are possible, as measured. At first glance, then, it is not obvious whether the net decrease in soot loading with N₂ dilution is due to a decrease in the particle formation rate or to an increase in the particle oxidation rate. However, the temperature changes in the soot forming region are much more drastic and fuel pyrolysis, being a high activation energy process, exhibits a strong temperature dependency. On the other hand, the temperature range in the oxidation region is 1800–1900 K, and, for the typical O₂ concentration of this zone, soot oxidation is not expected to exhibit a strong temperature sensitivity [19]. In conclusion, the N₂ dilution experiment lends further support to the hypothesis that the sooting tendency of a fuel in diffusion flames is controlled by its pyrolysis kinetics.

RESULTS AND DISCUSSION

As stated earlier, the smaller the smoke height or the mass flow rate of fuel at the sooting point, the greater is the tendency of a fuel to soot. Thus, regarding the mass flow rate of fuel at the sooting point (FFM) as an inverse measure of the pyrolysis rate of a given fuel, the results, plotted as log(1/FFM) versus 1/T, where T is a characteristic temperature of the process, should produce straight lines for each fuel, since hydrocarbon pyrolysis rates follow Arrhenius kinetics. Accordingly, Glassman and Yaccarino [12] successfully correlated the results of aliphatics by choosing as the characteristic temperature the adiabatic stoichiometric flame temperature in air properly adjusted for nitrogen dilution in the fuel and calculated by using the NASA CEC program [20]. It should be emphasized that this temperature was chosen as the most convenient and physically apparent correlating parameter. Due to radiative losses, and some small heat loss to the burner rim, the actual flame temperatures throughout are somewhat lower than the calculated adiabatic temperature. However, it is thought that the adiabatic flame temperature is a good surrogate temperature for the thermal situation which exists in the pyrolysis region of a diffusion flame. In fact, the fuel pyrolysis that leads to soot formation takes place in a lower temperature region, well upstream with respect to the Burke Schumann flame surface. The temperature in this region is controlled by the heat feedback from the reaction zone of the cylindrical portion of the flame, well below the heavily soot loaded flame tip; in fact, the radial temperature gradients are much steeper than the axial gradients. As reported by Boedeker and Dobbs [14], the temperature in the reaction zone in this region scales very well with the adiabatic flame temperature. This agreement is not surprising because finite rate chemistry and radiation losses are not major effects where the reaction zone and sooting region are thin.

The type of information obtainable from data plots of log(1/FFM) versus 1/T is twofold: (1)
at a fixed temperature the sooting tendency of different fuels can be compared to investigate fuel structure effects; and (2) the temperature sensitivity of the sooting tendency can be observed for each fuel. The present results were also plotted in this manner. Since overlapping of some of the data resulted in a rather confusing plot, the fuels were grouped according to structural affinity and the results were reported in four figures (Figs. 2-5), with the same scale on the axes for ease of comparison.

**Monoaromatics**

Figure 2 gives results for six aromatics; least square fits of previously reported data of aliphatics [12] were plotted for comparison. The aromatics show a significantly greater tendency to soot as compared to the aliphatics. There is good agreement between the data points for each fuel's highest temperature which corresponds to undiluted condition, and other results reported in the literature [2]. The experimental scatter is due to the following reasons: the transition to smoky flames is gradual and no "wings" [12] that could help identify more precisely such transition were detected in the upper part of the flame, and, the range of flame heights among the aromatics is very small. It is difficult to propose a satisfactory differentiation among the aromatics, but sooting tendency would appear to decrease in the order ethylbenzene, xylenes, toluene, benzene. This trend is in agreement with an interpretation of the results in terms of pyrolysis kinetics. In fact, on the basis of simple bond energy considerations one would expect that the alkylated aromatics generate a radical pool more readily than benzene and, therefore, soot more [8]. However, consideration should be given not only to the rates of pyrolysis but also to the product composition of such pyrolysies. The significantly higher sooting tendency

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![Fig. 2. Sooting tendency as function of adiabatic flame temperature. Monoaromatics.](image-url)
of aromatics lends support to the conjecture that resonance structures are fundamental in leading to direct precursors of the particle inception process [8]. The conjugated structure of an aromatic or of its fragments provides the needed stability at high temperatures with respect to decomposition via resonance stabilization. These conclusions stand irrespective of the particular polymerization mechanism leading to soot nuclei, on which there is no universal agreement.

In support of the pyrolysis based interpretation of sooting in diffusion flames it is important to note that the relative sooting trends observed here for fuels such as acetylene, the aromatics, butene and butadiene are also the same as those obtained by Frenklach and coworkers [21, 22] in shock tube experiments. The difference between the two pieces of work is that in shock tubes for a given fuel, as the temperature is raised beyond a certain point the sooting tendency begins to drop. No drop has ever been found with smoke height tests as the temperature is varied. The difference is readily explained in that in shock tube experiments the temperature field is essentially constant. In flame tests the fuel pyrolysis begins at a lower temperature as the fuel element approaches the flame front and the soot nucleation process is completed well before the flame temperature is reached. It is impossible to raise the fuel pyrolysis and precursor formation region to temperatures achieved in shock tubes.

The temperature sensitivity of the aromatics’ sooting tendency is significantly lower than that of the aliphatics. The pseudoactivation energy deduced from such plots is of the order of 30 kcal/mole; it is interesting to observe that the activation energy for the oxidative pyrolysis of benzene reported in the literature [23] is \( \sim 30 \) kcal/mole. On the other hand, the activation energy obtained for the aliphatics is in the range 80–118 kcal/mole and is roughly equal to the weakest bond energy in the fuel [12]. If the agreement is not just fortuitous, one might speculate that the oxygen diffused to the fuel side at the burner lip, as mentioned in the preceding section, does not play a role for the aliphatics, but may for the aromatics. Considering that the velocity at the burner for the aromatics is typically an order of magnitude lower than for the aliphatics, the oxygen penetration into the fuel jet may be more effective for the aromatics. At the temperatures at which pyrolysis is occurring in these diffusion flames, it is quite likely that oxygen does not catalyze the pyrolysis of aliphatics [24], but may catalyze that of aromatics whose pyrolysis initiation steps has a greater activation energy. Furthermore, it should also be pointed out that hydrogen atoms and hydroxyl radicals diffused from the flame zone into the fuel region may in general assist in the initiation of the pyrolysis of the fuel. Indeed this phenomenon would be strongly related to the temperature field. However, at least for the results reported below, the general trend indicates that it is not the initiation of the fuel process which controls the extent of soot formation, but the pyrolysis steps which follow and form the soot precursors. These latter steps do not appear to be affected by the fuel side H and OH concentrations that would exist due to diffusion. Sufficient H atoms are already present from the early pyrolysis initiation steps.

### Polycyclic Hydrocarbons

In Fig. 3 the results of dicyclic hydrocarbons are reported. No data points are available for undiluted conditions because there was always need for some nitrogen carrier in the evaporator used in this set of experiments. The relative trends of these fuels are in agreement with the few results previously reported [3, 4], although the latter were obtained on smoke point lamps. \( \alpha \)-methyl naphtalene is the most prolific sooter, followed in the order by tetralin and decalin. The first two, being aromatic, have a sooting behavior comparable to that of the simple aromatics; \( \alpha \)-methyl naphtalene appears to be somewhat more prone to soot than the others. A starting material containing two rings would be expected to yield a higher concentration of the larger “building blocks” of the soot nucleus; furthermore, the more weakly bound CH\(_3\) group should have a promoting influence, as the methyl group in toluene does with respect to benzene. On the
other hand, decalin, a dicycloalkane, shows an intermediate tendency between the aromatics and the aliphatics, and has temperature sensitivity typical of the aliphatics. Graham [25] studied the formation of soot from the pyrolysis of several hydrocarbons in a shock tube at temperatures from 1600 to 2300K. A maximum in the soot conversion of decalin was observed in the temperature range 1900–2000K, whereas at 1830K the soot yield was found to be very low. He suggested that at lower temperatures fragmentation is the dominant pathway, whereas at higher temperatures dehydrogenation reactions, resulting in aromatization of decalin into tetralin, successfully compete with fragmentation and soot conversion is limited by their rates. Furthermore, he reported for cyclohexane and cyclohexene yields one order of magnitude lower than the aromatics, and suggested that fragmentation is their only path to soot. It is interesting to observe that the present data show decalin falling between the aromatics and the other monocyclic hydrocarbons tested (data on cyclohexane and cyclohexene are shown in Fig. 5 and will be discussed later). Flow reactor studies [26] showed that the low temperature (<1200K) path of degradation of decalin leads to large amounts of light monoaromatics, methane, and ethylene. Under the same experimental conditions [27] it was also reported that tetralin dehydrogenates to naphthalene and 1,2-dihydronaphthalene. Once again, the results in Fig. 3 seem to support the concept that products of pyrolysis play a fundamental role in determining sooting tendencies.

Dienes

Figure 4 shows data pertaining to the dienes. Starting with the cyclohexadienes, they were
initially tested to validate eventually the hypothesis that conjugation should be a fundamental factor of the present molecule in evaluating its sooting tendency [8]. 1,3-cyclohexadiene, being more conjugated than the 1,4-isomer, was expected to be a more prolific sooter. In contrast, the experimental results do not indicate any difference; the data of 1,4-cyclohexadiene also confirm Graham’s findings of identical soot yields of this diene and benzene in shock tube pyrolysis [25]. Review of the literature shows that the cyclohexadienes immediately pyrolyze to benzene [28]. Quite remarkably, the data in Fig. 4 show that all three fuels have the same tendency to soot. Subsequently, the straight chain dienes were tested. This time greater conjugation determined significant differences in the tendency to soot: the conjugated 2,4-hexadiene soots more than the isolated 1,5-hexadiene, as expected. From the only pertinent pyrolysis study found in the literature [29], it appears that two allyl radicals form from the thermal cracking of 1,5-hexadiene. The allyl radical is a prototype of a resonance stabilized radical and, as such, should have a very active role in the soot formation process. This fact may explain the high sooting tendency of even the nonconjugated hexadiene, comparable to benzene’s. Turning to butadiene, the results presented here are in contrast with previously reported data [12] from this laboratory. After careful checks, it was concluded that the disagreement was due to the nature of the chemicals tested: gas chromatographic analysis of the gas labeled as butadiene in the previous study inexplicably showed a large amount of butene. Butadiene’s sooting tendency, as given by this more recent study, is lower only than that of the aromatics and the other dienes tested and comparable to that of decalin. Indeed, butadiene was proposed as a key precursor to soot formation [8] because of its polar resonance structure.
Finally, the sooting behavior of the dienes as compared with the aromatics may be explained by considering the pyrolysis of aromatics. It is conceivable that it may lead to both benzyl or phenyl radicals and resonance-stabilized fragmentation products such as the allyl and butadienyl radicals [30]. The aromatics may still have higher sooting yields because a greater variety of resonance stabilized radicals participate in the process of soot formation.

**Cyclic Aliphatic Hydrocarbons**

In Fig. 5 the results of C₃, C₅, and C₆ cycloalkanes and the C₅ and C₆ cycloolefins are reported. For comparison, the least square fits of olefins and aromatics previously shown are reported. The new data fall in the olefin band, with the exception of cyclopentene, which falls close to the aromatic band. The reported trends are in agreement with undiluted smoke points in the literature [2]. In the case of cyclopentene, basic kinetics results [31, 32] show that initially the fuel molecule is dehydrogenated to cyclopentadiene, which subsequently breaks down to form highly conjugated species, characterized by high yields of soot [33]. The present data show that cyclopentene's sooting tendency is nearly that of benzene. The apparent activation energy of 57 kcal/mole is close to the pure pyrolysis activation energy of the initial step to cyclopentadiene. On the other hand, cyclohexene shows a significantly lower tendency to soot. Küchler [34] found that cyclohexene pyrolyzes primarily to ethene and butadiene; it is not surprising then that cyclohexene falls between these two fuels in its sooting tendency. Intuitively one would not have expected cyclopentene to have a greater tendency to soot than cyclohexene.

Turning to the cycloalkanes, cyclopentane pyrolysis data [35] lend support to a dual,
simultaneous reaction pathway: a decyclization to ethene and propene, and dehydrogenation to cyclopentene. This picture is consistent with the location of cyclopentane in Fig. 5. With regard to cyclohexane, pyrolysis results [34] support again two reaction routes, one of dehydrogenation leading to cyclohexene, which in turn breaks into ethene and butadiene, and another one of fragmentation into propene. Once again, the sooting trends presented here behave accordingly. The relative behavior of cyclohexane, cyclohexene, and the aromatics is also confirmed by shock tube studies [25]. A comparison of present data on cyclopropane and Glassman and Yaccarino's results on propene [12] shows that they have essentially the same sooting behavior. Turning to the pyrolysis literature for support, it was found that Davis [36] reported that cyclopropane readily isomerizes to propene and the secondary pyrolysis of propene is one order of magnitude slower than the isomerization step. Since the slowest step is the controlling one, it is conceivable that cyclopropane is isomerized early enough in the flame so that is does not play any role in the sooting process, and is influenced only by the subsequent pyrolysis of propene. It is worth reemphasizing that for these fuels also the influence of pyrolysis on the sooting behavior may be related not so much to the rates as to the type of primary products of such pyrolysis.

Branched Alkanes

In Fig. 6 the results of isooctane, n-octane, isobutane, and n-butane are shown. The latter has already been reported in Fig. 2. Comparing the isomers, it is seen that the branched hydrocarbons have significantly greater tendencies to soot than the corresponding normal alkanes. Murphy [24] studied the pyrolysis of n-butane and isobutane and found that the normal com-

![Diagram](image_url)

Fig. 6. Sooting tendency as function of adiabatic flame temperature. Branched versus normal alkanes.
pound essentially formed ethene and the branched compound formed mostly propene and methane. It is therefore expected that isobutane will soot more than n-butane. Similarly, pyrolysis studies [37, 38] show that isoctane forms more propene, while n-octane forms largely ethene. Isooctane also tends to form more butene, methylacetylene, and allene than n-octane, all of which soot more than ethene. It is concluded from these isomeric comparisons that large branched chain hydrocarbons soot more than the straight chain hydrocarbons because the principal intermediates of pyrolysis have a greater tendency to soot.

CONCLUSIONS

The tendency of a fuel to soot under diffusion controlled conditions results from the competitive effects of pyrolysis of the fuel, leading to soot precursors and growth species, and heterogeneous oxidation of the soot particle, which in general begins inside the luminous flame zone. Comparison of flame results presented here and basic pyrolysis results reported in the literature support the contention that fuel pyrolysis plays the controlling role in the sooting tendency of diffusion flames. It is not only the rate of pyrolysis, but also the sequence and type of products in the pyrolysis steps which seems to affect the sooting tendency of fuels. Fuel structure effects are quite significant in diffusion flames. Aromatics and dienes show a greater propensity to soot and a much milder temperature dependence as compared with the aliphatics. It is possible that the aromatics may undergo an oxidative type of pyrolysis, in contrast with the other fuels for which pure pyrolysis is found to be relevant. Conjugation in the initial fuel or in pyrolysis intermediate is confirmed as a key soot promoting characteristic.

APPENDIX

Phenomenologically, for a diffusion flame

$$H = \bar{v} \cdot t_R,$$

where \( H \) is the height of the true diffusion flame, \( t_R \) is the residence time, and \( \bar{v} \) is the average velocity over this height, defined as

$$\bar{v} = v_B + \bar{v}_a = v_B + \frac{1}{H} \int_0^H v_a \, dz,$$

where \( v_B \) is the mass flow rate based velocity at the burner lip and \( v_a \) is the accelerative contribution to the velocity. Furthermore, the height of the flame is defined by the condition

$$t_R = t_D,$$

where \( t_D \) is a diffusion time, representing the time it takes for an oxygen molecule to reach the axis. For fixed burner diameter

$$t_D \propto \frac{1}{D T^2},$$

where \( D \) is the gas diffusivity and \( T \) represents an average temperature characteristic of the flame. As \( N_2 \) is added, the temperature \( T \) drops and, therefore, \( t_D \) increases; from (3), \( t_R \) should also increase. Rearranging (1) and (2) gives

$$t_R = \frac{H}{\bar{v}} = \frac{H}{v_B + \bar{v}_a} \propto \frac{v_B}{v_B + \bar{v}_a} = \frac{1}{1 + (\bar{v}_a/v_B)},$$

where the proportionality relationship is introduced from the experimental findings of linear relationship between true diffusion flame height and gas volumetric flow rates [13]. Examining Eq. (5) indicates that an increase in \( t_R \) should result from a decrease in the ratio \( \bar{v}_a/v_B \). In fact, as \( N_2 \) is added, \( v_B \), the velocity at the burner lip increases, whereas \( \bar{v}_a \) decreases, irrespective of the mechanism causing the acceleration in the flame (thermal expansion and/or buoyancy effects), because of the decrease in temperature in the flame.

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