

Oxidation/Pyrolysis Chemistry as Related to
Fuel Sooting Tendencies

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Introduction

The obvious practical importance of understanding soot formation processes has motivated a series of studies examining both the macroscopic, phenomenological parameters that affect soot formation such as flame type and temperature and the microscopic, chemical processes that may be responsible for the rate controlling soot initiation steps.

At Princeton University, premixed and diffusion flame experiments have been conducted and have revealed the relationship between the sooting tendency of hydrocarbon fuels and temperature (1,2,3). The tendencies exhibited by fuels are different when measured in the two types of flames. Under premixed conditions, an increased flame temperature has been found to decrease the formation of soot. The details of the initial fuel structure, such as the isomeric distribution of side chains, degree of conjugation and aromaticity are unimportant to the sooting tendency except insofar as they contribute to the total number of C-C bonds. The general conclusions that have been deduced are that soot forms in the post flame region from an essential precursor, probably acetylene, and the sooting tendency of a particular fuel depends primarily on the balance between the amount of soot precursor it forms (a function only of the number of C-C bonds) and the amount of precursor consuming OH radicals the fuel produces. The OH attack increases faster with temperature than does the soot precursor formation (1). The OH concentration is also proportional to the H/C ratio, which, too, is a function of the number of C-C bonds (1).

Diffusion flame experiments have led to the observation of almost completely opposite patterns. An increase in the diffusion flame temperature has been shown to increase the sooting tendency of a hydrocarbon fuel. The particular structure of the fuel affects the degree of soot formation through the mechanism by which the fuel pyrolytically decays. Since different fuels have different pyrolysis mechanisms, the nature of the initial fuel structure becomes a significant determinant in the degree of soot formation. Furthermore, soot is formed in the pre-flame, fuel region. Consequently, oxidation at the flame front consumes fuel, fuel fragments and soot particles. Particles break through the flame front and become observed as soot only when there are lowered temperatures in a localized area and insufficient oxygen to consume both the molecular hydrocarbons and the soot particles.

The details of the chemical mechanisms of the pyrolysis and oxidation processes that so strongly impact the sooting tendencies of various hydrocarbon fuels could not be revealed by the types of premixed and diffusion flame experiments that were performed. Insight into chemical mechanisms, however, has been obtained from chemical kinetic, flow reactor studies conducted at Princeton. Studies of the oxidation of benzene (4), toluene (5), ethyl benzene (6), propyl benzene (7,8), butyl benzene, alpha methyl naphthalene (10), butadiene (11), ethylene (12), propane (13), butane (14) and

other hydrocarbons have revealed many of the mechanistic steps by which these fuels decompose. A limited number of pyrolysis studies have also yielded mechanistic information for oxygen free conditions. Despite the information obtained from the flow reactor studies, the absence of a chemical, soot formation mechanism has prevented the linking of the flow reactor derived mechanisms with the pyrolysis and oxidation chemistry that must be responsible for the phenomenological observations of the flame studies.

A recently developed soot formation mechanism by Frenklach et al. (15), that evolved from a sequence of shock tube experiments on acetylene pyrolysis can serve as a partial framework for connecting known chemical mechanisms with macroscopically determined sooting tendencies. The mechanism proposes a sequence of events starting from acetylene, proceeding through butadienyl and vinyl acetylenyl radicals to the formation of a phenyl radical (Table 1). From the phenyl radical, the growth of large polycyclic aromatics leading to soot would proceed relatively easily. This soot formation sequence should be appropriate for the post-flame region of a sooting premixed flame and the pre-flame fuel region of a diffusion flame.

In this paper, a first attempt is made at using the postulated soot formation mechanism of Frenklach et al., as a framework for relating flow reactor derived oxidation and pyrolysis mechanisms to soot related, fuel and intermediates decomposition processes. In order to logically develop the relationship, the set of Princeton experiments will first be described, the results obtained from them succinctly stated and then the proposed chemical relationships discussed.

Experimental

In both the premixed and diffusion flames the effects of temperature and fuel structure on the propensity to soot have been examined by changing the amount of diluent, usually nitrogen. Fuel structure effects were examined by the careful selection of a wide variety of hydrocarbon compounds. However, the two types of flames are very different in the manner in which the fuel and oxidizer come together at the flame front. As a consequence, there are profound effects on the above mentioned relationships between temperature, fuel structure and sooting tendency.

In a premixed flame, fuel, oxidizer and diluent are mixed upstream of the flame front and arrive at the flame front as components of a homogeneous gas. In the Princeton experiments (1), preset quantities of nitrogen and oxygen were mixed with a variable amount of fuel and fed to a Bunsen type tubular burner. The sooting limit was determined by increasing the fuel flow rate while the oxygen and nitrogen flow rate were kept constant. When luminous continuum radiation was detected at the sides of the conical flame, the fuel flow rate was decreased just enough to cause the radiation to disappear. The average fuel flow rate associated with both the appearance and disappearance of luminosity was used to calculate the critical equivalence ratio for the onset of soot. To establish the critical equivalence ratio at another temperature, the same procedure was repeated with a different preset quantity of nitrogen.

A diffusion flame is unlike a premixed flame in that the fuel and oxidizer meet in a reaction zone as a result of molecular and turbulent diffusion. The Princeton diffusion flame studies(2,3) were conducted with a burner in which a central tube delivered fuel into an outer tube containing flowing air. An excess of oxidizer led to the elongated shape characteristic of an overventilated flame. The sooting tendency of a particular fuel was established using this burner by varying the volumetric fuel + diluent flow rate for a given amount of air. When visibly obvious soot particles exited

from an annulus around the top of the flame, the soot height, i.e. the length of the luminous zone measured from the burner lip to the flame apex, was measured. Sooting heights for different fuels with different amounts of added nitrogen or argon diluent were evaluated in order to establish the sooting propensity at different temperatures.

For the chemical mechanism studies, the Princeton flow reactor was used (16). The flow reactor is a tubular, high temperature, turbulent reactor that is designed to permit the examination of oxidation and pyrolysis processes without complications due to the diffusion of heat and mass. Species concentrations with respect to time for a dilute reacting flow are obtained by withdrawing samples with a water cooled probe at discrete, well characterized locations within the tube. Analysis of the chemical content of each sample is performed with either gas chromatography or gas chromatography/mass spectrometry as is needed. Concentrations at the various locations in the reactor are related to the extent of reaction by taking into account the flow velocities within the reactor. Experiments examining the oxidation and pyrolysis of various hydrocarbon fuels have all been conducted at one atmosphere pressure and in a 900 to 1200K temperature range. The temperature range of the flow reactor, though lower than the range of hydrocarbon adiabatic flame temperatures, is nevertheless quite relevant to the chemistry of soot formation processes. The 900-1200K range corresponds both to the temperature in a flame where the initial fuel decomposition occurs and also the temperature of the zone of a flame where soot particles are first observed (17).

Results

For premixed flames, the sooting tendency (as a function of the adiabatic premixed flame temperature) for a wide variety of hydrocarbons is shown in Figure 1 (1). The critical effective equivalence ratio, i.e. the ratio of the stoichiometric oxygen necessary to convert all the fuel to CO and H₂O to the experimental amount, is used as a measure of the sooting tendency in the premixed flame. The larger is the critical equivalence ratio, the smaller is the tendency of fuel to soot. Therefore, from Figure 1 it can be seen that ethane at all temperatures has a much smaller tendency to soot than does methyl-naphthalene. The single, most obvious trend in Figure 1 is that for all fuels, the sooting tendency decreases as the flame temperature is increased. Furthermore, the change in sooting tendency with temperature is roughly the same for all fuels regardless of fuel type. Consequently, a vertical slice through Figure 1 at any one temperature should permit an ordering of sooting tendencies that is representative of those at all temperatures.

Such an ordering is presented in Figure 2 for a flame temperature of 2200K (1). The abscissa, "number of C-C bonds", represents the total number of carbon to carbon bonds in the parent fuel molecule when each single carbon-carbon bond is considered to contribute one, each double bond contributes two and each triple bond contributes three to the total number of bonds. The predictive correlation of Figure 2, which is independent of a detailed knowledge of isomeric structures, conjugation and even aromaticity, implies that fuel structure is an inconsequential factor in soot formation in premixed flames. The results of these premixed flame experiments along with those that have examined the post-flame region as a function of initial fuel type (18), suggests that soot formation occurs in the post flame region from a universal soot precursor whose concentration but not nature is affected by the structure of the initial fuel.

The results of a diffusion flame study of the sooting tendency of hydrocarbons as a function of temperature is shown in Figure 3 (19). The

sooting tendency is measured by the inverse of the volumetric flow rate at the smoke height. The smaller the inverse flow rate the smaller the tendency to soot. The sooting tendency of different classes of species varies widely from class to class but is relatively constant within a class. For example, aromatic compounds such as benzene, ethylbenzene and methylnaphthalene soot much easier than do the small alkenes such as propene, butene and even cyclohexene. The classes of compounds also have very different sooting temperature dependencies as revealed by the slopes of each line in Figure 3. However, in contrast to the behavior of hydrocarbon fuels in premixed flames, fuels show an increasing sooting tendency with increasing flame temperature.

A structure independent correlation of the type available for premixed flames cannot be developed from the diffusion flame results. It appears that initial fuel morphology does play an important part in the tendency of a fuel to soot as is evidenced in Figure 3 by the groupings of sooting tendency according to class of hydrocarbon. Since hydrocarbon fuels will pyrolytically decompose at the temperatures present in the oxygen-free fuel stream a distance far from the flame front, the conclusion can be drawn that the effect of initial fuel structure on sooting tendency is manifested through pyrolysis processes.

Flow reactor studies of hydrocarbon fuels, unfortunately, cannot be so concisely summarized in three plots as were the flame results. Generally, each oxidation study is conducted at rich, stoichiometric and lean equivalence ratios at one or more temperatures. From the many species concentration profiles with respect to time that are obtained, mechanistic information is deduced. The mechanism of the high temperature oxidation of benzene/phenyl radical that was developed from a series of such flow reactor oxidation studies is displayed in Figure 4 (16). This mechanism, as well as the one for butadiene that follows, were chosen for display from among the many that have been obtained from flow reactor studies because of their particular relevance to important elements of the soot formation process.

The mechanism of Figure 4 indicates that benzene is oxidized in a step by step process involving C_6 , C_5 and C_4 stable radicals. At the temperature of the oxidation studies, 1000-1200K, oxidative attack was the predominant mode of decomposition, since purely pyrolytic processes are too slow. The benzene oxidation sequence as outlined ends with the ring opening formation of either butadiene or the butadienyl radical. The oxidation characteristics of butadiene have been the object of another, different set of flow reactor studies (11). These studies have resulted in the development of a mechanism that extends the benzene mechanism just presented. This butadiene/butadienyl oxidation mechanism is given in Figure 5.

Discussion

Before discussing the relationship between flame and flow reactor experimental results, the assumption must be made that the diffusion of species in flames affects the rates of reactions but not the basic pathways of a chemical mechanism that would occur in a reduced diffusion, flow reactor environment. Some preliminary, direct comparisons of flame species obtained from the probe sampling of a diffusion flame and flow reactor pyrolysis experiments appear to support this conclusion (20). Presumably, diffusion of species would also leave the basic mechanisms of oxidation and pyrolysis in premixed flame essentially unaffected.

Therefore, premixed sooting flames can be conceptually viewed as flames in which the fuel rapidly breaks down in an oxidizing environment to acetylene; the acetylene passes through the flame front, and then reacts to form soot. If the initial fuel is benzene, it is oxidized in the homogeneous

pre-flame region to mostly CO, H₂O and a small amount of acetylene. The acetylene that survives the flame front then grows through the Frenklach mechanism (15) back up to phenyl radicals and/or benzene. In some sense, the process is symmetric with respect to the flame front. The benzene oxidation mechanism derived from the flow reactor is applicable both to the rapid pre-flame benzene decomposition processes and the post-flame benzene and/or phenyl radical consumption reactions.

The pre-flame benzene decomposition oxidation reactions, if very rapid, will lead by the step by step mechanism of Figure 4 to a large buildup of acetylene. Since a large concentration of acetylene on the pre-flame side near the flame front would presumably lead to a large acetylene concentration in the post-flame region, these oxidation reactions are soot enhancing.

In contrast, any oxidation reactions in the post-flame region that consume species involved in the Frenklach soot growth mechanism will be soot retarding and perhaps even inhibiting. For example, vinyl acetylene, a key species in the soot formation mechanism, may be attacked by an O atom leading to the formation of allene and CO as indicated in Figure 5. Though the allene, through subsequent reactions may contribute species, such as acetylene, that can enter back into soot formation mechanism they do so at a lower molecular weight level with a consequent delay in the formation of soot. Therefore, the oxidation processes serve to drain species out of the soot formation route.

In a similar way, the formation of phenoxy or phenol from phenyl and/or benzene can occur in the post-flame region because of some O₂ and significant quantities of OH and O that are found there. The phenoxy quickly decomposes to cyclopentadienyl which itself will be oxidized. Thus the post-flame benzene consuming reactions interfere with the further growth of large molecules by removing or delaying the concentration growth of an essential soot building block, the phenyl radical. These reactions are therefore soot inhibiting.

Paradoxically, it appears that oxidative attack on some soot formation intermediates could actually contribute to soot formation. For example, butadienyl radical is postulated to be a key species in the route leading to the first aromatic ring. The butadienyl radical can decompose to vinyl acetylene as indicated in Figure 5 through reaction with O₂ or collision with a third body designated as M. The decomposition reaction with O₂, when the concentration of O₂ is high enough, may even be faster than the unimolecular decomposition. Since it is known from sampling in flames (21) that a considerable fraction of the initial O₂ persists into the post-flame region, the accelerative effect of O₂ on the rate of soot formation may be significant.

The benzene oxidation mechanism of Figure 4, when developed into a detailed mechanism of the type now available for smaller hydrocarbons and coupled with an advanced flame model, can potentially yield an analytic prediction of the amount of acetylene that is formed in the pre-flame region and which then survives into the post-flame zone.

In diffusion flames, soot formation can be viewed conceptually to be the result of fuel pyrolysis reactions occurring in the relatively oxygen free pre-flame, fuel stream. Consequently, the soot formation mechanism of Frenklach et al., which is, in fact, a pyrolysis mechanism, would be most appropriate for the fuel stream reactions of diffusion flames. However, in contrast to the situation for premixed flames, there is no experimental indication that hydrocarbon fuels must break down to acetylene before building back up to larger molecules. Pyrolysis reactions in the fuel stream that produce directly any of the larger members of the soot formation route would contribute to an increased sooting tendency. An indication of the routes

through which fuel decomposition might feed large species into the soot formation route could come from flow reactor pyrolysis experiments augmented by higher temperature mechanistic information available in the literature.

An obvious example of such a case is the pyrolysis chemistry of benzene. Flow reactor pyrolysis experiments have indicated that though it is difficult to decompose benzene thermally, when the molecules do break apart they form vinyl acetylene, butadiene and acetylene (22). Higher temperature experiments performed in a very low pressure pyrolysis apparatus (23) revealed the formation of these same intermediates as well as others. High temperature shock tube pyrolysis experiments corroborate both of these experimental findings and emphasize the importance of phenyl radical formation (24). Clearly, benzene fuel in a diffusion flame not only will decompose pyrolytically to the starting material in the soot formation mechanism, acetylene, but also provides some of the essential vinyl acetylene and phenyl radical building blocks necessary for the formation of the polycyclic aromatics. In view of the intermediates known to be formed during benzene pyrolysis, it is not surprising that the data of Figure 3 indicate that benzene soots very easily.

However, it is not necessary that the hydrocarbon pyrolysis processes form the exact C_2 , C_4 and C_8 species that appear in the soot formation mechanism. Sometimes, it is sufficient for the pyrolytic decomposition simply to produce stable intermediates which themselves appear to easily form the appropriate species. An interesting demonstration of this point results from a flow reactor examination of the major pyrolysis intermediates of iso-octane and n-octane (25). Though both fuels pyrolytic decomposed rather quickly, each one produced a different major intermediate. The pyrolysis of iso-octane was found to yield primarily iso-butene and some propene. The corresponding pyrolysis of n-octane yielded mostly ethylene and also some propene. The diffusion flame data of Figure 3 indicates that iso-octane has a significantly greater tendency to soot than does n-octane. In fact, the sooting tendency of iso-octane is close in magnitude to that of its primary pyrolysis intermediate, iso-butene. In contrast, the sooting tendency of n-octane approaches the reduced value of ethylene, its major pyrolysis intermediate. The comparison between the sooting tendency of the two isomeric octanes, and their pyrolysis intermediates is another example of the importance of initial fuel structure to sooting in a diffusion flame.

Experimental results on the addition of small amounts of oxygen to the fuel side of various sooting diffusion flames have yielded some interesting insights into the relationships between sooting tendency and chemical mechanism. The oxygen effect was found to be exceptionally strong in ethene, less so in propene, and negligible for the alkane fuels (26,27,28,29,30,31). It would appear that the normal radical pool formed during thermal pyrolysis of most fuels in diffusion flames is so large that the additional radical reactions due to the presence of small amounts of oxygen lead to no overall gain in the extent of the radical pool which governs the overall pyrolysis rate. This pyrolysis condition is true for all aliphatic hydrocarbons except ethene, and to some extent propene. For ethene, oxygen increases the radical pool extensively. Consideration of the bond strengths in ethene and propene would lead one to perhaps expect the trend postulated. Verification was shown (31) by computations in which a comprehensive chemical kinetic mechanism for the oxidation of butane (14), developed in part with flow reactor data, was adapted to apply to the pyrolysis of ethene, propene and acetylene. Although there are no experimental data for oxygen effects on accelerating the sooting of acetylene, from bond strength considerations one would expect a strong

effect and the flow reactor based computations do show substantial increase in the radical pool with oxygen addition. Similarly one would expect the same for benzene. Although no computations for benzene were performed, experimental results (29) show that oxygen accelerates the sooting of benzene.

There is, of course, a temperature effect when considering the role of oxygen in accelerating pyrolysis of fuels. The higher the temperature, the less is the accelerative effect (32,33). Most fuels show increased pyrolysis rates with oxygen addition at lower temperature (32,33). The comparisons made in the previous paragraph were for high temperatures (~100-1300 K). In laminar diffusion flames the temperature time history of a pyrolyzing fuel element is short compared to low temperature flow and static reactors. Since it has been established that the onset of soot formation in a diffusion flame coincides with the points on the temperature profiles corresponding to about 1300 K (17,34), it is very apparent that the high temperature comparisons are the ones of importance. This temperature sensitivity can lead one to conclude that the initiation step is accelerated in addition to increasing the radical pool. The computations (31) appear to confirm this statement. The general pyrolysis mechanism does not seem to change otherwise. Flow reactor experimental results confirm that there is no appreciable, if any, accelerative effect of oxygen on the pyrolysis of propane, propene or butane (33) at high temperatures and an appreciable effect on ethene (35).

Summary

The relationships between flame studies of the sooting tendencies of various hydrocarbon fuels and chemical mechanisms derived from flow reactor experiments have been developed. The mechanisms for the oxidation of benzene and butadiene, in particular, have been related to both sooting premixed and diffusion flames despite the large difference in basic flame structure. A recently developed soot formation mechanism has provided the linking framework between chemical mechanism and observable sooting tendencies. The same framework has permitted the application of flow reactor based chemical models to the prediction and explanation of the effect of oxygen addition on sooting diffusion flames.

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References

1. Takahashi, F. and Glassman, I., *Combust. Sci. & Technol.*, 1984, Vol. 37, pp. 1-19.
2. Glassman, I. and Yaccarino, P., *The Combust. Inst.*, 18th Symp. (Int'l.) on Combustion, 1981, pp. 1175-1183.
3. Gomez, A., Sidebotham, G. and Glassman, I., *Comb. and Flame* 58, 45-57 (1984).
4. Venkat, C., Brezinsky, K., and Glassman, I., *Int. Symp. Combust.* 19, 143 (1982).
5. Brezinsky, K., Litzinger, T.A. and Glassman, I., *Int. J. Chem. Kinet.* 16, 1053 (1984).
6. Litzinger, T.A., Brezinsky, K. and Glassman, I., *Comb. and Flame* 63, 251 (1986).
7. Litzinger, T.A., Brezinsky, K. and Glassman, I., *J. of Phys. Chem.*, 1986, 90, 508.
8. Litzinger, T.A., Brezinsky, K. and Glassman, I., *Combust. Sci. & Technol.*, 1986, Vol. 50, pp. 117-133.

9. Brezinsky, K., Litzinger, T.A. and Glassman, I., 21st Symp. (Int'l.) on Combustion, 1986.
10. Litzinger, T.A., Brezinsky, K. and Glassman, I., Eastern States Section/Combust. Inst. Paper #68, 1985.
11. Brezinsky, K., Burke, E.J. and Glassman, I., Int. Symp. Combust. 20, 613 (1985).
12. Westbrook, C.K., Dryer, F.L. and Schug, K.P., 19th Symp. (Int'l.) on Combustion, 1982, pp. 153-166.
13. Hautman, D.J., Schug, K.P., Dryer, F.L. and Glassman, I., Combust. Sci. & Technol. 25, 219 (1981).
14. Pitz, W.J., Westbrook, C.K., Proscia, W.M. and Dryer, F.L., Int. Symp. Combust. 20, 831 (1985).
15. Frenklach, M., Clary, D.W., Gardiner, W.C., Jr. and Stein, S.E., 20th Symp. (Int'l.) on Combustion, 1984, pp. 887-901.
16. Brezinsky, K., Prog. Energy Combust. Sci., 1986, Vol. 12, pp. 1-24.
17. Kent, J. and Wagner, H. Gg., Int. Symp. Combust., 20th, p. 1007.
18. Harris, S.J. and Weiner, A.M., Combust. Sci. & Technol., 1984, Vol. 38, pp. 75-87.
19. Glassman, I., COMBUSTION, Academic Press, 1987.
20. Sidebotham, G. and Hura, H., Princeton University, unpublished data.
21. Bittner, J.D. and Howard, J.B., Int. Symp. Combust. 18, 1105 (1981).
22. Weckman, E., Princeton University, unpublished data.
23. Smith, R.D. and Johnson, A.L., Comb. and Flame 51: 1-22 (1983).
24. Kiefer, J.H., Mizerka, L.J., Patel, M.R. and Wei, H.-C., J. Phys. Chem. 1985, 89, 2013-2019.
25. Brezinsky, K. and Dryer, F.L., Central States/Western Section/Combustion Institute, WSSCI Paper # 3-5A, 1985.
26. Chakeraborty, B.B. and Long, R., Comb. and Flame 12, 469 (1968).
27. Deardon, P. and Long, R., J. Appl. Chem. 18, 243 (1968).
28. Jones, J.M. and Rosenfeld, J.L.J. Comb. and Flame 19, 427 (1972).
29. Wright, F.J., Fuel 53, 232 (1974).
30. Schug, P., Manheimer-Timmat, Y., Yaccarino, P. and Glassman, I., Comb. Sci. and Tech. 22, 235 (1980).
31. Hura, H. and Glassman, I., Comb. Sci. and Tech. 53, 1(1987).
32. Walker, P.W., Reaction Kinetics (Spec. Periodical Rep., Chem. Soc. London) 1, 172 (1975).
33. Murphy, S.L., Brezinsky, K. and Glassman, I., Eastern States Section/The Combustion Institute Meeting, Paper No. 10 (1982). See also Murphy, S.L., Princeton University M.S.E. Thesis, 1982.
34. Gomez, A. and Glassman, I., 21st Symp. (Int'l.) on Combustion (1986).
35. Hura, H., Princeton University, private communication (1987).

Acetylene Soot Formation Mechanism

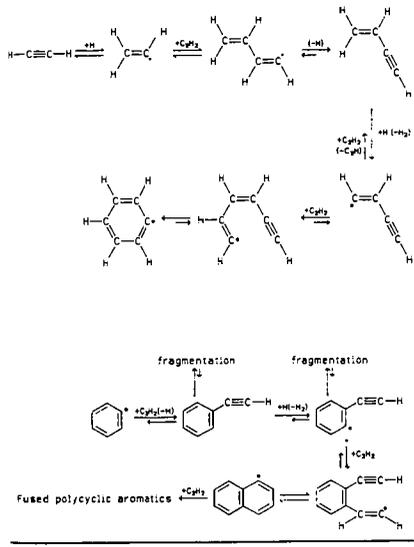


Table 1

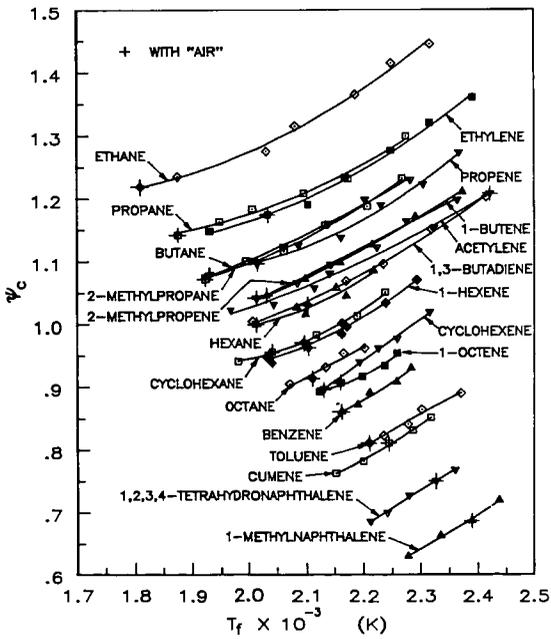


Figure 1. The critical effective equivalence ratio at sooting as a function of adiabatic flame temperature (from ref. 1)

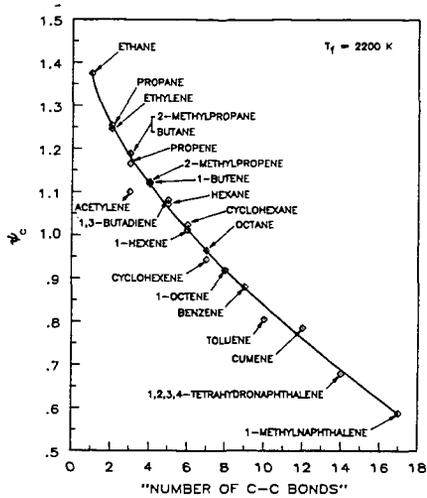


Figure 2. The correlation between the critical equivalence ratio at sooting and the number of C-C bonds (from ref. 1).

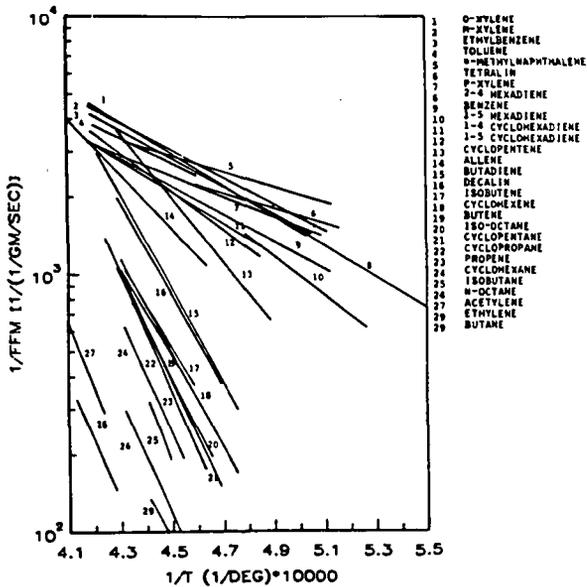


Figure 3. The sooting tendency of some hydrocarbon fuels as a function of the reciprocal of the calculated adiabatic flame temperature (from ref. 19).

