

## SMOKE LIMITS OF BUNSEN BURNER ETHYLENE-AIR FLAMES

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### ABSTRACT

The smoke limits and chemical composition of smoking ethylene-air flames were determined to gain understanding of the mechanism whereby flames emit smoke. Such information has bearing on carbon deposition in gas appliances and engines. Ethylene-air flames were chosen because of the pronounced tendency of flames of this fuel to smoke and its prevalence in send-out gases of gas utilities. A characteristic smoke limit for the fuel independent of burner parameters was not observed. Smoke limits were all richer in fuel than the constant yellow-tip limit. Two types of smoke limit flames were observed. One is very sensitive to flow, the other to fuel-air ratio. Analysis of the gases within the yellow zones of these flames and immediately downstream of these flames has failed to show any relation of these flames to cool flames.

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The circumstances under which carbon is formed in gas appliances or in jet and gasoline engines are of obvious importance. A broad program is under way at the Bureau of Mines seeking (1) to obtain and evaluate basic chemical information on the formation and burning of yellow emitters and carbon monoxide in rich flames, and (2) to identify smoke limits of gaseous fuels burning in free air. This paper is largely concerned with progress toward attaining the second objective although some information is offered with regard to the first.

Research on yellow-tip limits of flames in this laboratory<sup>1/</sup> has established constant yellow-tip limits that are characteristic of the fuel gas. A wide range of single and multicomponent fuels has been correlated and these data have been used to predict yellow tipping on gas burners. Spectroscopic studies of luminous hydrocarbon-air flames have also been made<sup>2/</sup> but the chemical nature of the yellow emitters and their precursors has not been identified. It is not known whether a given species and a specific mechanism of formation are common to all yellow flames or under what conditions the appearance of yellow must result in the escape of carbonaceous material from the flame. It is known that some yellow flames richer than the yellow-tip limit burn clean in free air, whereas others do not. Determination of smoke limits and a study of the temperature and chemical species composition in the yellow and blue zones of yellow-tipped flames should lead to basic information on the fuels, fuel-air ratios, and ambient temperatures that can be used in gas appliances without fouling surfaces, etc. Although this study is primarily centered on applications to gas appliances, information gained is applicable to other gaseous and liquid fuel combustors.

Experimental Procedure

Streams of ethylene and air were separately metered, mixed in suitable mixing chambers, and then fed to long cylindrical glass tubes which served as burners. The streams were ignited and permitted to burn in free air. After surveying the literature and making trial runs, it was decided that smoke limits are best determined by visual observation of Tyndall light in a suitably illuminated room. Smoking flames generally flicker very badly and are very luminous, making it difficult to observe traces of smoke escaping from the flame. However, these difficulties were overcome in the following manner. The hot gases leaving the flame were viewed in an evenly illuminated room against a black background. The observer looked over a shield which blocked off direct light from the luminous flame. A strong beam of light was directed crosswise to the observer's line of sight. Particulate matter in the nonluminous hot gases leaving the fire was made visible by reflection of this beam of light into the

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1/ J. Grumer, M. E. Harris and V. R. Rowe, Fundamental Flashback, Blowoff, and Yellow-Tip Limits of Fuel Gas-Air Mixtures. Bur. Mines Rept. Investigations 5225 (1956).

2/ A. G. Gaydon and H. G. Wolfhard, "Flames, Their Structure, Radiation and Temperature," Chapman and Hall, London, 1953.

eyes of the observer. The technique was found to be highly sensitive and reproducible. The smoke limit is the point where smoke is first observed leaving the flame and is expressed in units of flow versus fuel-air composition of the premixed stream. The procedure is similar to that employed in reference 3 and differs from the more usual definition of a smoke limit<sup>4/</sup> which is the minimum flow of pure fuel at which smoke is observed against a white background.

### Observations and Discussion of Results

#### A. Smoke Limits

Figure 1 contains several photographs of smoking ethylene-air flames. There are two types. Photograph A shows a type 1 smoke limit flame. These are short flames formed at low flow velocities and at low primary aeration (including zero percent air). The smoke appears in a steady stream at the top of a yellow flame. These flames are fairly steady, frequently showing nonperiodic changes in height. This particular flame varied in height from 12.7 cm. to about 10 cm. When the flame lengthened, the top of the flame broadened and changed in color from yellow to orange-black. Smoke issued from the top of the flame as a constant thin streak. In its shortened state the flame top was sharp and of the same yellow intensity as the body of the flame. No smoke could be seen at such times. Photograph B shows a type 2 smoke limit flame. These flames flicker greatly and resemble a turbulent diffusion flame. Shifting regions of orange-black tongues emitting smoke appear in the periphery of the flame. The over-all flame lengthens and shortens nonrhythmically. For example, this particular flame changed from a height of about 35 cm. to one of about 28 cm. Smoke appeared as puffs from various parts of the flame. Generally these puffs became visible some distance downstream from the flame and did not appear to be continuous with the flame. The height of this type of flame was very sensitive to minor changes in primary aeration. Photograph C shows a smoking ethylene-air flame considerably richer than the smoke limit. It appeared to the eye that there were two flames—a central one reaching from the port of the burner to the top of the flame, and a second hanging like an umbrella from the top of the flame and extending about halfway upstream toward the port. It seemed that combustion was stopped at the borders of the central flame, that perhaps secondary air was drafted into the combustion products, and the resultant mixture ignited. The over-all flame changed its shape frequently and irregularly and was about 26 cm. tall. This flame is of interest because it illustrates the possibility of combustion ending and beginning under suitable circumstances.

Measurements of these two types of smoke limits were made using a range of flame port diameters from 0.25 to 2.47 cm. The maximum height of smoke limit flames was also measured. The data are presented in Figures 2 and 3, respectively. There is no evidence of a smoke limit characteristic of the fuel gas such as was observed in studies of yellow tipping.<sup>1/</sup> As burner tube diameter and flow are increased, the smoke limits tend to approach the constant yellow-tip limit, indicating that there is a gradual transition from the phenomenon of yellow tipping to smoking, and that the smoking tendency of a fuel can be represented as a fuel-air ratio that is fuel-richer than the constant yellow-tip limit of the fuel.\*\* The curves of flame height and of flow versus fuel-air composition at the smoke limit show two regions. The type 1

<sup>3/</sup> T. P. Clark, Natl. Advisory Comm. Aeronaut. Research Mem. RME52G24 (1952).

<sup>4/</sup> R. L. Schalla and G. E. McDonald, Ind. Eng. Chem., 45, 1497 (1953).

\*\* The constant yellow-tip limit of a fuel has been shown in previous studies to be characteristic of the fuel and independent of the burner on which the fuel is being burned. It is the leanest fuel-air mixture at which yellow can be observed anywhere in the flame burning in free air. The value for ethylene is  $F_c = 1.88$ .

limit flames, which include the pure diffusion flame of 100 percent fuel, show no change of flame height and nearly constant flow rate for a wide range of fuel-air ratios. It is apparent that large changes in the concentration of primary air and the presence of secondary air do not influence these limits. As the primary mixture is further aerated, there is a transition to another type of limit flame where the limit is strongly dependent on the primary oxygen present. The transition point depends on the tube diameter and is at leaner mixtures for the larger tubes. This indicates that secondary air is being consumed by these flames.

In Figure 4, the time for a gas element at the axis of the flame to flow from the port to the end of the flame is plotted as a function of composition. The slopes of the curves decrease with decreasing primary air. This observation indicates that the height of a type 1 flame is not such that enough secondary air can diffuse into the flame for stoichiometric combustion. Figure 5 bears more evidence that the availability of secondary air does not make for complete combustion in type 1 flames. As the smoke limit is approached from the yellow side, the residence time of an axial element in the flame increases, indicating that time is being taken to gain secondary air to prevent smoking. However, in the region of smoking flames, time spent in the flame decreases as more smoke is produced. It appears that reaction is being stopped between secondary air that could be obtained by flame lengthening and combustibles.

#### B. Chemical Composition of Burning Gases in Smoking Flames

Photographs A and B of Figure 6 show flame structure that was obtained on a 2.47 cm. burner at conditions where the flashback and smoking flame regions intersect. A streak of smoke was observed issuing from the top of the flame. The flame in Photograph A was about 10 cm. long when it smoked and about 7-1/2 cm. long when it did not smoke. A slight decrease in fuel flow caused an inner core of flame to separate and move upstream into the burner as shown in Photograph B. As this separation progressed, the remaining flame on top of the burner in free air steadied and ceased smoking. The center core of the fire inside of the tube showed on its upstream face a horizontal blue burning zone preceding the yellow. Soot was observed on the inside walls of the glass tube around the yellow zone. This is important because it indicates that the initial stages of smoking occur very close in space and time to the blue burning zone. The blue zone is thin, as are the primary cones of usual blue flames. Reaction times must be correspondingly short. The yellow zones are much more extended, showing slower reaction time. Furthermore, this sequence of the zones on a time scale indicates that the yellow zone reactions are fed by the products of the blue zone combustion. This is not the sequence of events in a yellow 100-percent fuel flame where, along a stream tube, yellow combustion precedes blue combustion. Table 1 contains mass spectrometric analyses of samples which were withdrawn from regions within and adjacent to the enclosed flame. These regions were at the axis or near the wall and at the plane of the blue flame base and at the yellow zone. There are no or practically no oxyhydrocarbon compounds detected. Therefore these smoking flames have not been shown to involve reactions and products characteristic of cool flames. The major products of burning detected are simple ones, namely hydrogen, carbon monoxide, carbon dioxide and water. (Water was evaluated by striking a hydrogen and oxygen balance.) Acetylene and methane appear in concentrations up to roughly 2 percent. Other hydrocarbons are present in only trace amounts. There is no sign of a progressive buildup of high molecular weight materials. The species found are about the same as observed in samples taken from diffusion flames of methane<sup>5/</sup> and propane.<sup>6,7/</sup> But the ratios of CO<sub>2</sub>/CO are less than unity in the enclosed premixed flames listed in Table 1 and larger than unity in the diffusion flames studied in references 5-7. So it.

<sup>5/</sup> S. R. Smith and A. S. Gordon, J. Phys. Chem., 60, 759 (1956).

<sup>6/</sup> S. R. Smith, private correspondence.

<sup>7/</sup> Unpublished work, this laboratory.

Table 1.—Compositions of ethylene-air flame enclosed in 2.5 cm. I.D. tube, 15.9 percent ethylene.

	A	B	C	D
	0.48 cm. from wall, adjacent to blue	0.48 cm. from wall, adjacent to yellow, 1 cm. above blue	0.48 cm. from wall, adjacent to top of yellow, 3 cm. above blue	Probe at axis, in blue
Argon	0.2	0.7	0.7	0.3
Nitrogen	62.0	60.9	60.3	62.4
Oxygen	11.1	.65	.4	10.1
Hydrogen	5.7	11.0	11.8	6.6
Carbon monoxide	7.4	18.5	18.9	8.5
Carbon dioxide	.90	2.5	2.5	1.0
Methane	.8	1.7	1.9	.8
Ethylene	10.7	1.7	1.1	8.8
Acetylene	1.0	2.2	2.3	1.2
Methyl acetylene	.04	.04	.04	.05
Benzene	.0	.02	.02	Trace
Diacetylene	.01	.03	.02	.02
Ethane or formaldehyde	.1	.04	.04	.1
CO <sub>2</sub> /CO	.12	.135	.132	.118
CO/N <sub>2</sub>	.119	.304	.314	.136
CO <sub>2</sub> /N <sub>2</sub>	.015	.041	.042	.016
H <sub>2</sub> /N <sub>2</sub>	.092	.181	.196	.106
(C/N <sub>2</sub> ) orig.	.478	.478	.478	.478
(C/N <sub>2</sub> ) gaseous products	.530	.508	.506	.493
(C <sub>2</sub> H <sub>4</sub> in air) products	16.8	35.4	36.5	15.4

seems that oxygen availability as measured by the CO<sub>2</sub>/CO ratio does not change the types of compounds to be found in very rich hydrocarbon-air flames.

The submergence within the tube of the blue and yellow zones excludes secondary air from these two regions. Therefore the loss of gas phase carbon and presumably the formation of solid carbonaceous material in the flame can be followed by means of the carbon/nitrogen ratio in the flaming gases. A decrease of about 2 percent in the ratio was observed with the downstream distance in the sequence A-C, indicating some smoke formation. It is not possible to use these analyses to identify the precursors of solid carbon beyond noting that the precursors must be single carbon compounds. Referring to columns A-C, the C/N<sub>2</sub> ratio and the percent ethylene in air remaining in the products are higher in the flame gases than in the gases fed to the flame. Such discrepancies have also been observed in tests with rich propane-air flames.<sup>7</sup> Comparison of columns A and D indicates a radial transfer of gaseous carbon compounds. These differences can be explained on the basis of diffusion across the flame zone, along concentration gradients. For example, ethylene from the unburned gas will diffuse toward the burned gas because its concentration is lower there. Carbon dioxide and monoxide will diffuse toward the unburned gas for the same reason. The nitrogen content of both flame and unburned gas is high, so there is no high concentration gradient for nitrogen. An exchange of this sort will enrich the carbon content of the flame gases, since ethylene is a two-carbon molecule and carbon dioxide is the slowest diffusing of the four molecules just mentioned.

### Conclusions

A study of smoke limits and the composition of gases in smoking ethylene-air flames shows the following:

1. Smoke limits characteristic of the fuel gas and independent of burner diameter and flow rate do not exist. No smoke limits have been found which are leaner than the constant yellow-tip limit for the fuel. The latter is characteristic of the fuel-oxidant system only.

2. There are two types of smoke limit flames, the richer of these being primarily a function of flow rate, the leaner primarily a function of fuel-air ratio.

3. The availability of unlimited ambient secondary air does not prevent the escape of smoke from flames.

4. Analyses of gases within smoking ethylene-air flames do not show the presence of significant quantities of oxygenated hydrocarbons or of high molecular weight hydrocarbons.

### Acknowledgment

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### Nomenclature

$F$  = fuel-gas concentration, fraction of stoichiometric  
 $F_c$  = fuel-gas concentration for the constant yellow-tip limit, fraction of stoichiometric  
 $h$  = height, cm.  
 $\bar{U}$  = average flow velocity, cm./sec.

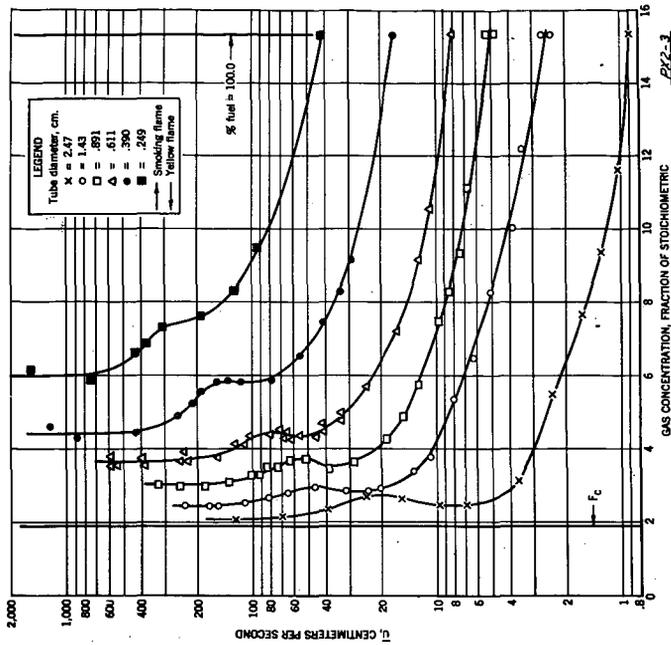
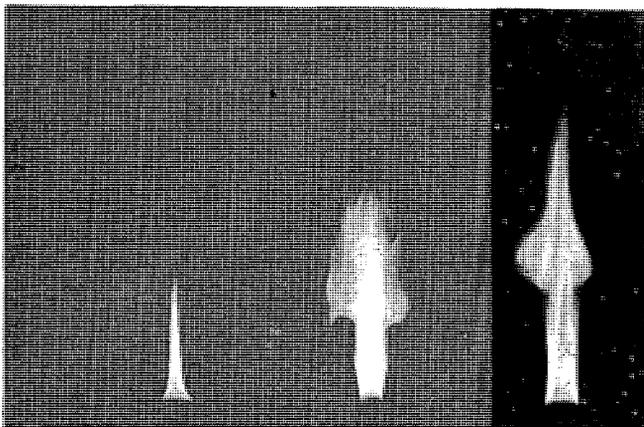


Figure 2.- Average flow velocity of smoke-limit flames of ethylene-air.



	A	B	C
Fraction of stoichiometric	9.96	2.44	5.52
Flow, cm./sec.	1.4	71.8	12.7

Figure 1.- Smoking flames of ethylene-air. Tube diameter = 2.47 cm.

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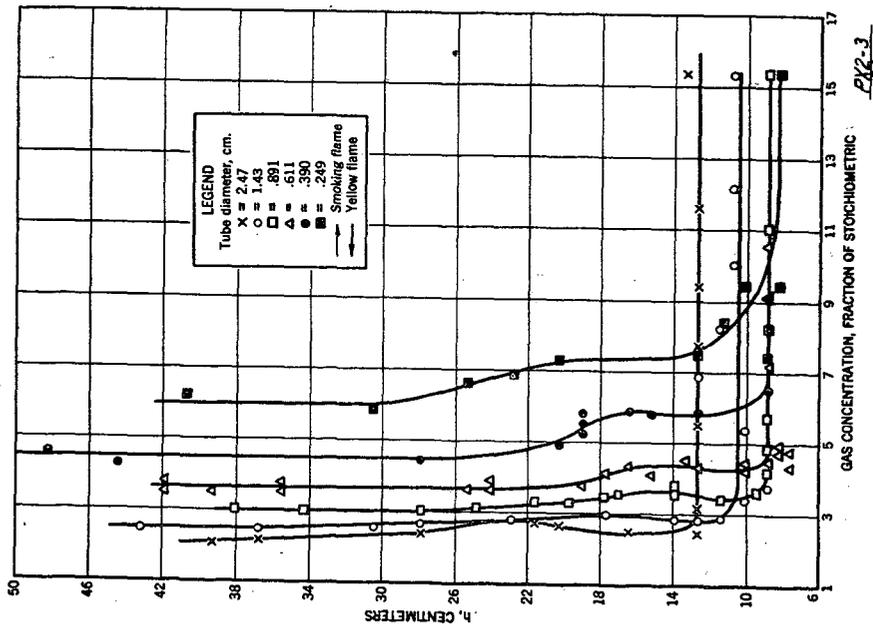


Figure 3.- Heights of smoke-limit flames of ethylene-air.

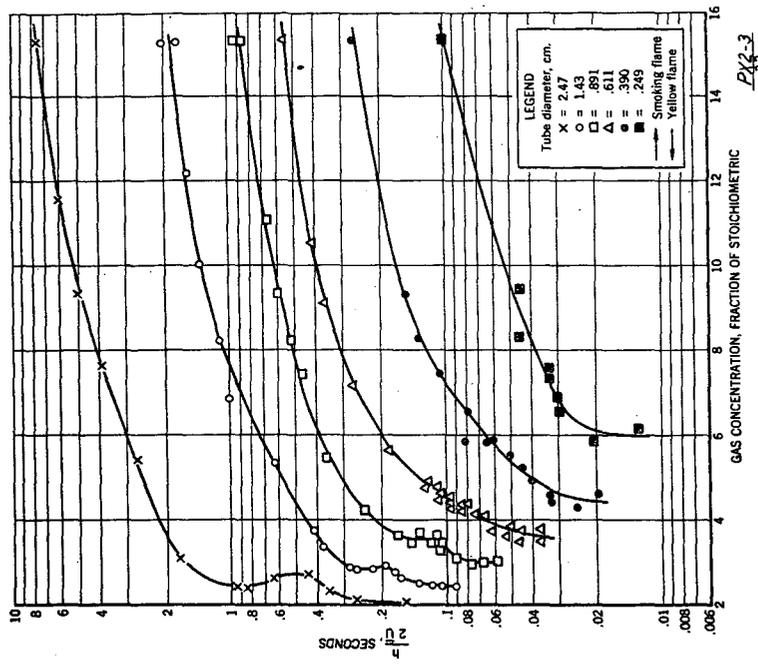


Figure 4.- Residence time in smoke-limit flames of ethylene-air.

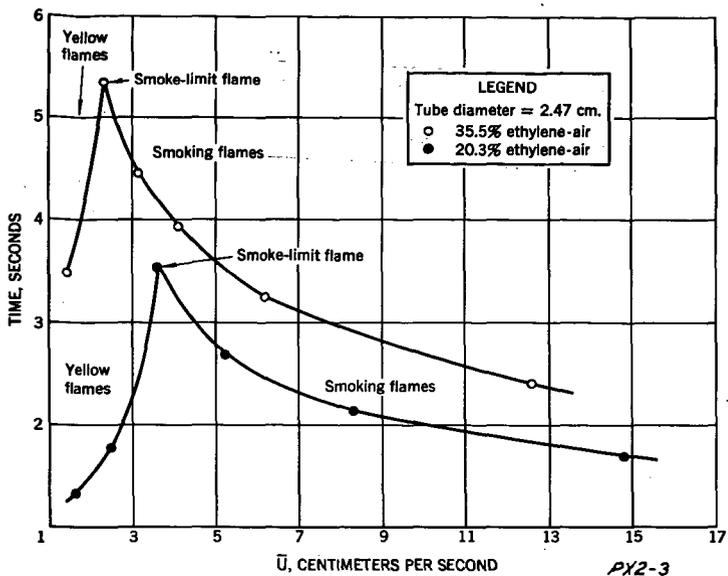
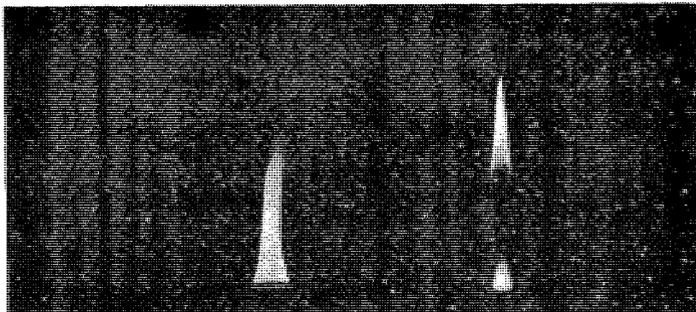


Figure 5.- Comparison of residence times for yellow and smoking ethylene-air flames.



	A	B
Fraction of stoichiometric	2.69	2.5
Flow, cm./sec.	5.8	5.7

Figure 6.- Smoking flames of ethylene-air at the flashback limit. Tube diameter = 2.47 cm.