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Soot Formation in Co- and Counter-flow Laminar Diffusion Flames of Binary Mixtures of Ethylene and Butane Isomers and Synergistic Effects

Ahmet E. Karataş,* Mario Commodo, and Ömer L. Gülder

Institute for Aerospace Studies, University of Toronto, 4925 Dufferin Street, Toronto, Ontario M3H 5T6, Canada

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Soot volume fractions of binary mixtures of butane isomers, ethylene−butane isomers, and propane−butane isomers were evaluated experimentally in diffusion flames on both co- and counter-flow burners. Soot volume fractions were measured by two-dimensional line of sight attenuation of a broadband arc lamp generated light in co-flow flames, whereas in counter-flow flames, attenuation of a small radius laser beam was used. Binary mixtures of iso-butane and *n*-butane did not show any synergistic effects on soot formation. On the other hand, either *n*-butane or iso-butane addition to ethylene caused a strong synergistic effect in both types of flames that the soot volume fractions were higher than those of the individual mixture components under the same flame conditions. Binary mixtures of propane and butane isomers, however, did not display any measurable synergistic effect on soot formation. These observations were discussed in the light of mechanisms proposed by previous investigators to explain the synergistic effects detected in the flames of binary mixtures. Current results cast doubt on the universality of the dominance of any of the mechanisms previously proposed to explain the synergistic effects observed with some binary hydrocarbon mixtures.

1. Introduction

Most of the soot formation studies focus on single-hydrocarbon fuels because of the complex nature of soot mechanisms in flames. On the other hand, mixtures of hydrocarbons, especially binary mixtures, are studied, although to a limited extent, to identify the probable soot formation channels associated with potential interactions between pyrolysis products of the hydrocarbons in the mixture. Several of these studies identified a synergistic effect when two pure hydrocarbons are mixed as the fuel. The synergistic effect in soot formation is described as the measured (or computed) increases of the soot yield of a binary hydrocarbon mixture over the soot concentrations of any of the two components in the mixture individually under similar flame conditions. The synergistic effect is observed if the addition of one single component fuel to another intensifies some production channels for the formation of soot by the interaction of the pyrolysis products of these fuels. Available fuel mixture results in the literature provide some insight into the precursors that might be the culprit for the synergistic effects. However, there exist significant disagreement among researchers about the results of the fuel mixture experiments and the interpretation of these results.[1−3]

Frenklach et al.[1] mixed several fuels, including allene, C_3H_4, acetylene, C_2H_2, and butadiene, C_4H_6, and they observed some synergistic effects in a shock tube study. Their computational results suggested that the mixture effects are caused primarily by the acceleration of acetylene-addition reactions. The flame temperature and acetylene concentrations in a diffusion flame of ethylene are expected to be relatively higher than those in a propane diffusion flame. One would expect that a reduction in sooting tendency would be realized when propane is added to ethylene.[2] However, an opposite behavior was observed such that propane addition to ethylene increased the soot formation. This synergistic effect was attributed to the pyrolysis products of propane.[2] It was argued that the soot formation rate in ethylene diffusion flames is limited by the rate of benzene formation. Propane addition to these flames, which results in propargyl production, broadens the possible reactions toward benzene and thereby increases soot formation. A further increase in propane percentage may decrease the acetylene concentration to a critical amount, below which the increase in soot formation is halted and reversed. This is due to reductions in acetylene concentrations that limit the growth of polycyclic aromatic hydrocarbons (PAHs). A less pronounced synergistic effect was observed for ethylene−ethane mixtures, whereas methane−ethylene mixtures displayed none.[2]

Roesler et al.[4] performed experiments on methane−ethylene mixtures to scrutinize the role of methane and, thus, the methyl radical, CH_3, as a contributor in the synthesis and destruction of some soot precursors, most notably, propargyl, C_3H_3, and acetylene. The observed synergistic effect not only stresses the role of propargyl in the stage of the first ring formation but also questions the domination of acetylene on the growth of PAHs. That is, the expected decrease in acetylene-addition reactions is surmounted by the direct production of larger rings than benzene (e.g., cyclopentadienyl, C_5H_5, recombination or benzyl, C_7H_7, addition to propargyl)

*To whom correspondence should be addressed. Telephone: 416-667-7700. Fax: 416-667-7799. E-mail: emre.karatas@utoronto.ca.
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and by the growth of these rings through the reactions of odd-carbon-numbered species.

Lee et al.[5] developed an experimental method to assess the efficacy of C_3 species in the PAH growth stage. They measured the ratio of heavier PAHs to relatively smaller PAHs for propane−ethylene mixtures and, at the same time, added benzene to the flame externally. Although benzene addition significantly trivialized the rate-limiting feature of benzene formation, the synergistic effect in soot formation for the mixtures of propane and ethylene remained unchanged. This result[5] questions the concept that the propargyl produced by propane is mostly active in the first ring formation and acetylene produced by ethylene dominates the growth of PAHs (HACA postulate), whose validity was also questioned by Roesler et al.[4]

By investigating the mixtures of many fuels that cannot straightforwardly produce propargyl, Yoon et al.[6] implicitly focused on the relation between propargyl and methyl. For instance, the synergistic effect of ethane−ethylene mixtures is explained by the behavior of ethane to readily produce methyl radicals as a result of the breakdown of the relatively weak C−C bonds. In a parallel experiment, it is shown that propene, C_3H_6, an intermediate species between propane and propargyl, does not cause any synergistic effect when it is added to ethylene.[6] These results indicate that the induction of C_3 fuels to propargyl by dehydrogenation may not be the cause for the synergy. Instead, the synthesis of propargyl through the reactions of acetylene and methyl radical may be responsible for the synergistic effect. However, the lack of synergistic effect that they observed for methane−ethylene mixtures suggests a deficiency in this hypothesis because methyl radicals are anticipated to be abundant in methane flames. The authors rationalize this by arguing that methane cannot produce methyl radicals at low temperatures because of the high activation energy of C−H bonds.[6] This explanation is plausible because the soot formation region in their experiments is at relatively low temperatures. A more recent study substantiates this hypothesis by reporting that the synergistic effect of methane−ethylene mixture but not that of the propane−ethylene mixture is sensitive to temperature.[3] Nevertheless, another possible reason that synergistic effects are hard to observe when adding methane to ethylene[2] is that the sooting tendency of pure ethylene is much greater than pure methane. Roesler et al.,[4] diluted the ethylene with nitrogen to reduce the soot concentration of the base flame and to make the synergistic effects more noticeable.

Trottier et al.[3] studied synergistic effects both experimentally and numerically in several binary mixtures: in methane−propane and methane−*n*-butane mixtures, they did not observe any synergistic effects. The observed effects in ethylene−propane, methane−ethylene, and ethane−ethylene mixtures are attributed to the interactions between the methyl radical and ethylene in the formation of vinyl radical, C_2H_3, and they suggested that the propargyl-based pathways may not be solely responsible for the synergistic behavior of certain fuel mixtures.[3]

Iso-butane contains three identical carbon−carbon bonds, thus giving only one possible initiation step for pyrolysis,

iso-$C_4H_{10} \leftrightarrow CH_3 + $ iso-C_3H_7.[7,8] On the other hand, *n*-butane has two channels for the initiation reactions: *n*-$C_4H_{10} \leftrightarrow 2C_2H_5$ and *n*-$C_4H_{10} \leftrightarrow CH_3 + $ *n*-C_3H_7.[9] As a result, the two butane isomers have significantly different pyrolysis products. Comparative thermal decomposition experiments of the two butane isomers showed that, in the pyrolysis of *n*-butane, ethylene is the primary product formed mainly by *n*-$C_4H_{10} \leftrightarrow 2C_2H_5$, whereas in iso-butane pyrolysis, C_1 and C_3 hydrocarbons dominate.[10,11] In view of the previous data on synergistic effects on soot formation with binary hydrocarbon mixtures and the associated rationale, the binary mixtures of butane isomers may produce synergistic effects because of their radically different pyrolysis products summarized above. In the current work, binary mixtures of *n*-butane−iso-butane, ethylene−butane isomers, and propane−butane isomers were studied experimentally on a co- and counter-flow burner at atmospheric conditions.

2. Experimental Section

Flames of two different geometries, co- and counter-flow laminar diffusion flames, are investigated to study the fuel mixture effect separately from possible flow and flame structure effects.[2]

The counter-flow burner used in this study consists of two McKenna burners that are positioned in opposed jet geometry together by two custom-made plates. These plates are connected with four connectors, which permit fine adjustments, so that the required burner separation can be obtained to a desired accuracy as well as assuring a perfect alignment of the nozzles. The intake gases first pass through sintered metal foams, where they are laminarized. Each nozzle of the opposed burner consists of inner and outer flow areas, with diameters of 19.1 and 31.8 mm, respectively. The separation distance between the fuel and air nozzle is fixed at 15.2 mm. The fuel is fed from the lower burner through the inner area, and the air is supplied from the upper burner. Nitrogen shielding is provided through the outer flow area to isolate the flame from the ambient air movements.

The co-flow laminar diffusion flame burner used in this study is of a design similar to that previously used.[12,13] The burner consists of a fuel tube with 10.9 mm inner diameter and 12.7 mm outer diameter, centered in an air nozzle with 88.9 mm inner diameter. Before the air exits the nozzle, it passes through packed beds of glass beads and porous metal disks to prevent flame instabilities. Air is provided from an in-house compressor and filtered. A flame enclosure made of flexible steel mesh protects the flame from air movements in the room, while appropriate holes provide optical access. Both co- and counter-flow burner assemblies are attached to positioning platforms with accurate and repeatable vertical and horizontal movement capability.

Soot concentration measurements in the co-flow burner were made using a 100 W mercury arc lamp (Newport Corporation, Oriel 66507 model with a built-in igniter) producing broadband light. The line of sight attenuation technique used in this study is based on the one described in Snelling et al.[13]

The technique allows soot volume fraction measurements to be taken for specific radial and height positions in the flame from two-dimensional flame maps. Two dimensional images were captured by a charge-coupled device (CCD) camera (Princeton Instruments MicroMAX system, 1024B, from Roper Scientific;

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model, 7404-0001; backlit CCD camera), which has 1024×1024 pixels. The radial data map was found through the use of the Abel inversion algorithm described by Dasch.[14]

Soot measurements in the counter-flow geometry were also made using a line of sight technique; however, because of severe beam steering with the two-dimensional system used for co-flow flame, we opted for line of sight measurements using a small diameter laser beam. For the counter-flow geometry, the two-dimensional system, because of longer probe path length through the flame, produces noisy measurements because of high temperature and density gradients, which affect the direction of the radiation pattern. Note that the flame diameter for the counter-flow geometry was several times larger than the flame diameter for the co-flow flame. A He–Ne laser source (Thorlabs HRP050 model, 5 mW, 632.8 nm, beam diameter of 0.8 mm, and linearly polarized) was passed through the centerline of the flame at the measurement locations, and attenuated light was captured downstream of the burner by a high-speed large active-area silicon photodiode (Thorlabs SM1PD1A model, spectral response of 350–1100 nm, anode-grounded, and detection area diameter of 0.9 cm). The area of the photodiode was large enough to capture the laser light for all beam-steering conditions. The photodiode is connected to a benchtop photodiode amplifier (Thorlabs PDA200C). The laser light is filtered by a bandpass filter centered at 632.8 nm (Thorlabs FL05632.8-3 model).

To calculate the soot volume fraction, the absolute value of $E(m) = -\mathrm{Im}[(m^2 - 1)/(m^2 + 2)]$, where $m = n + ik$ is the refractive index of soot that is required. In our study, $E(m)$ is considered constant, independent of wavelength, with a magnitude of 0.26 ($n = 1.57$ and $k = 0.56$).[15]

Soot formation in counter-flow burners is highly dependent upon the flame strain, the carbon flow rate of the fuel stream, and the flame temperature among other parameters. The strain rate in counter-flow geometry depends upon nozzle velocities, the nozzle separation distance, and the densities of the fuel and air streams. A global strain rate for counter-flow geometries, which is valid for unequal volumetric flow rates as well, is given as follows:[16]

$$K = -\frac{2v_O}{L}\left[1 + \frac{v_F}{v_O}\left(\frac{\rho_F}{\rho_O}\right)^{1/2}\right] \quad (1)$$

where L, v, and ρ are the separation distance of the two opposing jets, jet exit velocity, and jet fluid density, respectively. Subscripts O and F denote the oxidizer and fuel, respectively. When hydrocarbon mixtures of the non-isomer fuels are used in soot experiments on counter-flow geometry burners with a constant carbon flow rate in the fuel, because of differences in the carbon content and molecular mass of the mixture components, the velocity of the fuel nozzle will not be constant. This will result in a different strain rate than the base fuel. For the counter-flow burner experiments with mixtures of ethylene–butane isomers and propane–butane isomers, corrections were applied to bring the flames of different mixture ratios to the same level of global strain of the base fuel. The soot volume fraction for strain rates around the reference strain rate were measured by changing the burner separation while keeping other parameters constant. An example of the change in the maximum soot volume fraction with the strain rate is shown in Figure 1 for ethylene and iso-butane.

In co-flow geometry, the carbon flow rate in the fuel mixture and the air flow rate were kept constant throughout all co-flow experiments, with values equal to 3.02 mg/s and 3.8×10^{-3} m^3/s, respectively. Visible flame heights for the fuel mixture co-flow
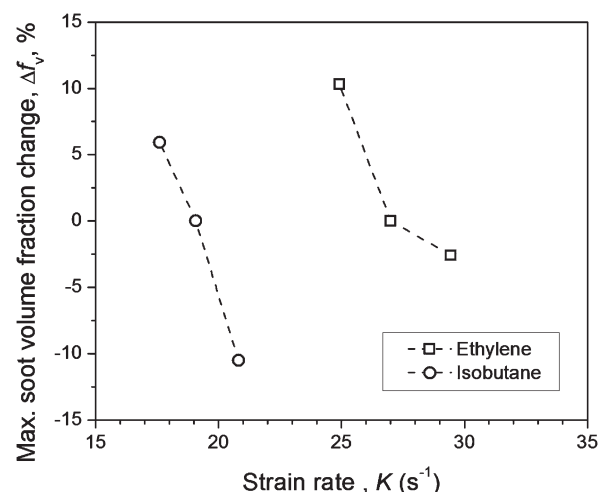
Figure 1. Effect of the strain rate on the maximum soot volume fraction on a counter-flow burner.

laminar diffusion flames were measured and found to be in good agreement with Roper's correlation.[17] In counter-flow geometry, the carbon fuel rate at the fuel nozzle was kept constant at 28.3 ± 0.1 mg/s and the air flow rate was adjusted to match the momentum of the fuel nozzle. The distance between the fuel and air nozzles was kept constant at 15.2 mm for all of the fuel mixtures investigated.

3. Results and Discussion

3.1. Mixtures of Butane Isomers. Line of sight soot volume fractions in counter-flow laminar diffusion flames of butane isomer mixtures are shown in Figure 2 at different positions along the centerline as a function of the butane isomer mixture ratio. Pure iso-butane and *n*-butane flames produce the highest and lowest amount of soot, respectively, and the mixtures are settled in between according to the mixture ratio. This means that there exists no measurable synergistic effect in soot formation when butane isomers are mixed as fuel. A similar picture emerged when the experiments were repeated on the co-flow burner, as shown in Figure 3. Integrated soot volume fractions of co-flow flames are reported as a function of the percentage of iso-butane in the mixture at several heights above the fuel nozzle. Soot volume fraction profiles show a linear trend for different mixture ratios, confirming the absence of the synergistic effect for mixtures of butane isomers. The measured visible flame heights for the investigated conditions ranged between 61.6 ± 0.7, with a negligible effect on the comparison of the different flames.

As mentioned in the Introduction, the initiation step of pyrolysis of iso-butane is iso-$C_4H_{10} \leftrightarrow CH_3 + $ iso-C_3H_7 because of three identical carbon–carbon bonds.[7,8] As a result of its chemical structure, on the other hand, there are two initiation channels in the pyrolysis of *n*-butane through the following reactions: *n*-$C_4H_{10} \leftrightarrow 2C_2H_5$ and *n*-$C_4H_{10} \leftrightarrow CH_3 + $ *n*-C_3H_7.[9] As a consequence of different initiation steps, the two butane isomers have significantly different pyrolysis products.[10,11] Thermal decomposition experiments from 975 to 1125 K on butane isomers report that iso-butane produces more C_1 (mostly methane and methyl radical) and C_3 species and *n*-butane produces more C_2 species (mostly ethylene).[10,11] It was found that hydrogen, methane, propene, and iso-butylene, C_4H_8, are the main products of pyrolysis of iso-butane, whereas ethane, propane, 1- and
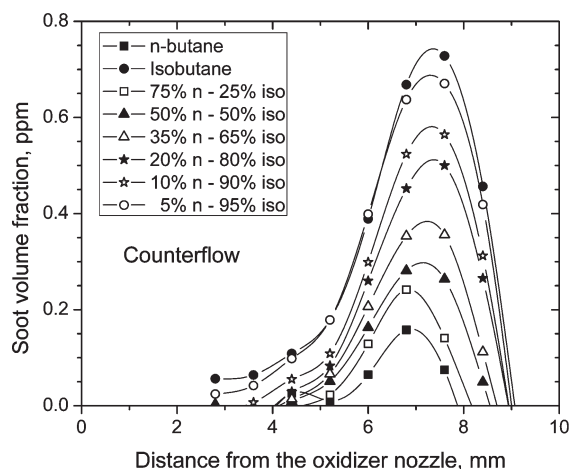
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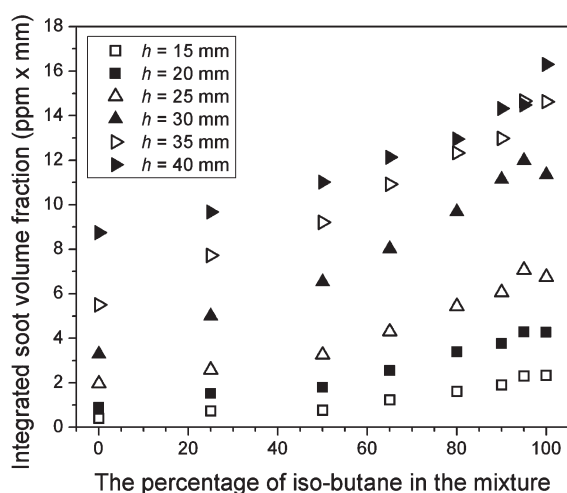(16) Seshadri, K.; Williams, F. A. *Int. J. Heat Mass Transfer* **1978**, *21*, 251–253.
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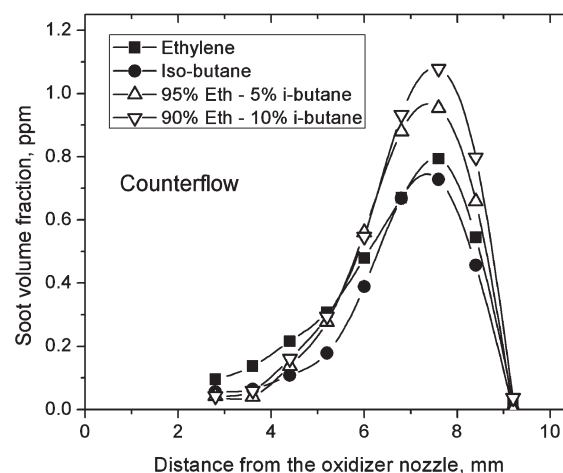
Figure 2. Soot volume fraction profiles of mixtures of butane isomers in the counter-flow flame.

Figure 3. Integrated soot volume fractions in co-flow flames of mixtures of butane isomers.

2-butylenes, butadiene, and C_5 hydrocarbons are formed in smaller quantities. On the other hand, hydrogen, methane, ethylene, and propene are the main pyrolysis products in *n*-butane, whereas ethane, butadiene, and 1- and 2-butylenes are formed in smaller amounts. As a first thought, it could be expected that ethylene from *n*-butane pyrolysis would interact with pyrolysis products of iso-butane (e.g., methyl radical, methane, and propargyl from iso-butylene) to yield synergistic chemical effects similar to the one displayed by the mixtures of ethylene−propane. Trottier et al.[3] argued that interactions between methyl radical and ethylene leading to the formation of vinyl radical through the reactions $H + C_2H_4 \leftrightharpoons C_2H_3 + H_2$, $OH + C_2H_4 \leftrightharpoons C_2H_3 + H_2O$, and $C_2H_4 + CH_3 \leftrightharpoons C_2H_3 + CH_4$ could be the culprit in the synergistic effects in ethylene−propane mixtures. The formation of the vinyl radical would lead to a synergistic behavior over the mixture range of the even-carbon-based reactions for the first aromatic ring formation.[3] However, current experiments did not show any synergistic effect of binary butane isomer mixtures on soot, although there would be an abundance of methyl radical from iso-butane pyrolysis and ethylene from *n*-butane pyrolysis. Observed results suggest that molecular aspects of soot formation may not solely be explained by the roles played by methyl radical, propargyl, or acetylene.

Figure 4. Soot volume fraction profiles of ethylene and iso-butane binary mixtures in the counter-flow flame.

More recently, McEnally and Pfefferle[18] added *n*-butane and iso-butane to a base methane co-flow diffusion flame (in a study to investigate the sooting tendency of C_4 alcohols). The centerline measurements of the major decomposition products showed that the iso-butane-doped flame produced significantly more propene and butene, C_4H_8, than the *n*-butane-doped flame. Propene and butene are expected to convert to benzene precursors, such as propargyl, more readily than ethylene.[19] In addition, the maximum centerline benzene concentration was measured about 20% higher for iso-butane-doped flame than the *n*-butane-doped counterpart.[18] These findings explain the much higher sooting tendency of iso-butane than that of *n*-butane under similar conditions, as shown in Figure 2.

3.2. Mixtures of Ethylene and Butane Isomers. Soot volume fraction profiles of the ethylene−iso-butane mixtures in the counter-flow flame are shown in Figure 4, for iso-butane mole fractions of 5 and 10% in ethylene. A correction was applied to account for the effects of nozzle velocity change on strain rate, while the carbon flow rate of the fuel mixture was kept constant. Although the strain rate was found to have a strong effect on the soot yield (Figure 1), the changes in the strain rate were subtle for the investigated fuel mixtures. On the basis of the results of Figure 1, the correction factors were calculated to be an increase of 0.9 and 1.85% in soot volume fraction for the addition of 5 and 10% butane, respectively.

A strong synergistic effect is apparent even with 5% iso-butane in ethylene. Similar behavior was observed in co-flow flames of ethylene−iso-butane mixtures. Radial profiles of soot concentrations are shown Figures 5 and 6, at flame heights of 15 and 25 mm.

As shown in Figure 2, *n*-butane produces much less soot than iso-butane under the same flame conditions (maximum soot volume fraction is about 5-fold higher for iso-butane than that of *n*-butane in counter-flame geometry). The branched paraffins produce more soot than normal paraffins as noted previously,[18,20] although both isomers have the same hydrogen/carbon ratios and almost identical adiabatic flame temperatures. The difference in sooting propensities of the two isomers is due to the widely different pyrolysis products.
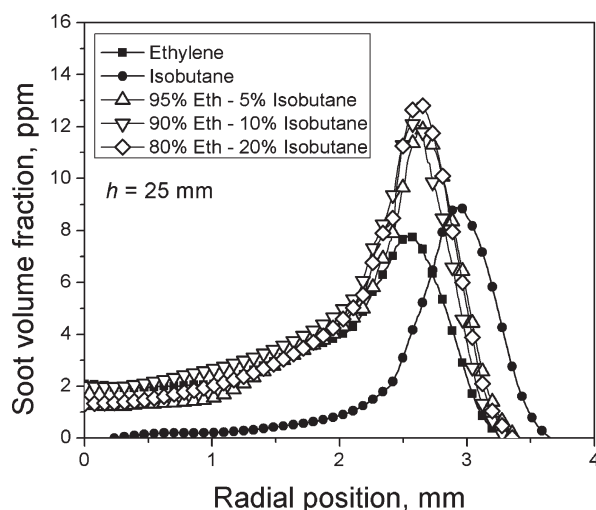
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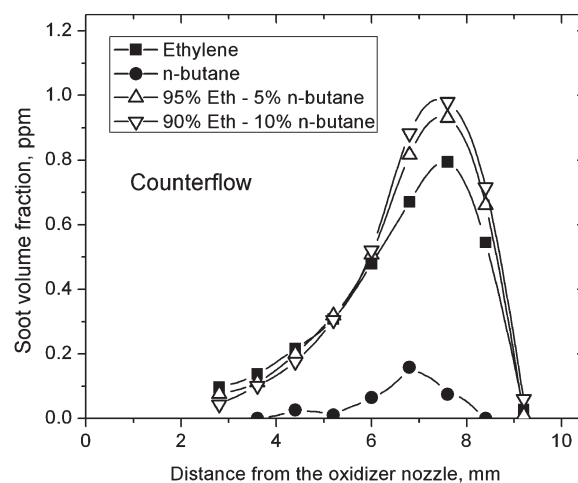(20) Gülder, Ö. L. *Combust. Flame* **1989**, *78*, 179–194.
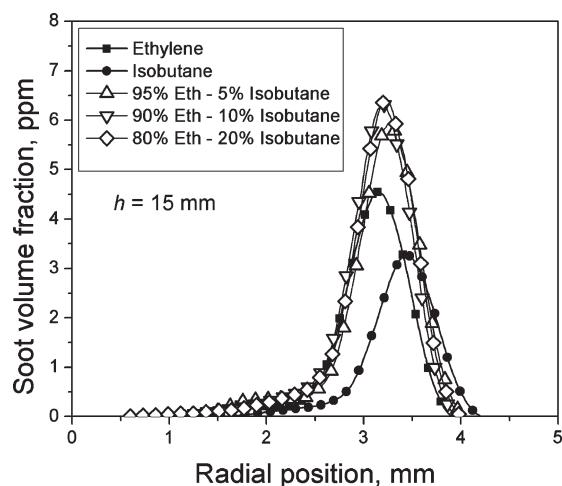
Figure 5. Radial profiles of the soot volume fraction in the co-flow flame at a flame height of 15 mm for binary mixtures of ethylene and iso-butane.
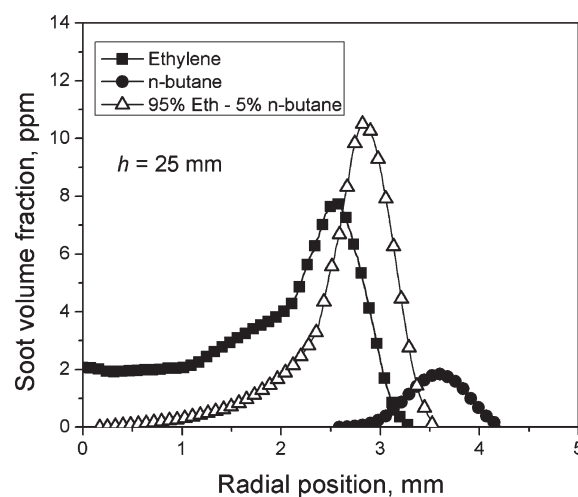

Figure 6. Radial profiles of the soot volume fraction in the co-flow flame at a flame height of 25 mm for binary mixtures of ethylene and iso-butane.

Figure 7. Soot volume fraction profiles of ethylene and *n*-butane binary mixtures in the counter-flow flame.

Figure 8. Radial profiles of the soot volume fraction in the co-flow flame at a flame height of 25 mm for binary mixtures of ethylene and *n*-butane.

Figure 9. Radial profiles of the soot volume fraction in the co-flow flame at a flame height of 35 mm for binary mixtures of ethylene and *n*-butane.

As discussed in section 3.1, ethylene is one of the major decomposition products of *n*-butane. Therefore, mixing *n*-butane into ethylene was not anticipated to cause any synergistic effect that would result from the presence of ethylene and *n*-butane pyrolysis products. However, the soot volume fraction increased substantially when small amounts of *n*-butane were added to ethylene (Figure 7) in a counter-flow geometry burner. The magnitude of the observed synergistic effect is comparable to that in ethylene−iso-butane mixtures. Given that flame temperatures of the mixtures are lower than that of pure ethylene, it is clear that the observed synergistic effect originates from chemical influences. Similar synergy was observed in co-flow flames of ethylene−*n*-butane mixtures. Examples of radial profiles of 5% *n*-butane in ethylene are shown in Figures 8 and 9 for axial flame heights of 25 and 35 mm. Again, observed increases in soot volume fractions with *n*-butane addition are comparable to those observed with iso-butane addition to ethylene in co-flow flames.
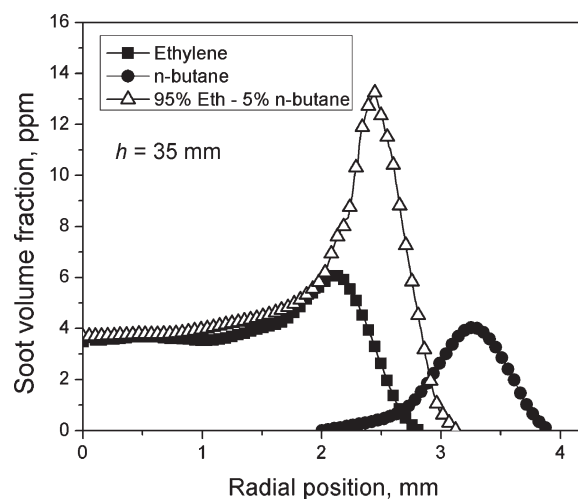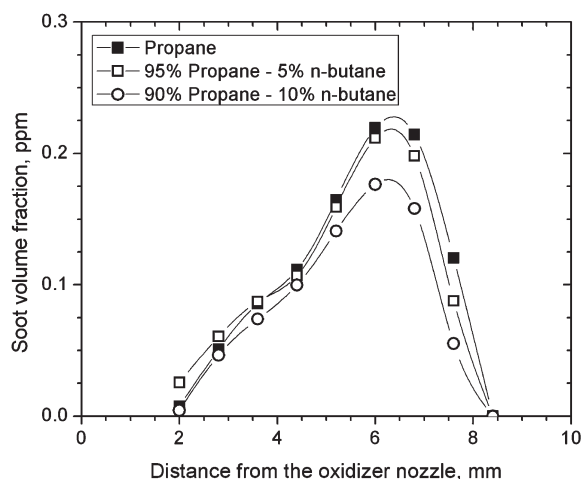
Both butane isomers produce small amounts of butadiene upon pyrolysis.[10,11] In the pyrolysis of ethylene, acetylene is one of the major decomposition products. Interaction between butadiene and acetylene is one of the plausible routes

Figure 10. Soot volume fraction profiles of propane and *n*-butane binary mixtures in the counter-flow flame.

that would contribute to nonlinear effects on soot formation in ethylene−butane isomer mixtures.[1]

The presence of a synergistic effect caused by chemical alterations is further justified considering that the soot volume fraction increases significantly with the addition of 5% butane isomers, but then further addition, such as 20% iso-butane, causes only a slight increase (Figures 5 and 6). Similar results were obtained with *n*-butane. This observation prompted us to do experiments with mixtures of propane−butane isomers to see whether the synergistic effect for the mixtures of ethylene−butane isomers originates from the activation of the same chemical pathways as the ones in the mixtures of propane−ethylene.

3.3. Mixtures of Propane and Butane Isomers. Ethylene−propane mixtures were shown to produce a strong synergistic effect.[2,3] In the pyrolysis of *n*-butane, one of the abundant products is ethylene.[10] Then, the mixtures of propane and *n*-butane are expected to produce a similar synergistic effect as the one observed in ethylene−propane mixtures. The base fuels are chosen as isobutane and propane for the mixtures of propane−iso-butane and propane−*n*-butane, respectively. This is because the sooting propensity of the fuels are in the order of iso-butane > propane > *n*-butane. The correction factors because of strain rate variations are calculated to be a decrease of 0.3 and 0.6% for the addition of 5 and 10% propane to iso-butane, respectively. Changes in soot volume fraction for the mixtures of *n*-butane and propane because of strain rate variations were not measurable. Therefore, no corrections were applied for the mixtures of *n*-butane and propane.
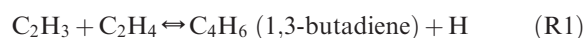
In our measurements, the addition of *n*-butane to propane did not produce any synergistic effect in counter-flow geometry flames (Figure 10). Similarly, the addition of propane to iso-butane did not produce any measurable nonlinear effect on soot formation (Figure 11).

For soot formation in diffusion flames of aliphatic hydrocarbon fuels, benzene formation seems to be the rate-limiting step; the concentrations of polycyclic aromatics and soot have been shown to be proportional to benzene concentrations.[21] One of the reaction pathways of benzene production
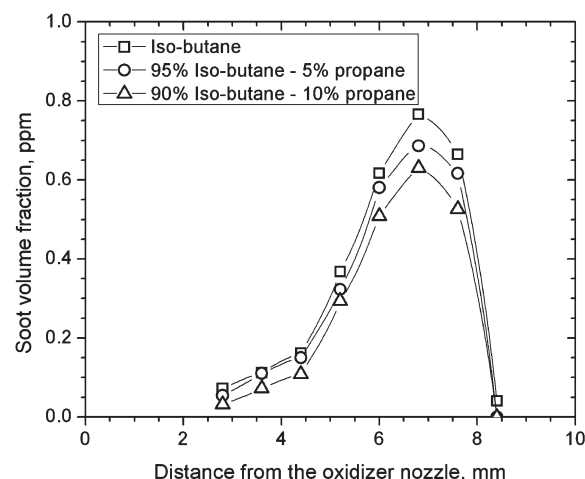
in *n*-butane pyrolysis at relatively lower temperatures is identified as[22]

$$C_2H_3 + C_2H_4 \Leftrightarrow C_4H_6 \text{ (1,3-butadiene)} + H \qquad (R1)$$

$$C_2H_3 + C_4H_6 \Leftrightarrow C_6H_8 \text{ (cyclohexene)} + H \qquad (R2)$$

$$C_6H_8 + R\bullet \Leftrightarrow C_6H_7 \text{ (cyclohexadienyl radical)} + RH \quad (R3)$$

$$C_6H_7 \Leftrightarrow C_6H_6 + H \qquad (R4)$$

Because ethylene is a secondary product of iso-butane breakdown, the benzene production in iso-butane diffusion flames may proceed mostly via propargyl combination and the interaction of methyl radical and propargyl, in contrast to benzene production in *n*-butane pyrolysis.

In a simulation of laminar diffusion flames of mixtures of ethylene−propane, a synergistic effect that was observed experimentally is attributed to the following benzene-forming reactions, which are acetylene-based: *n*-C$_4$H$_5$ + C$_2$H$_2$ ⇔ C$_6$H$_6$ + H and *n*-C$_4$H$_3$ + C$_2$H$_2$ ⇔ C$_6$H$_5$ (phenyl radical).[3] However, the experimental data and the numerical simulation did not show any synergistic effect in methane−*n*-butane and methane−propane mixtures. The absence of the synergistic effect in these two mixtures is attributed to the hypothesis that interactions of even- and odd-numbered carbon species are responsible for the sooting behavior.

Because *n*-butane pyrolysis produces ethylene, its interaction with propane in propane−*n*-butane mixtures is expected to yield nonlinear effects, as observed in ethylene−propane mixtures.[3] However, propane−*n*-butane mixtures displayed a linear behavior in current experiments.

The processes involved in the synergistic effects in binary fuel mixtures observed in several studies are remarkably complex. In addition, the presence of contradictory experimental evidence available in the literature and the conflicting explanations of such effects create a confused state. Current experimental results further cast doubt on the universality of the mechanisms proposed for explaining the synergistic effects observed in soot formation in flames of binary fuel mixtures. It seems that small changes in the composition of pyrolysis products may have significant effects on the soot

Figure 11. Soot volume fraction profiles of iso-butane and propane binary mixtures in the counter-flow flame.

(21) McEnally, C. S.; Ciuparu, D. M.; Pfefferle, L. D. *Combust. Flame* **2003**, *134*, 339–353.

(22) Gupta, G. K.; Dean, A. M.; Ahn, K.; Gorte, R. J. *J. Power Sources* **2006**, *158*, 497–503.

formation pathways, some of which may not have yet been identified or discussed.

It may be argued that the results presented in this study could be explained by the hypothesis previously proposed;[2,4] namely, a synergistic effect can arise when ethylene or acetylene is the base fuel. Pyrolysis of these fuels produces virtually no methyl radical because they have double or triple bonds between their two carbon atoms. The absence of C_1 products severely constrains propargyl formation via C_1 + C_2 addition reactions, which in turn constrains the formation of benzene and soot. The synergistic effect is observed when the flame is perturbed in any way that leads to the production of methyl radical and, therefore, relaxes this constraint. However, this hypothesis fails to explain: (a) the synergistic effects observed in methane−ethane mixtures,[3] (b) no effect observed in ethylene−propene mixtures,[6] and (c) the effects observed in propane or butane flames doped with oxygen.[23]

4. Concluding Remarks

Experimental data obtained on both co- and counter-flow diffusion flames of binary fuel mixtures showed that binary

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(23) Gülder, Ö. L. *Combust. Flame* **1995**, *101*, 302–310.

mixtures of *n*-butane and iso-butane do not display any synergistic effects in soot formation despite the fact that the two butane isomers have radically different pyrolysis products. On the other hand, binary mixtures of ethylene and butane isomers showed a strong synergistic effect in soot formation; 5% iso-butane or *n*-butane in ethylene increased the soot volume fraction significantly in both co- and counter-flow flames above that of the pure ethylene flames. The increase in the soot volume fraction was not linear; as the butane fraction in ethylene was increased to 20%, the soot volume fraction approached a plateau. Mixtures of propane−*n*-butane and iso-butane−propane did not show any measurable synergistic effect. These observations question the universal dominance of any of the mechanisms proposed for explaining the synergistic effects in soot formation in binary fuel mixtures. Further, the widely held belief that only few parameters control the rate of PAH formation should be revisited.