Measurements of combustion efficiency in nonequilibrium RF plasma-ignited flows

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Abstract

The paper presents results of combustion efficiency measurements using Fourier transform infrared absorption spectroscopy in premixed hydrocarbon–air and CO–air flows excited by a low-temperature transverse radiofrequency (RF) discharge plasma. The results demonstrate that significant fractions of these fuels are burned in RF plasma-generated and -stabilized flames (up to 100% of ethylene, 70% of methane, and 40% of CO). The results also show that fuel oxidation in the RF plasma-excited flows is most efficient in lean mixtures. Measurements of reaction product concentrations in hydrocarbon–air and CO–air mixtures show that significant amounts of fuel react under conditions when there is no flame detected in the test section. Under these conditions, fuel species oxidation occurs in plasma chemical reactions, without producing ignition. Also, experiments in CO–air flows demonstrated ignition and combustion at the equivalence ratios well below the lean flammability limit for CO. Finally, experiments in higher power RF discharges (500 W) showed that nonequilibrium plasma ignition occurs at flow velocities up to at least \( u = 60 \text{ m/s} \) and at flow residence times exceeding \( \sim 1 \text{ s} \). The effect of significant fuel oxidation, which is observed for lean fuel–air mixtures outside the flammable range, before the ignition occurs, provides additional evidence for the nonthermal fuel oxidation triggered by plasma-generated radicals. The present results, combined with previous experiments in which RF plasma ignition was demonstrated to occur in a low-temperature plasma, suggest the following nonequilibrium plasma ignition mechanism: (i) active radical species generation by the nonequilibrium plasma, (ii) plasma chemical reactions of fuel species oxidation with participation of these radicals, (iii) flow heating due to net exothermal plasma chemical fuel oxidation process, and (iv) subsequent thermal ignition and combustion.

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1. Introduction

Control of ignition and combustion processes in aircraft jet engines is of crucial importance for their performance over a wide range of operation parameters, such as altitude, flight speed, and thrust. This requires sustaining stable combustion and flame hold-
ing at widely different values of combustor static pressures, flow velocities, and equivalence ratios. In particular, it is well known that controlling flame stability becomes a challenge at low pressures (i.e., high altitudes), high flow velocities in the combustor, and for lean fuel–air mixtures [1–5]. Operation under these conditions may result in combustion instabilities, incomplete burning, and flame blowoff.

Recent work conducted at the Nonequilibrium Thermodynamics Group at the Ohio State University [6,7] demonstrated that large-volume ignition of premixed hydrocarbon–air flows by a uniform and diffuse RF discharge plasma can be achieved at significantly higher flow velocities (up to $u = 25 \text{ m/s}$) and lower pressures ($P = 60–130 \text{ Torr}$) compared to both a spark discharge and a DC arc discharge. The experiments also demonstrated flame stabilization by the RF plasma, without the use of any physical obstacle flame holders. Temperature measurements in the stable diffuse RF discharge using Fourier transform infrared spectroscopy show that the flow temperature in the plasma prior to ignition ($T = 250–550 \degree \text{C}$ at $P = 60–120 \text{ Torr}$) is considerably lower than autoignition temperatures for ethylene–air mixtures at these pressures ($T = 600–700 \degree \text{C}$). Also, spatially resolved temperature measurements show the transverse temperature nonuniformity in the RF discharge to be insignificant. Finally, visible emission spectroscopy measurements in $\text{C}_2\text{H}_4$–air and $\text{CO}$–air flows in the RF discharge detected the presence of radical species such as CN, CH, C$_2$, and OH, as well as O and H atoms. These results, in particular low ignition temperatures, suggest a nonthermal ignition mechanism, i.e., ignition via generation of chemically active radical species in the volume occupied by the plasma (15–20 cm$^3$).

To determine feasibility of this large-volume, low-temperature ignition and flame-holding method for engineering combustion applications, additional experiments, such as measuring the radical species and the combustion product concentrations, are required. The main objectives of the present work are to measure combustion efficiency (i.e., the fraction of fuel burned) and combustion product concentrations using infrared absorption spectroscopy in premixed hydrocarbon–air and CO–air flows excited by a low-temperature transverse RF discharge plasma. This would determine the range of flow parameters in which nonthermal ignition is most effective and may also provide insight into its mechanism.

2. Experimental

The present experiments have been conducted at a high-speed flow plasma combustion facility recently developed at Ohio State [6,7]. The schematic of the facility is shown in Fig. 1. A premixed hydrocarbon–air flow enters the $5 \times 1$-cm rectangular cross section, 20-cm-long test section through a 50-foot-long, 1-inch-diameter corrugated gas supply line. The facility can use either room air or bottled air. Spring-loaded shutoff valve and a flash arrester installed in the 1/4-inch-diameter fuel supply line enable quick flow shutoff and prevent the flame propagation into the fuel cylinder. Downstream of the test section, the flow is diluted with atmospheric air through a vent valve to prevent further combustion in the vacuum system and in the dump tank (see Fig. 1). The 1200 ft$^3$ dump tank is pumped out using an Allis-Chalmers 1300 cfm rotary vane vacuum pump. The test section static pressure ranges from 30 Torr to 0.5 atm. The mass-flow rate through the test section can be varied from below 1 to 12 g/s. The test section pressure and the mass-flow rate can be varied independently. This makes the experimental facility suitable for combustion studies both in high-speed, low-pressure and in low-speed, intermediate pressure flows. At the highest mass-flow rate and the lowest pressure, the experimental conditions correspond to the test section Mach number of $M \cong 0.8$. At the steady-state test section pressure of 100 Torr, the mass-flow rate through the vent valve is approximately 100 g/s. For the baseline flow conditions, at a pressure of $P = 100 \text{ Torr}$, mass-flow rate through the test section of $m = 10 \text{ g/s}$, and stoichiometric methane–air flow mixture (9.5% CH$_4$ in air), air dilution reduces the methane fraction in the flow into the dump tank to about 1%, which is well below the low flammability limit of 5% [8].

The test section made of high-temperature machineable mica ceramic and steel is shown in greater detail in Fig. 2. The flow enters the rectangular cross section test section through a 1/2-inch-long ceramic honeycomb flow straightener (300 holes per square inch), which also serves as an additional flash arrester, and passes between two RF electrode blocks. Each of the two $5 \times 3$ cm electrode blocks, manufactured of mica ceramic and flush mounted in the test sec-
Fig. 2. Schematic of the plasma-assisted combustion test section.

The plasma combustion facility has been designed for the use of spectroscopic flow diagnostics. In particular, the test section has four optical access window ports, two on each side, as shown in Fig. 2. This provides optical access to both the RF discharge/flame attachment region and the flow region ∼10 cm downstream of the discharge through MgF2 windows. As in our previous emission spectroscopy measurements [6], we used an optical multichannel analyzer (OMA) equipped either with a Princeton Instruments liquid nitrogen cooled 512 × 512 pixel CCD array camera or a PI-Max ICCD camera, and a Spectra Physics 0.5 m monochromator with a 1200 g/mm grating to detect radical species produced in the RF plasma. In the present experiments, we also used a Biorad 17SC dynamic alignment Fourier transform infrared (FTIR) spectrometer with a liquid nitrogen-cooled InSb detector spectrometer for absorption spectroscopy measurements, to determine combustion completeness and combustion product concentrations. The same FTIR spectrometer has been used in our previous paper [6] for plasma temperature measurements. In absorption spectroscopy measurements, we sample the flow through the static pressure tap placed at the downstream end of the test section (see Fig. 2) into a 17.5-cm-long cylindrical glass absorption cell with two CaF2 windows placed into an absorption compartment of the FT spectrometer (see Fig. 1). Before sampling the flow, the absorption cell and the supply lines are evacuated using a small vacuum pump. Then the sample is drawn off until the absorption cell and the test section pressures equilibrate, after which the absorption cell shutoff valve is closed (see Fig. 1). The absorption cell pressure and temperature are monitored using a pressure gauge and a thermocouple. In the present experiments, absorption spectra are recorded after the sample temperature reached room temperature. Basically, a small flow sample quickly cools off on its way to the absorption cell. The absorption spectra are measured at a resolution of 0.25 cm⁻¹ using an internal source (globar) of the FT spectrometer. To infer combustion product species concentrations from the absorption spectra, calibration spectra for the known amounts of CH₄, C₂H₄, CO, and CO₂ in the air flow have been taken, for every 0.25–0.5% increase in the percentage of these species in the flow. In the present paper, all measurements have been done using room air–fuel mixtures.

3. Results and discussion

Plasma ignition in the test section has been produced either by first striking a transverse RF discharge in the air flow and then adding fuel to the air supply line or by striking the discharge in the premixed air–fuel flow. In the entire range of pressures studied in our previous papers [6,7] as well as in the present experiments, the RF discharge was diffuse and stable. At the RF power of 200 W and within the pressure range of \( P = 70–100 \text{ Torr} \), the RMS voltage between the RF discharge electrodes was 1.8–1.9 kV. Fig. 3 shows photographs of a 250 W transverse RF discharge
plasma and the flame in a stoichiometric ethylene–air flow at $P = 70$ Torr and a 200 W transverse RF discharge plasma and the flame in a 20% CO–air flow at $P = 110$ Torr. After ignition occurs, the steady flame originates at the RF plasma, spans the cross section of the flow, and usually extends through the entire test section downstream of the discharge (see Fig. 3). The flame remains stable for as long as the RF discharge is on.

In our previous paper [6], we measured the temperature in the RF discharge in air before adding the fuel by FT emission spectroscopy, using CO added to the flow at a 1–2% level as a thermometric element. Fig. 4 summarizes the results of these measurements at the RF discharge power of 200 W, also showing the range of pressures at which adding a stoichiometric amount of ethylene or methane to the air flow results in flow ignition by the RF discharge. From Fig. 4, it can be seen that ignition is produced at rather low plasma temperatures, $T = 250–300 \degree$C in ethylene and $T = 350–400 \degree$C in methane. These temperatures are considerably lower than autoignition temperatures for these species, $600–700 \degree$C. For example, Fig. 5 [10] shows autoignition temperatures in ethylene–air mixtures at different equivalence ratios and pressures.

These results suggested that ignition in hydrocarbon–air flows excited by nonequilibrium transverse RF discharge occurs by a nonthermal mechanism. This suggestion is consistent with visible emission spectroscopy measurements, which showed the presence of O and H atoms, and OH radicals in RF air–fuel plasmas [6].

In the first series of experiments, we measured FT absorption spectra of ethylene–air mixtures (without plasma) and of the combustion products (with plasma-assisted ignition) at different equivalence ratios, keeping the mass-flow rate through the test section and the RF discharge power the same, $\dot{m} = 1.2$ g/s and 200 W, respectively. Fig. 6 summarizes the results of these absorption spectroscopy measurements at $P = 70$ Torr. The absorption spectra were taken in a range of equivalence ratios of $\phi = 0.3–4.4$; the spectra shown in Fig. 6 are for $\phi = 0.5, 1.0$, and 1.4. In all air–fuel mixture spectra, absorption bands of ethylene (between 2930 and 3220 cm$^{-1}$), CO$_2$, and water can be easily identified (see Figs. 6a–6f).
Magnified regions of the spectra with ethylene absorption bands shown in greater detail are plotted in Figs. 6b, 6d, and 6f. Carbon dioxide and water both appear in the fuel–air absorption spectra (see Figs. 6a, 6c, and 6e) since in these experiments room air has been used. It can be seen that in the lean ethylene–air mixture (at $\phi = 0.5$), nearly the entire amount of ethylene disappears from the flow after the RF discharge is turned on (see Fig. 6b). At the same time, CO$_2$ and water concentrations in the flow significantly increase, and CO absorption bands also appear in the spectra (see Fig. 6a). Clearly, under these conditions ethylene in the flow excited by an RF discharge is completely oxidized into CO, CO$_2$, and water.
Continuing the analysis of Fig. 6, it can be seen that in the stoichiometric ethylene–air mixture ($\phi = 1.0$), turning the RF discharge on results in a considerable reduction of ethylene amount in the flow (see Fig. 6d), although not in its complete removal, as in the lean mixture at $\phi = 0.5$ (see Fig. 6b). In addition, under these conditions, it can be seen that some amount of ethylene is converted into acetylene, which appears in the absorption spectra between 3230 and 3350 cm$^{-1}$ (see Fig. 6d). Therefore, ethylene oxidation under the stoichiometric conditions is not complete. Finally, in the rich ethylene–air mixture ($\phi = 1.4$), it is quite apparent that larger fractions of ethylene and acetylene remain unreacted in
the RF discharge excited flow, compared to the stoichiometric conditions (see Fig. 7f). Summarizing the qualitative analysis of Fig. 6, we can conclude that ethylene oxidation into CO, CO$_2$, and water in the RF discharge excited flows is most efficient in lean and least efficient in rich mixtures.

In the second series of experiments, we measured FT absorption spectra of methane–air mixtures and of the combustion products at the same mass-flow rate and RF power, $m = 1.2$ g/s and 200 W. Fig. 7 summarizes the results of these measurements at different equivalence ratios, at $P = 90$ Torr. In methane–air, the absorption spectra were taken in a range of equivalence ratios of $\phi = 0.4$–1.3; the spectra shown in Fig. 7 are for $\phi = 0.6$, 0.9, and 1.15. In all air–fuel mixture spectra, absorption bands of methane (between 2850 and 3200 cm$^\text{-1}$), CO$_2$, and water can be easily identified (see Figs. 7a–7f). Magnified regions of the spectra with methane absorption bands shown in greater detail are plotted in Figs. 7b, 7d, and 7f. Qualitatively, the results are similar to the results obtained in ethylene–air mixtures. At $\phi = 0.6$, a significant reduction of methane amount and its oxidation into CO, CO$_2$, and water can be observed (see Figs. 7a and 7b). At $\phi = 0.9$, the methane amount reduction is considerably smaller (see Fig. 7d), and at $\phi = 1.15$ it becomes very small (see Fig. 7f). Also, in the reach mixture, at $\phi = 1.15$, acetylene appears in the absorption spectra, although in a much smaller amount compared to the ethylene–air flows (see Figs. 6e and 7e). Again, we conclude that methane oxidation in the RF discharge excited flows is most efficient in lean and least efficient in rich mixtures.

From the absorption spectra such as shown in Figs. 6 and 7, one can determine the fraction of fuel (either ethylene or methane) left unreacted in the RF discharge excited flow, $f$, by comparing the intensities of individual absorption lines with and without RF discharge sustained in the flow,

$$ f = \frac{n_{\text{RF}}}{n} = \frac{\ln(I_{\text{abs}}/I_{\text{b}})}{\ln(I_{\text{abs}}/I_{\text{b}})} . $$

(1)

In Eq. (1), $I_{\text{b}}$ is the baseline transmitted signal intensity, $I_{\text{abs}}$ and $I_{\text{RF}}$ are transmitted signal intensities with and without RF discharge, and $n_{\text{RF}}$ and $n$ are the number densities of the fuel species with and without RF discharge. The relation between the signal intensities and the number densities in Eq. (1) is very simple since the absorption spectra of the initial air–fuel mixture and of the reaction products are both measured at the same pressure in the absorption cell (equal to the test section pressure), and at the same temperature (room temperature). The value of $f$ was determined using several vibration–rotation absorption lines (typically 4 to 6) and averaging the result. Typically, the

Fig. 8. Percentage of fuel left unreacted in the flow. Shaded areas indicate conditions under which a flame is detected in the test section.

$f$ values obtained for different lines differed by only a few percent.

Fig. 8 shows the percentage of fuel left in the flow, calculated from the absorption spectra using Eq. (1), as a function of the equivalence ratio. Shaded areas in Fig. 8 indicate conditions under which a flame is detected in the test section. Note that in these experiments detecting the flame in the test section has been quite simple, both visually and spectroscopically. First, unlike the RF plasma, which was always confined to the region between the electrode blocks, the flame typically extended through the test section downstream of the RF discharge (see Fig. 3). Second, the most pronounced features of the hydrocarbon–air flame emission were the blue-green C$_2$ emission (Swan band system, $\Delta v = 0, \pm 1$) and the blue CH emission (4300 A band system) [6], which were missing in the spectra of RF plasma emission when ignition was not produced.

From Fig. 8, it can be seen that, indeed, the fraction of fuel left unreacted in the flow is lowest in lean mixtures, i.e., at the low values of the equivalence ratio (close to zero in ethylene–air flows and 30–55% in methane–air flows at $\phi \leq 0.8$). As the equivalence ratio increases, the fraction of fuel remaining in the flow also grows, up to nearly 100% in ethylene–air at $\phi = 4.4$ and in methane–air at $\phi = 1.3$. The range of equivalence ratios at which significant fuel oxidation occurs is much wider for ethylene than for methane. Most interestingly, very significant reduction of fuel amount in both ethylene–air and methane–air mixtures has been detected for lean mixtures, under the conditions when there was no flame detected in the test section (i.e., at $\phi < 0.75$–0.8, see Fig. 8). In other words, under these conditions fuel species oxidation, nearly complete in ethylene/air flows, occurs without ignition produced in the test section. Note that our
previous measurements [6] showed that the air plasma temperature before the fuel is added to the flow is quite low, 250–300 °C at $P = 70$ Torr and 350–400 °C at $P = 90$ Torr (see Fig. 4), much below autoignition temperature. Therefore, this strongly suggests that fuel oxidation under these low-temperature conditions, which occurs without ignition and therefore cannot be thermal, is triggered by the radical species generated in the RF plasma, such as O and H atoms and OH radicals [6]. Since the net process of fuel species oxidation is exothermal, it has to result in heat generation and heating of the flow. The results shown in Fig. 8 qualitatively suggest that when the temperature of the flow, heated by this plasma chemical process, becomes sufficiently high (which happens as the available fuel amount and the equivalence ratio are increased), thermal ignition would occur and combustion would be sustained in the test section. We would like to emphasize that the observed effect of nearly complete fuel oxidation in the lean RF plasma-excited flows, without producing ignition, cannot be explained by localized heating of the flow in small arc filaments (“hot spots”) which could form in the RF discharge. Indeed, the entire flow cannot pass through such a hot spot. A somewhat more modest effect of partial oxidation of fuel species is also observed in rich mixtures, also when the flame is not detected, at $\phi > 2.0$ in ethylene–air (see Fig. 8). This is also consistent with the qualitative scenario of fuel oxidation by the plasma-generated radicals. In this case, the heat of reaction of the net oxidation process may be insufficient to heat the fuel-rich, high specific heat mixture up to the ignition temperature.

The mole fractions of the reaction products, such as CO, CO$_2$, methane, and ethylene, have been determined by comparing the experimental absorp-

![Fig. 9. Mole fractions of ethylene oxidation/combustion products at different equivalence ratios. Shaded area indicates conditions under which a flame is detected in the test section. $P = 70$ Torr.](image1)

![Fig. 10. Mole fractions of methane oxidation/combustion products at different equivalence ratios. Shaded area indicates conditions under which a flame is detected in the test section. $P = 90$ Torr.](image2)
section are lower than the temperatures under near-stoichiometric conditions.

The third series of experiments was conducted in lean CO–air mixtures ($\phi = 0.03–0.7$), at the same mass-flow rate and the RF power, $\dot{m} = 1.2$ g/s and 200 W, and at two different test section pressures, $P = 110$ and 70 Torr. The main objective here was determining the combustion efficiency and lean flammability limits of CO–air flows ignited by the RF plasma. In these experiments, the presence of the flame was identified by the blue CO$_2$ emission (carbon monoxide flame bands [11]) extending downstream of the RF plasma region (see Fig. 3), also detected in our previous measurements [6]. Figs. 11 and 12 show the percentage of CO burned and the CO$_2$ concentrations as functions of the equivalence ratio. Shaded areas in Fig. 11 indicate conditions under which a flame is detected in the test section. As in the experiments with hydrocarbon–air mixtures (see Fig. 8), the largest CO fractions down to 5% are observed in lean mixtures, at $\phi < 0.17$, while H atom line (656 nm) emission peaks at $\phi \sim 0.5$. Note that under these conditions the reacted fuel fraction is highest (nearly 100%, compare Fig. 8 and Fig. 13), while ignition is not achieved and a flame is not detected. On the other hand, CH (4300 A band system) and C$_2$ (0 $\rightarrow$ 1 Swan band, 563 nm) emission intensities peak at $\phi \sim 0.9$, respectively, i.e., under the conditions when a flame is detected in the test section and when O, H, and OH emission intensities are significantly reduced. These measurements showed that there is a strong correlation between CH and C$_2$ emission and ignition in the test section. At higher equivalence ratios, as the burned fuel fraction decreases (see Fig. 8), that the present nonequilibrium plasma ignition and flame-holding method may produce stable burning in very lean air–fuel mixtures, well below the lean flammability limits.

In an attempt to identify key radical species responsible for plasma-assisted ignition, we also took visible emission spectra of the RF plasma in ethylene–air flows at $P = 70$ Torr, and in CO–air flows, at $P = 70$ and 110 Torr. It is understood that these emission spectroscopy data can be used only for qualitative analysis of ignition kinetics since they cannot provide quantitative information on radical species concentrations. Therefore, we used these data only to identify radical species which may play key roles in the nonthermal plasma oxidation mechanism, and thereby to provide guidelines for development of optical diagnostics to measure concentrations of these key species. The emission spectroscopy results for ethylene and CO are summarized in Figs. 13 and 14. From Fig. 13, it can be seen that in ethylene–air flows, O atom line (777 nm) and OH ($A^2\Sigma^+ - X^2\Pi$ band system, 306 nm) emission intensities are highest in lean mixtures, at $\phi < 0.4$, while H atom line (656 nm) emission peaks at $\phi \sim 0.5$. Note that under these conditions the reacted fuel fraction is highest (nearly 100%, compare Fig. 8 and Fig. 13), while ignition is not achieved and a flame is not detected. On the other hand, CH (4300 A band system) and C$_2$ (0 $\rightarrow$ 1 Swan band, 563 nm) emission intensities peak at significantly higher equivalence ratios, $\phi \sim 0.6–0.8$ and $\phi \sim 0.9$, respectively, i.e., under the conditions when a flame is detected in the test section and when O, H, and OH emission intensities are significantly reduced. These measurements showed that there is a strong correlation between CH and C$_2$ emission and ignition in the test section. At higher equivalence ratios, as the burned fuel fraction decreases (see Fig. 8),
both CH and C₂ emission intensities are somewhat reduced. Very similar results have been obtained in methane–air flows. Qualitatively, one may conclude that O and H atoms, as well as OH radicals generated in the plasma are among species controlling completeness of plasma-assisted oxidation of these hydrocarbon fuels at lean conditions, before ignition occurs. On the other hand, since CH and C₂ emission peaks only after ignition is achieved and a flame is sustained in the test section, CH and C₂ radicals are unlikely to be among key species for plasma chemical hydrocarbon fuel oxidation reactions.

The results obtained in CO–room air mixtures and summarized in Fig. 14 are quite similar. The highest CO fraction reacted in the plasma is achieved at the low equivalence ratios, \( \phi < 0.4 \) (see Fig. 11), when both O atom and OH emission are highest (see Fig. 14). On the other hand, the H atom emission relatively weakly depends on the equivalence ratio. Again, this suggests a qualitative conclusion that O atoms and OH radicals initially produced in the RF discharge by electron impact dissociation of oxygen and water vapor may play a significant role in nonthermal plasma CO oxidation kinetics, before ignition occurs. Note that previous measurements of explosion limits in CO–O₂ mixtures [12] demonstrated a critical role of hydrogen-containing species (such as hydrogen or water vapor) in kinetics of CO ignition. In particular, it has been concluded that the dominant chain branching kinetic mechanism involves hydrogen-based radicals such as OH and H atoms. Ref. [12] also concluded that the chain branching mechanism involving O atoms,

\[
\text{CO} + \text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} + \text{O},
\]

becomes important only at very high temperatures. Since the present experiments have been conducted using room air, they cannot isolate the effect of O atoms on kinetics of CO oxidation in a nonequilibrium RF plasma. However, comparison of the results obtained using dry air–CO mixtures and room air–CO mixtures may provide new insight into the CO ignition kinetics under the conditions when a low-temperature plasma provides a continuous source of O atoms generated by electron impact dissociation of oxygen,

\[
e^- + \text{O}_2 \rightarrow \text{O} + \text{O} + e^-.
\]

To predict the amount of radicals generated in the RF air plasma and to compare it with the experimentally measured amounts of oxidized fuel, we conducted modeling calculations using a kinetic model of nonequilibrium air plasma [13], with 1% water vapor concentration. Briefly, the model incorporates electron impact processes of vibrational and electronic excitation of nitrogen and oxygen, including excitation of \( \text{N}_2(A^3 \Sigma) \), \( \text{N}_2(B^3 \Pi) \), \( \text{N}_2(C^3 \Pi) \), \( \text{O}_2(a^1 \Delta) \), and \( \text{O}_2(b^1 \Sigma) \) states, dissociation of \( \text{N}_2 \), \( \text{O}_2 \), and water vapor, and generation of excited atoms, \( \text{O}(^1 \text{D}) \), \( \text{O}(^1 \text{S}) \), \( \text{N}(^2 \text{D}) \), and \( \text{N}(^2 \text{P}) \). The rates of these processes are calculated from the experimental cross sections by solving the Boltzmann equation for plasma electrons [14,15], coupled with the one-dimensional kinetic equations for the ground state and the excited species concentrations and one-dimensional flow equations [13]. The model also incorporates vibrational relaxation processes and collisional quenching processes of electronically excited species, including processes resulting in additional molecular dissociation, such as

\[
\text{N}_2(A^3 \Sigma) + \text{O}_2 \rightarrow \text{N}_2 + \text{O} + \text{O}.
\]
In the final (fourth) series of experiments, we measured combustion products concentrations in lean ethylene–air flows ($\phi = 0.6–0.7$), at different mass-flow rates through the test section, $\dot{m} = 1.2–3.6$ g/s and a higher RF discharge power, 500 W. The main objective of these measurements was to determine combustion efficiency in RF plasma-ignited flows at higher flow velocities. The results are presented in Fig. 15. At $P = 70$ Torr, it can be seen that in the entire range of flow velocities tested, $u = 20–60$ m/s, the fraction of ethylene left unburned in the flow does not exceed 20% (see Fig. 15). In these experiments, the estimated lower bound RF discharge energy loading per unit mass necessary for ignition is 500 W/3.6 g/s = 139 kJ/kg (or 0.04 eV/molec). This is less than 5% of the heat of combustion reaction for a stoichiometric ethylene–air mixture, 3025 kJ/kg. At a lower test section pressure, $P = 50$ Torr, the results show that at flow velocities of $u > 50$ m/s the unburned fuel fraction sharply increases, up to 60–80% (see Fig. 15). This allows a rough estimate of the ignition delay time under these conditions of $\tau \sim 5$ cm/50 m/s $\sim 1$ s, which may well be the key constraint on the minimum flow residence time in the plasma. Further reduction of the ignition delay time and the use of nonequilibrium plasma ignition at higher flow velocities and pressures may require generation of higher radical species concentrations in the plasma, which would have to be achieved without significant increase of the plasma power budget. In this respect, the use of high-voltage (20–30 kV), short pulse duration (10–20 ns), high repetition rate (50–100 kHz) pulsed discharge appears promising. Recent results obtained in our group demonstrate superior stability of this type of discharge compared to DC and RF discharges, both in high-pressure, low-speed flows (up to $P = 0.3–0.5$ atm) [16] and in low-pressure supersonic air flows ($P = 10$ Torr, $M = 3–4$) [17,18]. Also, kinetic modeling analysis of high reduced electric field, nonequilibrium discharge plasma in air [14,15] suggests that it has much higher efficiency of electronic excitation and molecular dissociation by electron impact compared to self-sustained DC and RF discharges, which may considerably increase radical species concentrations produced in the plasma. Further low-temperature plasma ignition experiments using this type of discharge are underway.

4. Conclusions

The paper presents results of combustion efficiency and combustion product concentration measurements using FTIR absorption spectroscopy in premixed hydrocarbon–air and CO–air flows excited by a low-temperature transverse RF discharge plasma,
in a wide range of equivalence ratios. The results demonstrate that significant fractions of these fuels are burned in RF-plasma-generated and -stabilized flames (up to 100% of ethylene, 70% of methane, and 40% of CO). The results also show that ethylene, methane, and CO oxidation into combustion products, such as CO, CO$_2$, and water in the RF plasma-activated flows is most efficient in lean mixtures and least efficient in rich mixtures. Measurements of reaction product mole fractions in hydrocarbon–air and CO–air mixtures show that significant amounts of fuel disappear, and substantial amounts of combustion products, CO and CO$_2$ (up to several percent), are generated under the conditions when there is no flame detected in the test section ($\phi < 0.75–0.8$ in lean ethylene–air and methane–air flows and $\phi < 0.17$ in lean CO–air flows). Under these conditions, fuel species oxidation occurs via plasma chemical reactions, without ignition produced in the test section. Finally, experiments in CO–air flows demonstrated ignition and combustion at equivalence ratios down to $\phi = 0.17$, well below the lean flammability limit of $\phi = 0.42$.

The effect of significant fuel oxidation with CO and CO$_2$ generation, which is observed for lean ethylene, methane, and CO mixtures outside the flammable range, provides additional evidence for the nonthermal fuel oxidation triggered by plasma-generated radicals. The present results, combined with our previous experiments [6] in which RF plasma ignition was demonstrated to occur at low temperatures, suggests the following nonequilibrium plasma ignition mechanism: (i) active radical species generation by the low-temperature plasma, (ii) plasma chemical reactions of fuel species oxidation with participation of these radicals, (iii) flow heating due to net exothermal plasma chemical fuel oxidation process, and (iv) regular thermal ignition and combustion. Emission spectroscopy measurements suggest that O and H atoms, as well as OH radicals generated in the plasma may be among key species for plasma chemical fuel oxidation and subsequent ignition. Preliminary kinetic modeling calculations suggest the presence of a plasma chemical chain branching mechanism multiplying primary radicals generated in low-temperature hydrocarbon–air and CO–air plasmas.

Experiments in higher power RF discharges (500 W) showed that nonequilibrium plasma ignition occurs at flow velocities up to at least $u = 60$ m/s and at flow residence times exceeding ~1 s. However, much additional work is needed to map the range of parameters, such as test section pressures, flow velocities, and discharge powers at which this ignition mechanism plays a role, and to evaluate its feasibility for the use in engineering combustion applications. Some critical advantages offered by nonequilibrium plasma ignition are quite apparent: ignition occurs in the entire volume occupied by the plasma, which may be quite large (up to at least a few tens of cm$^3$ [16–18]); the plasma stabilizes the flame without the use of flame holders. However, the key issues to be addressed to determine feasibility of this ignition method are (i) scalability and stability of the plasma, especially at higher pressures and in high-speed flows, and (ii) reducing the plasma power budget, which is currently estimated to be a few percent of the heat of combustion reaction.

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References


