Soot Formation in Diffusion Oxygen-Enhanced Biodiesel Flames

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Abstract

The focus of this work is the experimental investigation of soot formation in coflow flames formed of two fatty acid methyl esters (FAMES) by employing the light extinction/scattering technique. Three different sets of experiments were conducted in this study. In the first set, radial soot volume fraction (f_v) profiles of flames of vaporized neat canola methyl ester (B100CME) and neat soy methyl ester (B100SME) fuels both using air as the oxidizer were obtained. In the second set of experiments, the effect of oxygen content in the oxidizer stream on soot formation was studied in both FAME formed flames by increasing the oxygen content in the oxidizer stream from 21% to 35%, 50% and 80%. In the third set of experiments, the effect of fuel blending on the formation of soot particulates was studied in flames formed using CME blended with No.2 diesel. The blends consisted of 80% biodiesel and 20% diesel (B80), and 50/50% (B50) biodiesel/diesel. The flames were scanned in the radial direction at various heights above the burner (HAB). For the B100CME-air flame the measured soot volume fraction f_v peak was 4.04 ppm and was located at the symmetry axis at a HAB of 16.25 mm. For B100SME-air, the f_v peak was measured to be 4.22 ppm at approximately the same flame height as in the CME-air flame. For the B100CME oxygen enriched-air flames the peak values at 35%, 50% and 80% were 6.50, 5.82 and 3.22 ppm, respectively. It was observed that by increasing the oxygen content in the B100CME flame from 21% to 35% oxygen, the f_v peak increases by approximately 61 percent. However, a further increase in oxygen content in the oxidizer stream suppressed soot formation. A similar trend in the f_v was observed for B100SME oxygen-enhanced flames. Furthermore, the increase of diesel fuel in the blending of B50CME resulted in significantly higher f_v values compared to the B80CME. The addition of oxygen content in the oxidizer stream in these blended fuel flames (from air to 35%) resulted in an increase in the f_v peak of approximately 47 and 71 percent, respectively. Centerline temperatures were measured at various HAB for selected flames.

Keywords: Soot formation, Biodiesel, Carbon particulates

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1. Introduction

Biodiesel (BD) has the potential to significantly address environmental concerns by reducing greenhouse gas emissions, interrupt the dependence on petroleum-based fuels and tremendously contribute to the local economy. A biodiesel fuel (BDF) which can be prepared from vegetable oils and animal fats is considered a clean, biodegradable and renewable fuel and potentially the best alternative to petroleum-based fuel. BDF is defined as a mixture of mono-alkyl esters of long-chain (C16-C18) fatty acids, usually methyl esters, obtained by the transesterification of the triglycerides contained in vegetable oils and animal fats [1]. Today, petroleum-based fuels meet 36% of U.S. energy demand [2] with 70 percent directed to fuels used in transportation including gasoline, diesel and jet fuel. Diesel fuel is predominantly used by light to heavy-duty trucks [3] and due to its high aromatics content, it is responsible for massive particulate matter emissions in the flue gases, which in turn trigger major health and environmental issues. The application of BD and biodiesel/diesel blends in diesel engines has been shown to be not only feasible, but also favorable in terms of lubricity and most-regulated pollutant emissions [4]. Due to the great potential of BDF in the transportation industry [5], some studies have reported on the measurement and characterization of particulate matter and gaseous emissions collected from the exhaust flows in internal combustion engines and gas turbines [6,7]. In recent years, BD research efforts has been focused on the synthesis processes, type of catalyst, and performance of this alternative fuel [8-12]. Numerous studies have been conducted on the thermo [13,14], catalytic pyrolysis [15-17], and heat of combustion, and these properties have also been studied by varying the blending percentages of BDF with petroleum-based fuel [18].

The present experimental study is aimed at understanding the soot formation in controlled coflow laminar diffusion flames formed using two fatty acid methyl esters including: B100CME (100% Canola Methyl Ester), B100SME (100% Soybean Methyl Ester), fuel blending includes B50 and B80. The fuel blending ratio (BD/ No.2 ULSD) is indicated by a “B” with a subsequent number. The number following the “B” represents the percentage of BD in the mixture, for instance B100CME represents a 100 percent canola methyl ester or neat BD. The effect of soot formation is also studied in these oxygenated fuels by increasing the oxygen content in the oxidizer stream from air to 35%, 50% and 80%. The study is conducted using a nonintrusive laser extinction technique. In the present study canola and soybean biodiesels were used mainly due to their large scale availability, and therefore the impact they can have as alternatives to petroleum-based fuels. Canola and soybean oils have lower level of saturated fats compared to other vegetable oils resulting in a BD with very low Cloud Point (CP) which allows the methyl esters to perform better than other BDF at lower temperatures [19]. The CP for CME and SME is 0°C and 1°C, respectively [19]. The CP is defined as the temperature that allows small, solid crystals to form in a fuel as it is cooled. Oil generated from canola feedstocks is considered an excellent lubricant in engines operating under extreme heat and steam conditions [20, 21]. The oil adheres to metal surfaces better than any other oils generated from other feedstocks. The production rate of a certain type of a BDF is largely a factor of the ability to produce its feedstock at a large scale. Canada is the largest producer of canola seed producing 7 million tons each year [20]. In 2008 it was reported that Canada produced 1.6 million tons annually of canola oil [22, 23]. The United States and Brazil are the major producers of soybeans in the world. The total production of BD in the U.S. in June 2014 was 100 million gallons [24]. A total of 822

million pounds of feedstocks were used to produce BD in the U.S. alone in the month of June 2014 with soybean oil ranking as the largest biodiesel feedstock with 467 million pounds [24].

Studies of engines running with diesel fuel and soybean oil BD comparing the performance and emissions at certain engine running conditions have been performed by Canakci et al. [25]. In that study it was shown that CO emissions were 18% lower for neat soybean BD compared to neat petroleum-based diesel. In the same study it was shown that the concentration of NO_x emissions is reported to increase in the flue gas by 12% when running with a soybean BD (due to the content of oxygen in the BD) compared to the neat petroleum-based diesel. The particulate matter (PM) from neat soy and canola BD is also shown to be significantly reduced in size during a combustion process [26]. These reductions are principally due to the oxidation rate of BD which can be as much as six times that of diesel. Most recently the study of soot nanostructure from a light-duty diesel engine running with various blending ratios of fuel (ULSD/SME) was reported by Vander Val et al. [27]. Through high resolution transmission electron microscopy that work aimed to study the physical presence of soot nanostructure as fullerenic shells and/or graphitic lamellae correlated to BD blend ratio.

Studies using diesel engines can provide useful information such as structural characteristics of the particulate matter and gaseous species emitted from diesel engines collected from the exhaust subsequent to the combustion process. However, the products in the exhaust normally undergo a dilution process of clean dry air. Dilution ratio and residence time in the dilution tunnel can lead to products in the exhaust with particle size distribution and chemical compositions that are different. However, fundamental studies directly inside a controllable laminar diffusion flame can suppress some of the physical variables that are encountered in such complex combustors, allowing for a better understanding of the fuel and its characteristic

combustion properties. Until recently only very few fundamental studies on the thermal and pollutant emissions have been conducted on BD formed flames [28-32] and on droplet BD combustion [33]. The study of soot formation and other pollutant emissions resulting from BD flames is a nearly unexplored area.

During the last decade new and improved oxygen generation technologies are making the application of oxygen-enhanced combustion (OEC) and or oxy/fuel combustion more affordable and attractive [34]. It is established in the literature that OEC can increase performance in a combustion process. In a typical combustion process (using air as the oxidant) the presence of soot increases the radiant heat transfer efficiency properties which can be significantly further improved by OEC [34]. Over the last decade, OEC and oxy-fuel combustion have been successfully incorporated into a variety of industrial processes, including glass furnaces, boilers, and incinerators [34]. It is known that burning hydrocarbons (liquid fuels/natural gas) with oxygen-enriched air significantly improves the thermal efficiency of the process by increasing the temperature of the flame, flame stability, in addition to a massive reduction in the flue gas volume [34]. Another advantage of OEC addresses the continual increase in the emphasis on the environment. A combustion process with a higher percentage of oxygen can significantly reduce the amount of NO_x formed. Given the feasibility of oxygen for increasing (effect on soot and temperature in flame) radiant heat transfer and hence the performance of a combustion process, it is imperative to study and understand the soot particle formation in oxygen and oxygen-enriched air flames formed using these new emerging and alternative form of energy (biodiesel fuel).

2. Experimental setup and procedures

Figure 1 contains the overall experimental setup used in this study including the coflow burner, liquid fuel injection and pre-vaporizer, laser extinction approach and BD flames characteristics.

The coflow burner employed in this study is a slightly modified version of the one originally developed for soot volume fraction measurements in methane/ethane flames by Santoro et al. [35]. The co-annular burner is placed on a two-dimensional, step motor driven positioner (Fig. 1a). For laser extinction measurements a computerized control – data acquisition system scans the soot distribution of the flame in radial directions at various positions height above the burner (HAB). The burner consists of two concentric tubes of 11 mm and 82 mm in diameter, with the vaporized fuel flowing through the central tube, and the oxidizer supplied to the lower section of the burner by four axially symmetric inlet ducts flowing through the outer channel (Fig. 1b). The oxidizer duct has inner and outer diameters of 12.7 mm and 82 mm. The oxidizer stream with oxygen content varied from 21% to 80% was prepared by mixing flows of industrial bottled oxygen (98% Airgas) and laboratory dry air. A flow rate of 36 lpm is used for the oxidizer. A 3-mm diameter glass bead bed and a honeycomb disk are used to evenly distribute the oxidizer flows inside the burner. The oxidizer flow is initially introduced into a vacant chamber in the bottom section of the burner separated by a stainless steel mesh. The mesh retains a bed of 3 mm diameter glass beads further distributing the flow. Finally, a 51mm thick ceramic honeycomb section (1.5mm cell size) is used directly above the glass beads to establish stable uniform oxidizer flow. For oxygen-enhanced combustion the flows (air/O₂) are initially introduced into a vacant chamber containing glass beads to completely mix the flows before they are introduced into the burner. Figure 1c contains representative photographs of coflow flames formed using B100CME at various oxygen content in the oxidizer stream from 21% to 80%. Figure 1d contains characteristics of flames formed at B80CME, B50CME and B100SME. Additionally, a more complete set of photographs of the flames studied herein is presented in Supplementary Data-1. Liquid BD is pumped into a pre-vaporization chamber, Fig. 1a. The chamber is

externally heated and fully insulated; the inner temperature can be continuously monitored and maintained at the desired temperature to evaporate the liquid fuel. A heated and insulated line connects the outlet of the pre-vaporizer with the burner. The liquid BD is supplied at a constant rate of 6 ml/hour employing a syringe pump (Model EW-74900-00 1-Channel from Cole-Parmer, Inc.). The wall of the fuel evaporator assembly and fuel line were successively heated by an array of three heating tapes set to 350, 475, and 500°C. The temperature settings were accomplished using temperature controllers. The liquid BD was introduced into the pre-vaporization chamber set at 350°C. The other two heating tapes set at higher temperatures were placed downstream in the fuel line connecting the outlet of the prevaporizer with the burner to prevent condensation of the vaporized fuel. High temperatures for vaporizing a liquid fuel can induce cracking and polymerization reactions, causing significant changes in the chemical composition and therefore in the soot propensity of the fuel. The biodiesel's thermal stability in this study was ensured by maintaining the vaporized fuel temperature lower than 275°C as suggested by Lin et al. [36]. In our experiments this effect was verified by measuring the temperature of the gas flow at the fuel nozzle in the burner. Moreover, visual inspection of unburned fuel extracted from the fuel line showed no carbonization or visual indication of severe fuel cracking during the vaporization process. The low volatility of a BDF can cause difficulties for flame ignition and sustainability, thus, in order to stabilize the flame it was necessary to introduce a small (<0.1 lpm) nitrogen flow as a carrier gas into the fuel line. The heating tape wrapping the wall of the pipe carrying the flow of nitrogen was set to 400°C. The oxidizer line was also preheated to 200°C (wall temperature). Liquid fuels such as No. 2 diesel and BD (CME and SME) employed in this study are composed of a variety of constituents (Table 1 and 2). BDF is principally composed of unsaturated fatty acids while diesel is composed mainly of

saturated hydrocarbons (no double bonds) and aromatic compounds (ringed structures containing 6 carbons and alternating single and double bonds). For instance, SME is composed of methyl palmitate (13%), methyl stearate (5%), methyl oleate (25.0%), Methyl linoleate (52%) and methyl linolenate (5%) by weight (Table 1). No. 2 diesel is composed of saturated hydrocarbons (Paraffins, monocycloparaffins, bicycloparaffins, and tricycloparaffins) and aromatic hydrocarbons (alkylbenzenes, teralins, dinaphthenobenzenes, naphthalenes, acenaphthenes, acenaphthylenes, and phenanthrenes). Diesel fuel average percent composition by volume is shown in Table 2. Compared to diesel fuel, BD have higher cetane numbers, contain approximately 11% oxygen by weight, and lack aromatic compounds [37]. Flame temperature measurements of selected flames were also carried out in this study. All temperatures were taken using fast-response K-type thermocouples (Omega Engineering, Inc) made of bare chromel and alomel. The K-type thermocouple had a bead diameter of 0.7-mm with the exposed junction. The rapid insertion technique was used [38,39]. The thermocouples were mounted on a traversing insertion mechanism and connected to a data acquisition board.

3. Soot volume fraction measurements

The laser extinction/scattering method is an attractive optical technique that allows for nonintrusive and instantaneous measurement of soot volume fractions (f_v) within the flame volume and has been widely employed in the combustion community. In previous studies of laminar diffusion flames, tomographic reconstruction has been proven useful in providing spatially resolved measurements of f_v based on line-of-sight extinction measurements [40-42]. For soot particles in the Rayleigh size limit (particle diameter/light wavelength $\ll 1$) (Bockhorn, 1994) [43] f_v averaged along the line-of-sight was calculated using the following expression:

$$\frac{I}{I_0} = \exp\left(-\frac{K_{EXT} L f_v}{\lambda}\right) \quad (1)$$

191 From this relation f_v is obtained as:

$$f_v = \frac{\lambda \ln\left(\frac{I_0}{I}\right)}{K_{EXT} L} \quad (2)$$

192 Where, L is the path length, I_0 is the incident laser intensity, I is the transmitted laser intensity, f_v
 193 is the soot volume fraction, and K_{ext} is the extinction coefficient. The K_{ext} is obtained from the
 194 refractive index of soot. Many measurements of the refractive index of soot have been reported
 195 during the last decades [44,45]. Some studies in this particular area have reported that refractive
 196 indices may be independent of fuel [46] others have shown that a refractive index can be a
 197 function of flame position and C/O ratio [46, 47]. In the present study the soot measurements
 198 employed an extinction coefficient of 4.9 that corresponds to the refraction index, $m=1.57-0.56i$
 199 (Dalzell and Saforim, 1969) [48].

200 In order to scan the soot profiles, the coflow burner was mounted on a two-dimensional, stepping
 201 motor positioning system. A personal computer data acquisition system was used to control the
 202 operation of the positioning system and to conduct the light extinction measurements. Laser
 203 beam extinction experiments were performed using a compact stabilized HeNe laser (Model
 204 HRS015 from Thorlabs Inc.). The resulting output power at 632.99 nm was <5mW with long-
 205 term drift less than 0.3% in 8 hours. The stabilized laser beam is focused into the flame and
 206 deflected back using two 50.8 mm diameter lenses (Newport Inc.) equally spaced to provide

one-to-one imaging, similar to our previous works for studying soot formation in flames formed using traditional fuels [40, 41]. The intensity of the transmitted light was measured using an optical power/energy meter (Model 1928C from Newport Inc.). Ambient light was suppressed from the laser intensity measurements by an on-line filter (Model 10LF10-633 from Newport Inc.). The effectiveness of flame radiation blocking was verified in the control scans with and without a flame.

The reactor is run by a computer program to perform repetitive sampling at pre-specified locations defined in terms of the dimensions of the scanning area and the step size. After each step, the data acquisition system takes measurements at the current location for a pre-specified period of time, averages them and saves already preprocessed data, before moving to the next scanning point. The “experimental errors” in our measurements of the soot volume fraction were minimized by obtaining soot volume fraction profiles of an ethylene-air flame. The precision of the laser extinction setup was validated using the results available in the literature for that particular flame. The intensity of the transmitted light (I/I_0) after the laser beam passed through the flame at different radial positions was measured. The transmittance was measured for various flame heights. Soot volume fractions were then obtained by using the collected transmittance. The transmitted light and soot volume fractions at the two flame positions correlate well to published values in the literature [35, 49]. The field distribution function was obtained using a three-point Abel deconvolution algorithm [50].

4. Results and Discussion

The present experimental study is aimed at understanding the soot formation process in controlled coflow laminar diffusion flames formed using two FAMES (B100CME and B100SME), fuel blends including B50CME (mixture of 50% BD and 50% No.2 diesel) and

B80CME (mixture of 80% BD and 20% No.2 diesel) by employing the light extinction/scattering technique. The effect of soot formation is also studied in the mentioned fuels by increasing the oxygen content in the oxidizer stream from air to 35%, 50% and 80%. Soot volume fraction profiles for all flames were acquired using the nonintrusive laser extinction technique. Centerline temperature measurements were also conducted for selected flames along the symmetry axis of the flames at different HAB using a thin-tip fast-response thermocouple, by means of the rapid insertion technique [38,51].

4.1 Soot volume fraction measurements in flames formed using B100CME and B100SME, with air and oxygen-enriched air as oxidizers

Soot volume fraction (f_v) measurements using the laser extinction technique were first conducted with neat BDF formed from canola and soybean oils (B100CME and B100SME). Figures 2a and 3a contain soot volume fraction profiles along the radial direction of the flame at various HAB for B100CME-air and B100SME-air flames. Similarly, figures 2(b, c, d) and 3(b, c, d) present profiles of soot volume fraction for B100CME and B100SME oxygen-enhanced flames. Inspection of figures 2 and 3 show that all curves display similar f_v evolution along the axial direction over the entire flame. Soot is first detected at the lower zone of the flame near the fuel-oxidizer interface forming a “wing” like structure, overlapping the luminous envelope of the flame where the highest temperatures in the radial direction are expected. The double wing-like profiles characteristic of the lower zone develop into a single peak distribution in the mid zone of the flame, which continue shrinking in the axial direction and eventually vanish for all radial locations near the tip of the flame. For the B100CME-air flame (Fig. 2a), the soot volume fraction peak was measured as 4.04 ppm and was located at the symmetry axis at approximately HAB=16.25 mm. For B100SME-air (Fig. 3a), the f_v peak was found to be 4.22 ppm located also

on the symmetry axis at approximately HAB=18.75 mm. It is interesting to note that the peak soot volume fractions for B100CME and B100SME do not vary significantly. In the literature it is shown that flame temperature variations could impact the soot particle inception limits [52]. A work of Gomez et al. studied the effects of fuel-type and temperature on soot formation along the centerline of axisymmetric laminar diffusion flames [53]. In that work it was suggested that the soot formation process is highly temperature dependent. Figure 7a and (b) represent measured temperature profiles along the centerline axial direction of a B100CME and B100SME, respectively. A comparison between the two flame temperature profiles reveals that the general trends and values are nearly the same. The flame temperature variations between the B100CME-air and B100SME-air are not very significant and may explain a similarity in the mechanisms of soot formation between these two fuels. The temperature profiles are also similar for the BD oxygen enriched-air flames. Furthermore, studies on soot formation reported by Love et al. [30] showed that soot volume fractions obtained in vaporized B100SME and B100CME premixed flames do not significantly vary between the two fuels compared to that of the petroleum-based fuel (diesel). In that study it was reported that the f_v peak for the B100SME-air is approximately 1.15 ppm (HAB = 10 cm) and the f_v peak for B100CME has a value of 1.3 ppm (HAB = 5 cm). In the same study it was shown that the formed premixed flame temperature peaks between these two fuels do not significantly vary. For the B100CME a highest temperature of 1850K (HAB = 5cm) was reported. For the B100 SME the highest temperature was 1820K and occurred at HAB = 10 cm. Soot inception can also be affected by a mechanism other than flame temperature such as fuel chemistry. The content of constituents in a fatty acid methyl ester varies according to the feedstock employed and can significantly affect the physical, chemical, and fuel properties [54]. In the present study both CME and SME are composed of methyl

palmitate, methyl stearate, methyl oleate, Methyl linoleate and methyl linolenate (Table-1). On the other hand, animal fats (AF) contain methyl myristate, methyl palmitoleate, methyl heptadecanoate in addition to all of the constituents present in the CME and SME.

However, the f_v peak value for B100CME-air flame is approximately 11 times higher than the f_v peak reported by K.O. Lee et al.[42] for a CH₄-air flame using the same burner configuration. And approximately a f_v peak value that is approximately 13 times higher for a B50CME-air flame. It is well established in the literature that combustion of heavier hydrocarbon compounds such as diesel fuels has a tendency to produce high quantities of soot compared to lighter hydrocarbon fuels such as methane. The work of Kitamura et al. showed that the beta-scission reaction plays an important role in the degradation pathway of the fuel molecules in the diesel [55]. Such reactions are responsible for generating a higher density of PAH species and as a result, significantly increasing the availability of precursors for soot inception and soot formation in a flame medium. This effect is quite visible in our soot measurements. On the other hand, the f_v peak for B100CME-air flame is approximately 2.5 times smaller than the peak value reported by Tran [56] for pure ultra-low sulfur diesel in a wick generated flame of similar dimensions. In comparison to No. 2 diesel fuel, the absence of aromatic compounds in CME and SME is believed to be the reason for the lower particulate matter emissions. The tendency of a BDF to form less sooty flames, opposed to a diesel fuel, can also be attributed to the nature of the fuel itself (hydrocarbon oxygenated compounds). Kitamura et al. proposed a detailed reaction mechanism for studying the effect of the oxygen molecule (bounded in the long chain fatty acids esters) and how it affects soot tendency [55]. It was suggest that the oxygen molecules present in the ester tend to remain bounded to the nearest carbon atom in the carbon chain promoting the formation of ketones and aldehydes. These

species are highly resistant to oxidation and are only oxidized by powerful oxidizing agents which have the ability to break the bonds. Soot studies by McEnally et al. by doping small concentrations of aldehydes and ketones in a coflow CH_4/N_2 nonpremixed flame showed that the carbonyl group tend to reduce the soot tendency of the overall flame [57]. The plots in Fig. 2(b-d) show the f_v peak values for B100CME at 35%, 50% and 80% oxygen as 6.50 ppm, 5.82 ppm and 3.22 ppm, respectively. Similarly, figure 3(b-d) shows the f_v peak values for B100SME at 35%, 50% and 80% oxygen as 4.94 ppm, 4.4 ppm and 3.25 ppm. It is observed that by increasing the oxygen content in the B100CME flame from 21% to 35% the f_v peak increases by approximately 61 percent. However, the further increase of oxygen content in this type of flame yields significantly reduced f_v peak values. That is, for B100CME using 50% and 80% oxygen in the oxidizer stream results in f_v peak value reductions of 10 and 44 percent, respectively. The further increase of oxygen content in the oxidizer stream significantly suppresses soot formation. The effect of oxygen content suppressing soot formation is also visible for the B100SME based flame but not as strong as the B100CME based flame (Fig. 3).

The introduction of oxygen enrichment in the oxidizer stream to form the coflow diffusion flame significantly modifies the physical and thermal properties of the flame. As the oxygen content is increased, the flame volume is compressed and the overall flame temperature is increased. The strong variation of the physical structure of the flame as the oxygen enrichment is increased is obvious from our soot volume fraction and temperature profiles. Inflame axial temperatures were measured at different locations along the symmetry axis of the flame upstream from the fuel nozzle. Figure 7 shows typical flame temperature profiles for B100CME and B100SME flames operated at 21%, 50% and 80% oxygen content in the oxidizer stream. The temperature measured in-flame by the thermocouple bead is exposed to heat losses caused by radiation, conduction

and convection. Recognizing that different investigators use different methods and procedures for the correction of thermocouple measured temperatures; profiles of temperatures formed using the raw readings “uncorrected values” are presented. A simplified yet well accepted approach was employed for correcting thermocouple measurement errors. A more complete approach requires proper values for the various heat transfer properties and velocity of the flame gases. In this approach the Nusselt number correlation for obtaining the convection heat transfer coefficient is based on a non-reacting flow. Hindasageri et al. employed a unique transient technique for accurately determining the heat transfer coefficient in premixed methane-air flames without the use of thermophysical properties and velocity of gases [58]. It was reported that the heat transfer coefficients can have an average deviation of 20% from the available heat transfer correlations present in the literature for cylinders and spheres exposed to non-reactive convective flows. However, temperature profiles formed using “corrected” values are incorporated as supplementary data (Supplementary Data-2). The general trends for the temperature profiles “uncorrected” vs. “corrected” are very similar. To correct thermocouple measured flame temperatures the method proposed by Jha et al. was employed [31]. Corrections can be estimated by using an energy balance equation on the thermocouple bead [31]. For the axial velocity an analytical expression proposed by Roper et al. [59] was employed. In that expression the constant acceleration value of 25 m/s^2 due to buoyancy for a controlled laminar diffusion hydrocarbon/air flame was employed similar to the work of Zelepouga et al. [41]. It is worth noting that since the studied flames are laminar there is little effect on the change of the value of the corrected flame temperatures by varying the axial gas velocity even by several folds. The axial centerline flame temperature (for both B100CME and B100SME) increased sharply just above the edge of the burner’s mouth right after the fuel nozzle exit (Fig. 7). The recorded flame temperatures near the burner’s mouth were 480°C (CME-air), 560°C (CME-50% O_2 + 50% N_2) and 780°C (CME-80% O_2 + 20% N_2),

Fig.7(a). The flame tested with the highest oxygen content (CME-80%O₂ + 20%N₂) contains the strongest temperature gradient. The centerline flame temperature for that particular flame varies from ~780°C just above the burner's mouth to ~1150°C near the flame's tip. The total flame height for the CME-80%O₂ + 20%N₂ is less than 10 mm indicating that soot inception, growth and oxidation mechanisms are much stronger under oxygen-enriched conditions. These results show that oxygen enrichment in the oxidizer stream can significantly (up to a certain point) alter the flame temperature and as a result increase the rates of fuel pyrolysis. The increase of the rate of fuel pyrolysis can strongly contribute to the augmentation in the formation of soot precursors (soot inception) in the lower part of the flame and consequently yield flames with high soot volume fraction peak. A brief examination of the soot volume fraction profiles compared to those of the measured local flame temperatures at each flame height reveals that the higher the temperatures, the higher the oxidation rate of the soot particles. This trend confirms that the addition of oxygen in the oxidizer stream of the coflow diffusion flames alters the flame reaction zone yielding essential variations in soot concentration. A quite similar trend was also found in our previous works for traditional fuels [34]. However, the further increase of oxygen content in the oxygen/nitrogen mixture formed flame in our experiments appears to suppress soot formation. It has been shown that the introduction of diluted fuel in the fuel line and/or oxygen-enriched air in the oxidizer stream can strongly influence the flame flow fields (reduction in flame volume) and significantly reduce soot formation in flames. The work of Sugiyama suggested that soot yield reduction in a laminar coflow nonpremixed flame is attributable to the changes in the flame velocity and flame shape [60]. Furthermore, from our soot volume fraction profiles (figures 2 to 6) it can be observed that the further increase of oxygen in the oxidizer stream (above 35%) significantly suppressed soot formation. Furthermore, the trends of our soot

volume fraction profiles are in line with the findings reported by Du and Axelbaum that soot inception can be dramatically affected by flame structure through changes in fuel pyrolysis and oxidation rates adjacent to the pyrolysis zone [61]. In our present study it is observed that the overall soot formation effect for oxygen enhanced flames is a trade-off between the augmented fuel pyrolysis rates resulting from higher flame temperatures, and the reduced residence time of the soot within the flame due to the shrinkage of the reacting zone. In the work of Li et al. a visual comparison of the appearance of the flame structure “flame streak” of a burning droplet stream showed that the “flame streak” contains very visible blue segments when only using neat BD (B100). This is mainly owed to the fact that a BDF has an oxygenated compound containing two oxygen atoms. The blue characteristic in the “flame streak” was visible only at the beginning and ending of the droplet burning process. “Flame streaks” formed with diesel and blended fuels did not contain very visible blue zones and this is mainly attributed to the fact that diesel has a higher tendency for soot formation yielding flames with strong soot luminosity that overcomes that of the blue flame [33]. These reported findings are in line with our observations that biodiesel-air flames tend to be characterized as having a thin blue zone flame just above the edge of the burner’s mouth (Supplementary Data-1/Figure1). The burner employed in this study is similar as the one employed by K.O. Lee et al. for measuring soot volume fractions in methane flames [42]. A visual comparison between the K.O. Lee et al. methane flames and the neat CME/SME-air flames shows that a thin blue flame is strongly visible only in the BD flames. This correlates very well with the findings reported by Li et al. on the flame appearance of BD flames [33]. Furthermore, a visual comparison of the flame structure formed using CME/oxygen enriched-air and CME-air shows that the CME/oxygen flames have a much brighter yellow luminous zone (Supplementary Data-1/Figure1). However, the thin blue zone flame becomes

less visible as the oxygen content is increased in the oxidizer stream. It is interesting to note that the temperature profiles for the lower oxygen enriched air flames contain a concave up curve in the upper part of the flame. The temperature profile for the CME-air flame shows the concave up curve at approximately $HAB = 12$ mm; while for the CME-50%O₂ the effect is located at $HAB = 7.5$ mm. In the works of Hayashida et al. it is reported that such an effect is attributed to soot deposition onto the surface of the thermocouple bead [62,63]. From the soot volume fraction profiles in the present study, Fig. 2, for B100CME flames it can be observed that the location of the concave up curve effect on the temperature profile correlates to the profile containing higher soot volume fraction peaks. The temperature profile for the CME-80%O₂ flame does not contain any concave up curve effect (figure 7). Attempts were made to measure the temperature of flames formed using blended fuels (DB/No.2 Diesel) including B80CME/B50. During the temperature measurements of the flame formed with the blended fuel it was observed that the surface of the thermocouple bead became quickly covered with large fragments composed of soot particulates as the soot field evolved in the direction of the flame's tip. The heavier accumulation of soot on the surface of the thermocouple could result in inaccurate flame temperature measurements. The temperature profiles for the blended flames exhibited a contrary behavior to that of the neat BDF. The accumulation of black materials on the surface of the thermocouple bead was significant for the blended fuel flames formed with air and as the initial introduction of percentages of oxygen in the oxidizer stream took place. Specifically, the flame temperature (axially along the centerline) increases from the edge of the fuel nozzle and suddenly begins falling in the upper part of the flame as the soot field evolved.

4.2 Soot volume fraction measurements in flames formed using CME blended with diesel fuel, with air and oxygen-enriched air as oxidizers

Transesterified vegetable oils have a number of advantages over petroleum-derived diesel fuel. However, the utilization of raw BD in the existing compression ignition engines during long-term tests does not follow up on trends observed for short-term testing. The best application of these renewable fuels is by blending them with diesel fuel. A better understanding of the characteristic soot propensity of BD and different biodiesel-diesel blends can provide useful information in order to enhance the fundamental understanding of combustors running with fuel blends with increased BD content. Various studies have been conducted with BD blends in engines [64-67]. In the present work, the soot propensity of BD and different biodiesel-diesel formed flames is studied. CME is chosen as the BDF to be blended with various percentages (volumetric) of No. 2 diesel in this study. The blends consisted of B80 and B50. For the B80CME-21%O₂, B50CME-21%O₂ f_v peak values of 4.32 and 4.68 were obtained (Fig. 4a and 5a), respectively. The f_v peak of 4.04 was measured for the B100CME-21%O₂ flame (Fig. 2a). While the percentage of oxygen remained fixed in the oxidizer stream (21%O₂ + 79%N₂), the increase of diesel percentage in the fuel blending mixture resulted in a high soot volume fraction peak compared to the value obtained for the B100CME-air flame. This trend is in line with the studies conducted using diesel engines, which show that while maintaining some physical and chemical properties, as the blending percentage of BD in diesel fuel increases, the emission of PM tends to decrease significantly [68-70]. It is well accepted in the literature that the tendency of a fuel to form soot particles is mandated by the availability of incipient soot nucleation during the combustion of a fuel. Soot inception and nucleation strongly depend on the molecular structure of the fuel [71]. Diesel fuel is composed mainly of saturated hydrocarbons (no double bonds) and aromatic compounds (ringed structures containing 6 carbons and alternating single and double bonds (Table 2). The complex molecular structure of

the diesel fuel (saturated hydrocarbons and aromatics) allows for a unique reaction zone (high rate of pyrolysis reactions) capable of producing more potential paths for soot nucleation and formation [70]. The study of Chien et al. on the emission effects of biodiesel/Diesel blending in a diesel engine showed that BD has much lower PAH content resulting in ultrafine PM in the exhaust line [70].

The effect of oxygen content in the oxidizer stream on the soot formation was also studied in the blended-fuel flames by varying the oxygen from air to 35%, 50% and 80%. Figures 4 and 5 contain soot volume fraction profiles for B80CME and B50CME flames formed using various oxygen contents in the oxidizer stream at various HAB. Figure 4 (a) 21%, (b) 35%, (c) 50%, and (d) 80% oxygen for the B80CME and Fig. 5 (a) 21%, (b) 35%, (c) 50%, and (d) 80% oxygen for the B50CME flames. For the B80CME flames the f_v peak values at 21%, 35%, 50% and 80% oxygen are 4.32, 6.35, 7.41 and 5.22 ppm. The change of oxygen content in the oxidizer stream from 21% to 35% resulted in the increase of the f_v peak by approximately 47 percent. As the oxygen content increased in the oxidizer stream from 35% to 50% oxygen the f_v peak increased by approximately 17 percent. However, a further increase in the oxygen content in the oxidizer stream (from 50% to 80%) resulted in the decrease of f_v peak value by approximately 29 percent. For the B50CME flames the f_v peak values at 21%, 35%, 50% and 80% oxygen are 4.68, 7.87, 6.80 and 5.59 ppm, respectively. Figure 6(a to d) represents a summary on the effect of oxygen concentration in the oxidizer stream on f_v peak values for tested neat BD (CME/SME) and of the blended fuel mixtures (CME/No. 2 Diesel) formed diffusion flames. It can be observed that the variation of oxygen content in the oxidizer stream has two different and opposing effects on the sooting tendency in the formed flames. Within a certain oxygen threshold the increase of oxygen concentration can act as an inhibitor to soot by increasing the fuel pyrolysis and hence soot

formation rates. In the contrary, a further increase of oxygen concentration in the oxidizer stream (above a certain oxygen threshold) significantly compresses the flame volume, increases the flame temperature thus increasing the particle oxidation rate and hence acting as soot suppressor. This effect is very visible from our summary profiles of soot peaks (Fig. 6) and flame measured temperatures at various oxygen contents in the oxidizer stream (Fig. 7).

4.3 Total Soot

Total soot content within a flame was estimated by integrating the f_v field distribution in the radial and axial direction over the entire flame volume as suggested by Zelepouga et al. [41]. Results are shown in Table 3. By inspecting Table 3, it becomes evident that the increase of No. 2 diesel fuel content in the fuel mixtures causes an increase in the overall soot concentration within the flame for all the tested oxygen contents. The integration scheme to obtain the total soot content on a mass basis is defined as in equation (3) and employed by Zelepouga et al. in coflow laminar diffusion flames of methane with oxygen and oxygen-enriched air [41]. The total soot content of the flame (by mass) was calculated based on the results from the integration of the f_v distribution and by selecting an average density for the solid carbonaceous materials within the flame. In the literature the density values of the carbon materials generally ranges from 1.74 to 1.84 g/cm³ [72].

$$F_V = \rho_s \int_0^{H_f} \int_0^R f_{(r,z)} 2\pi r dr dz \quad (3)$$

Where ρ_s is the density for carbon material, H_f is the flame height and R is the radius of the flame. Although the thermal and dilution effects are inevitably introduced to the tested flames by altering the oxygen content in the oxidizer flow, B100CME and B100SME showed indistinct behaviors regarding the total soot produced by flames of similar conditions when compared with each other.

On the other hand, for B80CME fuel, it was observed that the utilization of oxygen-enhanced air as oxidizer has a soot enhancing effect as judged by the total soot load of the flame, only when the oxygen content is increased from 21% to 35%. Conversely, a further oxygen increase in the oxidizer stream (50% and 80%) lead to significantly lower soot loads. Generally, the behavior observed for the total soot content of B80CME flames closely follows the previously described trend for peak f_v values. For B50CME flames operating at oxygen contents (21% to 50%) does not show a dominant soot suppressing or enhancing effect. Moreover, for all the fuels, the 80% oxygen flames were observed to produce significantly less soot than their counterparts operating with air. The reduction for B100CME and B100SME was calculated to be 78% and 75% respectively, while for the biodiesel-diesel blends; B50CME and B80CME, the reduction was approximately 48% and 72%, respectively. The lower sooting tendency of B100CME and B100SME when compared to the biodiesel-diesel blends (B50CME, and B80CME) is most likely resulting from the lower concentration of soot precursors in the early stages of the flame (as shown in f_v profiles).

Moreover, we hypothesize that the reduction of the sooting tendency for B100CME and B100SME compared to their blends is due to the increased concentration of O/C atomic ratio that occurs when forming the flames with a BDF. Oxygenated fuels tend to produce elevated CO concentrations resulting in less carbon available to form particulate precursors. While the CO formation cannot entirely account for the reductions in soot observed for B100SME and B100CME, the differences in the molecular structure of these oxygenated fuels compared to traditional No.2 diesel can partly explain the differences in the PM emissions (Tables 1 and 2).

In the measurements of soot volume fractions in flames using the laser extinction technique several assumptions are made that may produce uncertainties that usually cannot be

precisely corrected. However, the method is considered an excellent tool as it provides a relative comparison of the soot propensity between flames formed by varying different parameters within a single set of experiments. The first uncertainty that could occur in our calculations of soot volume fractions could be due to the accuracy of the values of the assumed constants employed. For instance, in our data analysis of the soot measurements we use an extinction coefficient with a value of 4.9 that corresponds to the refraction index $m = 1.57 - 0.56i$. This value has been widely attributed to the work of Dalzell and Sarofim [48] and has been extensively employed in soot-studies including in the measurements of soot volume fractions in methane-air and in methane/oxygen and in oxygen enriched-air flames [73, 41, 42]. The extinction coefficient constant k_{ext} is obtained from refractive index of soot. The refractive index is defined as the ratio of the refractive index of the particle to the refractive index of the medium. The work of Smyth and Shaddix provides an excellent discussion on the history of the various values of refractive indices of soot used for data analysis in flames. In that work it was concluded that errors can be attributed to the degree to which scattering affects extinction measurements and its possible variation within a flame [74]. Although, some investigators in soot related studies have reported that refractive indices are independent of fuel [75], others, however, have proposed that a refractive index can be a function of flame position and C/O ratio [46, 47, 76]. Charalampopoulos suggested that using a constant refractive index value over an entire flame region (where significant variations of soot fields are present) can cause errors on the number densities and soot particle size determinations of as much as 25% and 15%, respectively [76]. Another uncertainty could be due to the accuracy of the value of the density used for calculating the total soot in the flames. In the literature the density values of carbon material generally range from 1.74 to 2.0 g/cm³ [41]. We employed a value of 1.8 g/cm³. This value was used by K.O.

Lee et al. in nonpremixed methane oxygen enhanced-air flames [42]. A not precise determination of the adequate number of soot volume fraction profiles necessary to capture the soot peak could also result in some uncertainties of the total amount of soot. Therefore, greater care was devoted to obtain an appropriated number of soot volume fraction profiles within a flame to most accurately obtain the total amount of soot produced. For instance, we obtained thirteen soot volume fraction profiles in a CME-air flame within a distance of 15 mm. The additional profiles are not presented in the plots for clarity, but the results are presented in the Table 3.

5. Conclusions

Soot formation in flames formed using various gaseous/hydrocarbon fuels in laboratory scale counter-flow and coflow flames have been extensively studied and documented in the literature. In those studies several parameters have been tested aiming at inhibiting or suppressing soot formation in flames. More recently the introduction of oxygen enriched-air in the oxidizer stream for studying soot formation in such flames has also been studied. In contrast, the literature contains very limited information on the formation of carbon particulates from flames formed using pre-vaporized fatty acid methyl esters (FAMES). BD or FAMES are considered a clean, biodegradable and renewable fuel that has the potential to significantly interrupt the dependence on petroleum-based fuels. However, given the importance and the significant impact that this fuel contains; the understanding of soot formation in flames has received little attention, not to mention the effect on soot formation that can result by fuel blending (FAMES/diesel) and the increase of oxygen content in the oxidizer stream in formed flames. In this present work soot formation is experimentally investigated in laminar jet, non-premixed coflow flames formed using BDF from canola and soybean oils. The laser extinction/scattering technique is employed.

The effect of blending (CME blended with No.2 diesel: B80CME and B50CME) and the variation of the percent of oxygen content in the oxidizer stream (21% - 80%) on soot formation was investigated. It was found that the initial increase of oxygen content in the oxygen/nitrogen mixture formed flames promotes soot formation; however, a further increase of oxygen content suppresses soot formation in the tested flames. Furthermore, the increase of oxygen content in the oxidizer stream compresses the flame volume and considerably stabilizes a flame formed using neat BD and blended with ULSD (No. 2 diesel). It was found that the total soot for the neat BD flames (B100CME and B100SME) does not significantly vary compared to the other parameters such as the variation of oxygen content in the oxidizer stream and fuel blending. The flame temperature variations between the B100CME and B100SME are not very significant and may explain the similarity in the soot tendency between these two fuels. Soot inception can also be affected by a mechanism other than flame temperature such as fuel chemistry. We hypothesize that this effect could be due to the similarity of the five major methyl ester compositions present in the fuels. This work also reveals that the f_v peak values tend to be significantly higher in flames formed using CME/SME compared to a gaseous/hydrocarbon fuel. For instance, the measured f_v peak value for a base B100CME-air flame is approximately 11 times higher than the f_v peak reported in the literature (by Lee O-K et al.) in a methane-air flame. The exact same burner configuration was used in these two studies. It is observed that by increasing the oxygen content in the B100CME flame from 21% to 35% the value of the f_v peak increases by approximately 47 percent. The increase in oxygen content in the tested flames increases the temperature of the flame resulting in the increase of fuel pyrolysis rates, significantly augmenting the formation of soot precursors in the lower part of the flame, which in turn leads to a higher density of soot particles in the upper part of the flame. A further increase

of oxygen content suppressed soot formation and reduced f_v peak values. That is, the f_v peak values for B100CME for 35%, 50% and 80% oxygen were measured as 6.50 ppm, 5.82 ppm and 3.22 ppm, respectively. A similar trend is observed for the other tested BDF. However, a further augmented oxygen concentration also restricts the reaction zone to the lower part of the flame, limiting the residence time for soot agglomeration and consequently limiting the total and peak soot volume fractions within the flame. The effect of fuel blending using CME with various percentages (volumetric) of No. 2 diesel showed that the total soot increased. The values of the total soot concentrations for some of these tested flames are nearly doubled as the oxygen content in the oxidizer stream is increased. Diesel fuel has complex molecular structure (saturated hydrocarbons and aromatics) that can result in a high rate of pyrolysis reactions capable of producing more potential paths for soot inception and formation. Our results show that indeed the soot production significantly enhances as the blending percentage of CME with No. 2 diesel is increased.

Temperature measurements were also conducted along the symmetry axis of selected flames at different heights using K-type fast-response thermocouple. Comparing the soot volume fraction with the measured local flame temperatures at each flame position reveals that the higher the temperatures, the higher the oxidation rate of the soot particles, and hence the lower the f_v peak values.

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Table 1

	SME (wt. %)	CME (wt. %)	Chemical Formula	Chemical Structure
Methyl Palmitate	13	5	C ₁₇ H ₃₄ O ₂
Methyl Stearate	5	3	C ₁₉ H ₃₈ O ₂
Methyl Oleate	25	62	C ₁₉ H ₃₆ O ₂
Methyl Linoleate	52	20	C ₁₉ H ₃₄ O ₂
Methyl Linolenate	5	10	C ₁₉ H ₃₂ O ₂
Methyl Myristate	---	---	C ₁₅ H ₃₀ O ₂
Methyl Palmitoleate	---	---	C ₁₇ H ₃₂ O ₂
Methyl heptadecano ate	---	---	C ₁₈ H ₃₆ O ₂
Total Fuel Composition (wt%)	100	100		

Table 1. Physical Properties and Chemical Structure of Constituent Fatty Acid Methyl Esters Present in Studied Biodiesel Fuel

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Figure 1

Figure 1. Schematic of the experimental setup for obtaining soot volume fraction profiles in coflow diffusion flames formed using biodiesel and biodiesel/diesel blends (a). Detailed view of the coflow burner (b); c) representative photographs of coflow flames formed using B100CME at various oxygen content in the oxidizer stream from 21% to 80%; d) flames formed at B80CME, B50CME and B100SME. The blended fuel mixture was formed using the biodiesel from canola and soybean oils with No. 2 Diesel (volume basis).

Figure 1.

Figure 2

Figure 2. Spatial distribution of soot volume fraction for B100CME flames, operated at 4 oxygen concentrations in the oxidizer stream: (a) 21%, (b) 35%, (c) 50%, (d) 80% at various heights above the burner (HAB).

Figure 2.

Figure 3

Figure 3. Spatial distribution of soot volume fraction for B100SME flames, operated at 4 oxygen concentrations in the oxidizer stream: (a) 21%, (b) 35%, (c) 50%, (d) 80% at various HAB.

Figure 3.

Figure 4

Figure 4. Spatial distribution of soot volume fraction for B80 CME flames, operated at 4 oxygen concentrations in the oxidizer stream: (a) 21%, (b) 35%, (c) 50%, (d) 80% at various HAB.

Figure 4.

Figure 5

Figure 5. Spatial distribution of soot volume fraction for B50 CME flames, operated at 4 oxygen concentrations in the oxidizer stream: (a) 21%, (b) 35%, (c) 50%, (d) 80% at various HAB.

Figure 5.

Figure 6

Figure 6. Summary of soot volume fraction peak values for (a to d) B100SME, B100CME, B80CME and B50CME formed flames, as a function of the oxygen content in the oxidizer stream.

Figure 6.

Figure 7

Figure 7. Measured temperature profiles along the centerline axial direction in flames; a) formed using B100CME and b) B100SME for various oxygen contents in the oxidizer stream.

Figure 7.