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Use of Carbon Dots to Boost Energy Content of Biodiesel to Enable Next-Generation Hybrid Heavy Vehicles for Ground Transpotation While Improving Safety

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16. Abstract
The transition to renewable energy is driven by both environmental and geopolitical factors. In the transportation sector, this has manifested through electrification and increased adoption of biofuel. Full electrification is sufficient to power light duty vehicles, but heavier vehicles are more likely to require a hybrid model. , Heavy duty vehicles require the most torque at low speed and low engine rpm. While biodiesel has many positive aspects, its specific energy density is about 40 MJ/kg while petro-diesel is closer to 45 MJ/kg. Increasing the energy density of biodiesel is a critical aspect in enabling widespread adoption, and this project aims to directly tackle this issue. Higher energy density means a lower volume of fuel is required, and this significantly reduces the extent of any fire. This project will develop “Green Nanofuel” where nano structured energetic and catalytic materials are used with liquid fuel to increase the energy density and fuel economy while reducing the required volume, GHG and PM emission. Previous studies by the PI have shown that a carbon-based nano-additive can significantly modify the energy density of liquid fuels, and these behaviors can be tailored based on the specific requirement. Year one research investigated the combustion characteristics of diesel-biodiesel blends and gel-like carbon dots (G-CDs) based nanofuels using a suspension droplet method and shadowgraph imaging. Diesel-biodiesel blends, ranging from B5 to B75, derived from waste cooking oil and animal fat, exhibited two combustion stages: a steady combustion stage followed by a puffing stage. Puffing peaked at B25, while B10 demonstrated the highest combustion rate. Biodiesel blends showed improved combustion rates over neat diesel. However, pre-ignition time increased with biodiesel content, posing ignition challenges. Nanofuels infused with G-CDs, ranging from 0.01 percent to 1.00 percent by weight, were analyzed in single-component n-Dodecane and multi-component Jet-A fuels. G-CDs improved combustion rates by up to 19 percent, particularly at concentrations between 0.075 and 0.10 percent by weight, due to enhanced heat transfer and secondary droplet. However, concentrations exceeding 0.50 percent led to nanoparticle aggregation, hindering vaporization and reducing combustion efficiency. In multi-component fuels, puffing intensity and frequency significantly impacted combustion behavior, with optimal performance observed at G-CDs concentrations between 0.05 and 0.10 percent. The findings highlight the potential of G-CDs as combustion enhancers and their application in biodiesel to improve combustion performance, energy efficiency, and emissions reduction while ensuring practical feasibility in fuel applications.

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Table of Contents

List of Figures

Disclaimer

Abstract

The transition to renewable energy is driven by both environmental and geopolitical factors. In the transportation sector, this has manifested through electrification and increased adoption of biofuel. Full electrification is sufficient to power light duty vehicles, but heavier vehicles are more likely to require a hybrid model. , Heavy duty vehicles require the most torque at low speed and low engine rpm. While biodiesel has many positive aspects, its specific energy density is about 40 MJ/kg while petro-diesel is closer to 45 MJ/kg. Increasing the energy density of biodiesel is a critical aspect in enabling widespread adoption, and this project aims to directly tackle this issue. Higher energy density means a lower volume of fuel is required, and this significantly reduces the extent of any fire. This project will develop "Green Nanofuel" where nano structured energetic and catalytic materials are used with liquid fuel to increase the energy density and fuel economy while reducing the required volume, GHG and PM emission. Previous studies by the PI have shown that a carbon-based nano-additive can significantly modify the energy density of liquid fuels, and these behaviors can be tailored based on the specific requirement. Year one research investigated the combustion characteristics of diesel-biodiesel blends and gel-like carbon dots (G-CDs) based nanofuels using a suspension droplet method and shadowgraph imaging. Diesel-biodiesel blends, ranging from B5 to B75, derived from waste cooking oil and animal fat, exhibited two combustion stages: a steady combustion stage followed by a puffing stage. Puffing peaked at B25, while B10 demonstrated the highest combustion rate. Biodiesel blends showed improved combustion rates over neat diesel. However, pre-ignition time increased with biodiesel content, posing ignition challenges. Nanofuels infused with G-CDs, ranging from 0.01 percent to 1.00 percent by weight, were analyzed in single-component n-Dodecane and multi-component Jet-A fuels. G-CDs improved combustion rates by up to 19 percent, particularly at concentrations between 0.075 and 0.10 percent by weight, due to enhanced heat transfer and secondary droplet. However, concentrations exceeding 0.50 percent led to nanoparticle aggregation, hindering vaporization and reducing combustion efficiency. In multi-component fuels, puffing intensity and frequency significantly impacted combustion behavior, with optimal performance observed at G-CDs concentrations between 0.05 and 0.10 percent. The findings highlight the potential of G-CDs as combustion enhancers and their application in biodiesel to improve combustion performance, energy efficiency, and emissions reduction while ensuring practical feasibility in fuel applications.

Chapter 1 Introduction

The increasing energy demands driven by rapid industrialization and urbanization, along with stringent emission regulations and the depletion of conventional fossil fuels, have intensified the search for renewable, reliable, cost-effective, and environmentally friendly alternatives. In the transportation sector, this shift has led to the growing adoption of both electrification and biofuels. While electrification is well-suited for light-duty vehicles, heavy-duty transportation will likely require a hybrid approach during the technology transition. As a result, biodiesel has emerged as a key area of research, either as a replacement for or a supplement to conventional petroleum-based fuels [1-6].

Biodiesel was the second most produced and consumed biofuel in the United States in 2021, accounting for approximately 11% of total U.S. biofuel production and 12% of total consumption [7]. In that year, 1.64 billion gallons of biodiesel were produced, with soybean oil-based biodiesel contributing about 68% of the total. Biodiesel can be blended with petroleum diesel in various concentrations, including B100 (pure biodiesel), B20 (20% biodiesel, 80% petroleum diesel), B5 (5% biodiesel, 95% petroleum diesel), and B2 (2% biodiesel, 98% petroleum diesel), with B20 being a commonly used blend in the United States.

Biodiesel offers several advantages, such as low sulfur and aromatic content, high flash point, inherent lubricity, biodegradability, and compatibility with existing fuel distribution infrastructure [4-6]. It also reduces most regulated exhaust emissions. However, technical challenges remain, including the reduction of NOx emissions, lower ignition probability, improvement of energy density, and enhancement of oxidative stability and cold-flow properties. One of the key limitations preventing the widespread adoption of biodiesel for heavy-duty diesel vehicles is its approximately 10% lower energy content and lower ignition probability compared to petroleum diesel.

Recent research has explored the potential of carbon nanoparticles as fuel additives to improve biodiesel and diesel fuel performance while reducing emissions [5-6]. These nanoparticles offer unique properties, including a high surface area-to-volume ratio, enhanced combustion rates, and increased energy density. Additionally, certain nanomaterials can modify the chemical and thermal properties of fuels, leading to improved combustion characteristics. Studies have shown that blending biodiesel with carbon nanoparticles can enhance engine performance and reduce emissions. Carbon nanoparticles have also been investigated for their potential fire safety benefits [8-15]. However, concerns regarding their environmental and health impacts have limited their widespread use [16]. To address these concerns, researchers are now focusing on biocompatible and biodegradable carbon nanoparticles as a viable alternative for commercial fuel additives [16].

Previous studies conducted by this research group have examined the effects of various carbon nanoparticles—including activated carbon nanoparticles (CNPs), multi-walled carbon nanotubes (MWNTs), graphene nanoplatelets (GNPs), and acetylene black (AB)—on the combustion behavior of liquid fuels such as diesel, Jet-A, and crude oil [8-15]. The findings indicate that carbon nanoparticles exhibit a concentration-dependent influence on combustion dynamics, acting either as combustion enhancers or as flame suppressants depending on their concentration [16]. At concentrations below 0.50%, carbon nanoparticles accelerate combustion rates and reduce ignition delay, whereas at higher concentrations, they can suppress evaporation and increase ignition delay. Certain carbon nanoparticles, such as MWNTs, can serve as heterogeneous nucleation sites that promote puffing and micro-explosions, enhancing fuel consumption in flames. Conversely, other nanoparticles, such as AB, may form a shell around burning droplets, suppressing puffing and micro-explosion phenomena. These effects are strongly dependent on the thermophysical properties of the nanoparticles. Generally, small spherical carbon nanoparticles at concentrations of 0.10% or lower have shown potential to improve combustion characteristics [16].

Growing awareness of the environmental and health risks associated with carbon nanoparticles has driven research toward biocompatible and biodegradable alternatives [17]. These sustainable carbon nanoparticles offer significant potential for enhancing biodiesel performance and supporting its broader adoption, particularly in higher-concentration diesel-biodiesel blends, to overcome the combustion performance limitations of biodiesel compared to petroleum diesel.

In the first year of the project, research efforts were dedicated to investigating the combustion characteristics of diesel-biodiesel blends and integrating biocompatible and biodegradable carbon nanoparticles into the liquid fuel matrix to enhance combustion performance. This phase focused on two main objectives: (1) characterizing diesel-biodiesel blend droplet combustion and (2) evaluating carbon dots (CDs) as fuel additives.

These research efforts have led to the publication of one research journal paper, one review journal paper, one conference paper, and two conference presentations. The findings are expected to contribute to the theoretical modeling of complex multicomponent fuel combustion, including nanofuels, and to support further advancements in the development of carbon-based nanoadditives for improving biodiesel combustion performance.

Chapter 2 Major Activities and Results

2.1 Combustion characteristics of Diesel-biodiesel blends

The combustion characteristics of diesel-biodiesel blends, prepared from commercial diesel and second-generation biodiesel derived from waste cooking oil (WCO) and animal fat, were experimentally analyzed. The study utilized a suspension droplet method with a cross-multifiber system and shadowgraph imaging, based on an experimental setup developed by the Ratner research group [8-19]. Second-generation biodiesel was selected due to its potential to lower biodiesel production costs and provide an effective waste management solution, reducing environmental pollution while offering economic benefits [4].

Blends with varying biodiesel content (5%–75% v/v) were investigated, including commercially accepted blends (B5, B20) and higher-concentration blends (B25, B50, B75), along with neat diesel (B0) and pure biodiesel (B100). This study is significant as it covers a broader range of biodiesel concentrations than previous works, providing critical insights into combustion behavior. The key findings are summarized below:

- Two combustion stages were observed: a steady combustion stage followed by a puffing stage as shown in Figure 2.1. The onset, duration, and characteristics of the puffing stage varied with biodiesel concentration, influencing overall combustion dynamics.

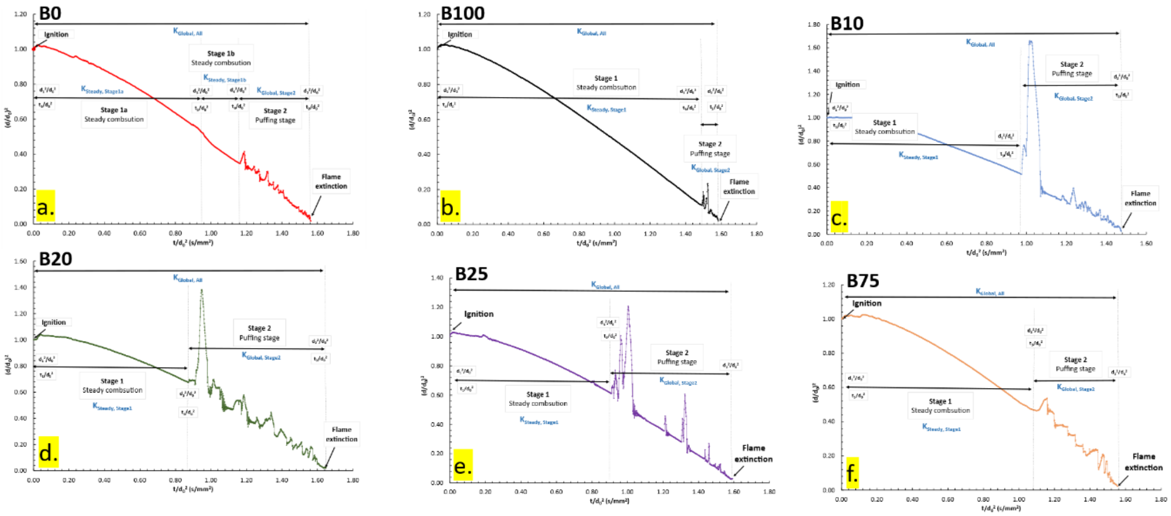

Figure 2.1 Evolution of normalized droplet size (d^2/d_0^2) over normalized time (t/d_0^2): a) B0, b) B100, c) B10, d) B20, e) B25, f) B75 (19). Here, d_0 is the initial droplet diameter and d is the instantaneous droplet diameter [19].

- The characteristics of the puffing stage were analyzed based on puffing occurrences, puffing intensity, and puffing effectiveness. The frequency of puffing increased with biodiesel concentration up to 25% but decreased at higher concentrations (see fig. 2.2a). Increased puffing events enhanced fuel mass transport to the flame zone, improving combustion efficiency. Puffing intensity, defined by changes in droplet size and fuel mass loss, peaked at 10% biodiesel concentration before decreasing at higher concentrations (see fig. 2.2b). Puffing effectiveness, which measures the rate at which fuel mass is transported via secondary droplet formation, increased up to 25% biodiesel concentration and then decreased for higher blends (see fig. 2.2c). These puffing parameters exhibited a non-linear trend with increasing biodiesel content, significantly influencing combustion rates.

- The highest combustion rate was observed for B10, attributed to a favorable combination of puffing characteristics that enhanced fuel-air mixing and combustion dynamics (see fig. 2.3).
- Pre-ignition time increased linearly with biodiesel content, with B0 exhibiting the shortest pre-ignition time and B100 the longest (see fig. 2.4). This trend highlights a known limitation of biodiesel blends regarding lower ignition probability.
- Droplet burning time followed an inverse trend to combustion rate; higher combustion rates corresponded to shorter burning times (see fig. 2.5).
- The distinct combustion behaviors of diesel-biodiesel blends provide valuable insights into optimizing biodiesel utilization in fuel mixtures. The findings contribute to further research on incorporating higher biodiesel content and exploring nanoparticle additives to enhance combustion performance.

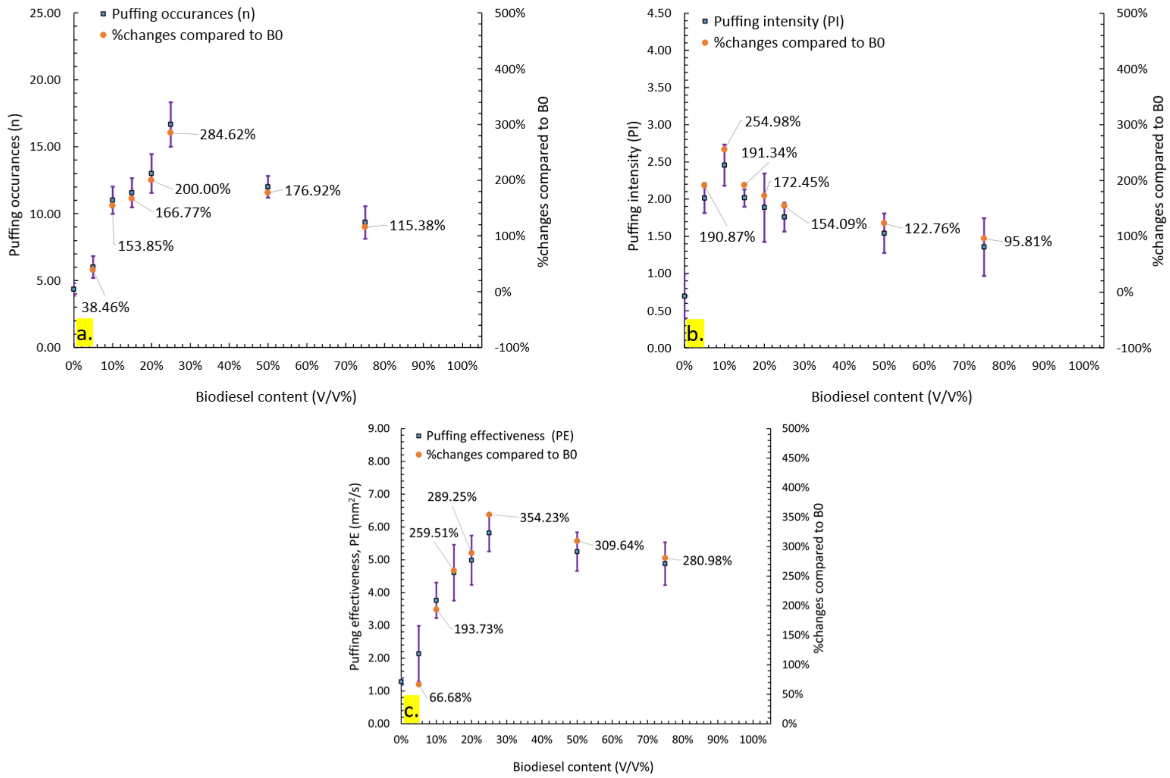

Figure 2.2 Puffing characteristics of diesel-biodiesel blends: a) puffing occurrences, b) Puffing intensity, c) Puffing effectiveness [19].

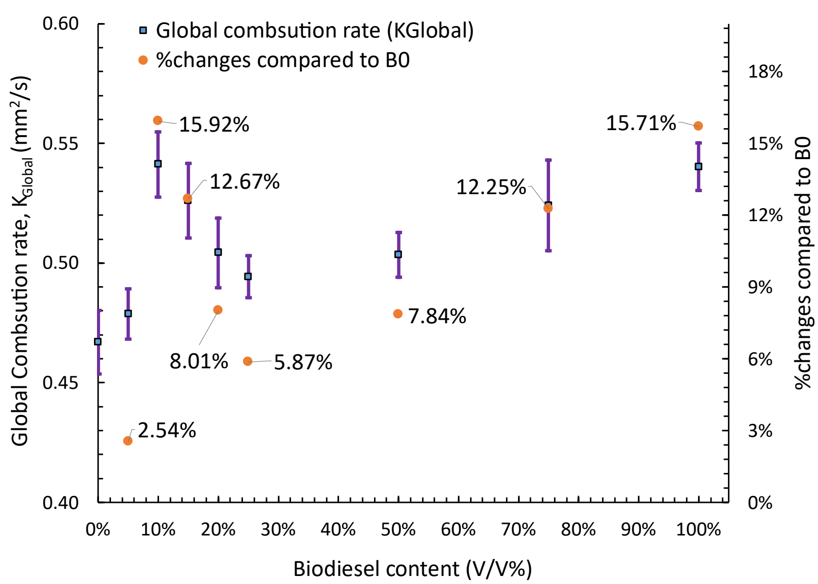

Figure 2.3 Combustion rates of diesel-biodiesel blends and neat fuels [19].

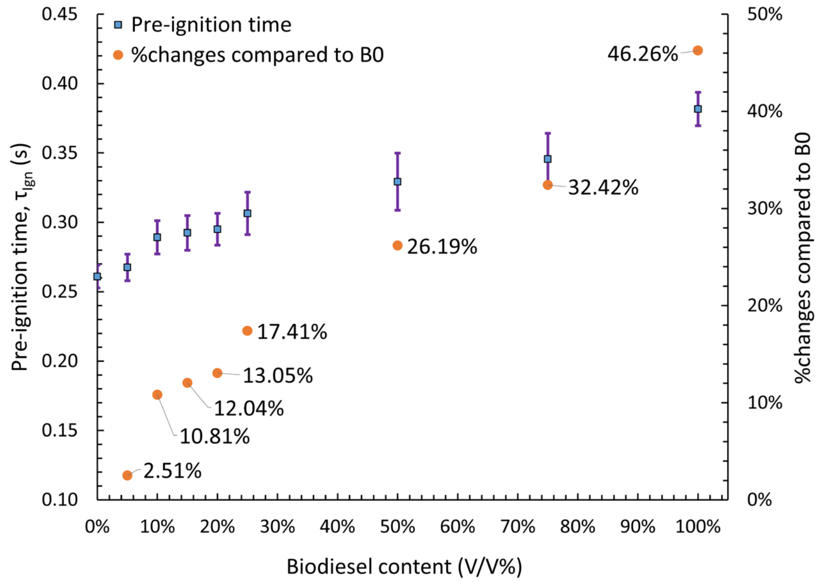

Figure 2.4 Pre-ignition time of diesel-biodiesel blends and neat fuels [19].

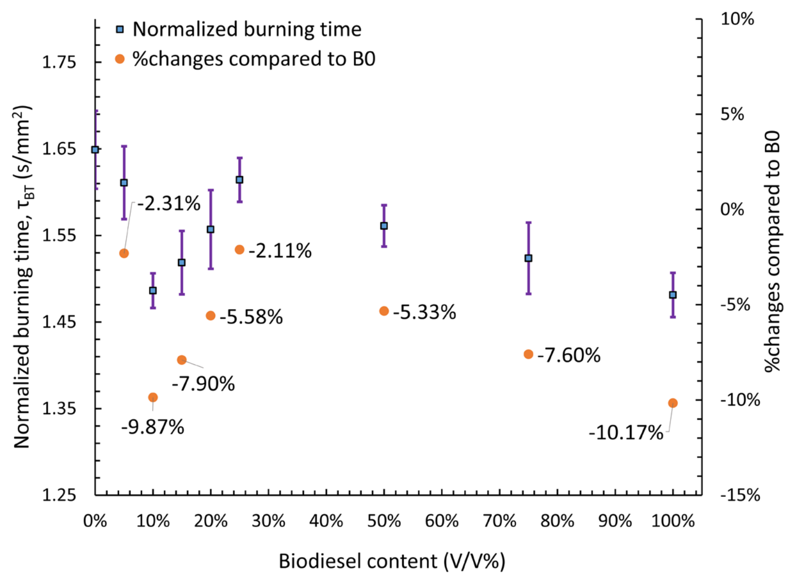

Figure 2.5 Normalized burning time of diesel-biodiesel blends and neat fuels [19].

2.2 Combustion characteristics of Carbon dots based nanofuels

Nanofuels, colloidal suspensions of nanoparticles (NPs) in liquid fuels, enhance combustion efficiency, power output, and emissions reduction by improving ignition delay, heat release, and fuel-air mixing. Among them, carbon dots (CDs) stand out for their suitable thermophysical properties, biocompatibility, biodegradability, and previous evidence in fuel applications [17, 18]. Observations regarding the effects of gel-like carbon dots (G-CDs) and surfactants on evaporation, aggregation, combustion, and fuel stability in single- and multi-component fuels will be discussed here.

2.2.1 Effect of Surfactant on Base Fuel Combustion

To isolate the influence of surfactants from G-CDs, which are typically used as stabilizers in nanofuel preparation, experiments were conducted on n-Dodecane and Jet-A fuels using Span 80 as the surfactant at concentrations of 0.05%, 0.50%, and 2.50% w/w. The key findings are as follows:

- Low Surfactant Concentrations (≤0.50% w/w):
    - DS0.50 burned smoothly, similar to neat Dodecane (see fig. 2.6a).
    - JS0.50 exhibited early puffing due to Span80-induced superheating (see fig. 2.6b).
- High Surfactant Concentration (2.50% w/w):
    - DS2.50 showed delayed puffing but remained mostly stable (see fig. 2.6c).
    - JS2.50 experienced intense, early puffing with droplet oscillations and secondary droplet ejection, reducing droplet lifetime (see fig. 2.6d).

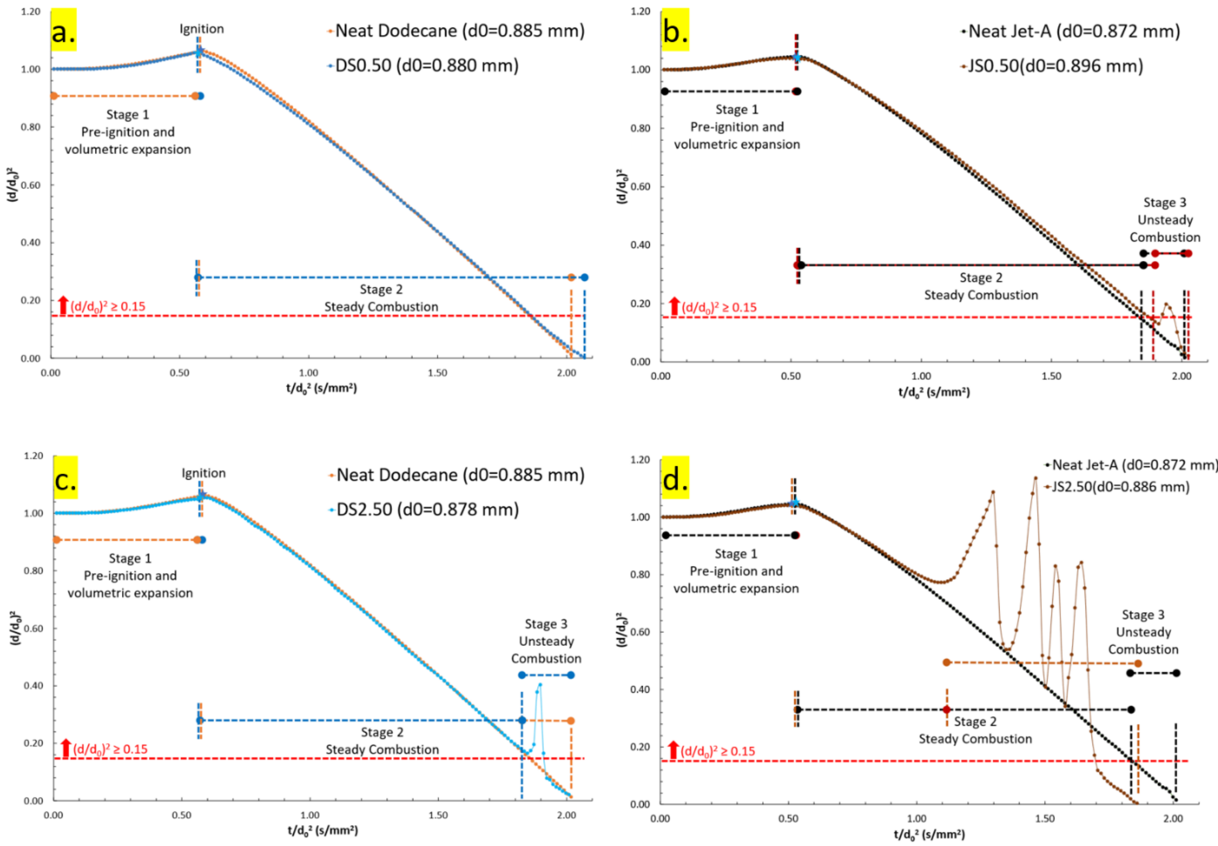

Figure 2.6 Evolution of normalized droplet size (d^2/d_0^2) over normalized time (t/d_0^2) of base fuel and surfactant mixture: a) neat Dodecane and DS0.50 (representation of single experiment), b) neat Jet-A and DS0.50 (representation of five repetitions), c) neat Dodecane and DS2.50 (representation of single experiment), d) neat Jet-A and JS2.50 (representation of five repetitions) [17]. Here, d_0 is the initial droplet diameter and d is the instantaneous droplet diameter.

- Combustion Rate:
  - At ≤0.50% w/w, no significant changes (<5%) in combustion rates or pre-ignition times (see fig. 2.7).
  - At 2.50% w/w, Jet-A's global combustion rate increased 15.03% due to enhanced fuel transport through puffing (see fig. 2.7b).

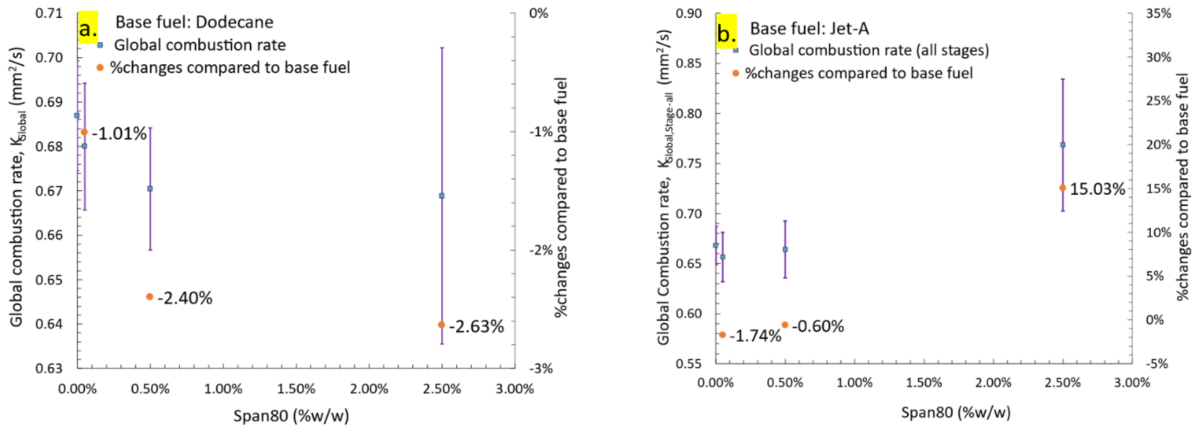

Figure 2.7 Combustion rates of base fuel and surfactant mixtures: a) Dodecane-surfactant mixtures, b) Jet-A-surfactant mixtures [17].

- Span80 had minimal impact at low concentrations but significantly altered multicomponent fuel combustion at higher levels.

2.2.2 Combustion Characteristics of G-CDs Based Nanofuels

The combustion behavior of G-CDs-doped fuels was evaluated in single-component (n-Dodecane) and multi-component (Jet-A) fuels to determine concentration-dependent effects. The key conclusions were:

- Effect of G-CDs Mass Concentration on Single-Component Fuel (Dodecane):
  - All droplets followed the d^2-law, maintaining a near-spherical shape (see fig. 2.8a-b).
  - No bubble formation or puffing was observed.
  - Non-linear concentration-dependent trends were observed for combustion rate and pre-ignition time (see fig. 2.8c-e).
  - The highest combustion rate was at 0.075% w/w G-CDs (DCD0.075).
  - At ≤0.10% w/w G-CDs, pre-ignition time decreased (by 7.00%–10.00%) due to enhanced heat transfer.

- At 0.10%–0.50% w/w, pre-ignition time increased due to reduced evaporation.
- At 1.00% w/w, particle aggregation further increased pre-ignition time (~9.63%).
- At ≤0.10% w/w G-CDs, combustion rate increased (4.00%‒16.00%), peaking at 0.10% w/w (16.46%).
- At >0.50% w/w, aggregation hindered vaporization, reducing combustion rate (~5.63% decrease at 1.00% w/w).

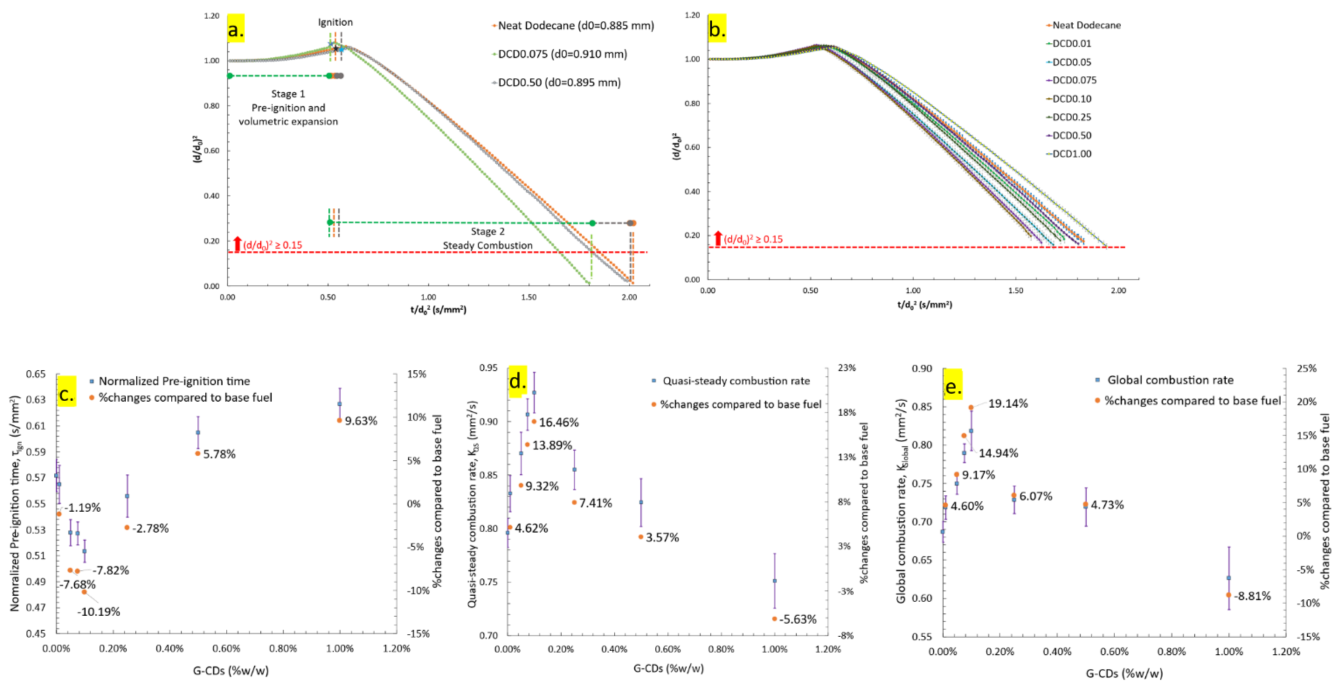

Figure 2.8 Evolution of normalized droplet size (d^2/d_0^2) over normalized time (t/d_0^2) of n-Dodecane based nanofuels: a) neat Dodecane, DCD0.075, DCD0.50 (representation of single experiment), b) Average d^2-plot comparison of neat Dodecane, DCD0.01, DCD0.05, DCD0.075, DCD0.10, DCD0.25, DCD0.50 and DCD1.00; Average d^2-plot is the representation of five repetitions with error bar showing the standard deviation from the mean. c) Pre-ignition time trend of nanofuels and neat fuel, d) Steady combustion rate trend of nanofuels and neat fuel, e) Global combustion rate trend of nanofuels and neat fuel [17].

- Effect of G-CDs Mass Concentration on Multi-Component Base Fuel:
    - Nanofuel droplets did not follow the d^2-law (see fig. 2.9).
    - The puffing stage was observed in all nanofuels.
    - Non-linear concentration-dependent trends were noted for combustion rate and pre-ignition time (see fig. 2.10).
    - The highest combustion rate was observed at 0.05% w/w G-CDs (JCD0.05).
    - The greatest reduction in pre-ignition time was at 0.05% w/w G-CDs (8.38% decrease) (see fig. 2.10a).
    - Pre-ignition time increased beyond 0.25% w/w due to particle aggregation (maximum increase: 9.62% at 1.00% w/w).
    - In the Steady Stage, for concentrations ≤0.10% w/w, combustion rates increased by 4.00%–20.00% (see fig. 2.10b). The peak combustion rate increase was observed at 0.075% w/w (19.76%). However, at concentrations >0.50% w/w, particle aggregation negatively impacted combustion, reducing the combustion rate by 5.38% at 1.00% w/w and increasing pre-ignition time by 9.62%.
    - In the Weak Puffing Stage, the highest combustion rate enhancement occurred at 0.10% w/w (20.45%), with puffing events facilitating additional fuel mass transport, thereby enhancing heat absorption and transfer (see fig. 2.10d). No plateau in combustion rates was observed up to 0.50% w/w, but at 1.00% w/w, aggregation led to a combustion rate reduction of 7.74%.
    - During the Strong Puffing Stage, strong puffing events resulted in higher puffing intensity and frequency, with combustion rates increasing by 6.00%–27.00% for

concentrations between 0.01% and 0.50% w/w (see fig. 2.10e). Beyond 0.50% w/w, combustion rates remained higher than the base fuel, with the highest combustion rate enhancement observed at 0.075% w/w and 0.10% w/w G-CDs.

- 0.075% w/w and 0.10% w/w G-CDs concentration had the highest enhancement in overall combustion rate (see fig. 2.11).
- The effect of G-CDs on multi-component fuels differed significantly from their effect on single-component fuels. In single-component fuels, heat absorption, heat transfer, and nanoparticle aggregation were the dominant factors. In multi-component fuels, additional factors such as puffing initiation and frequent puffing occurrences played a crucial role in combustion behavior. Increased G-CDs concentration led to higher puffing intensity and frequency, significantly impacting combustion performance.

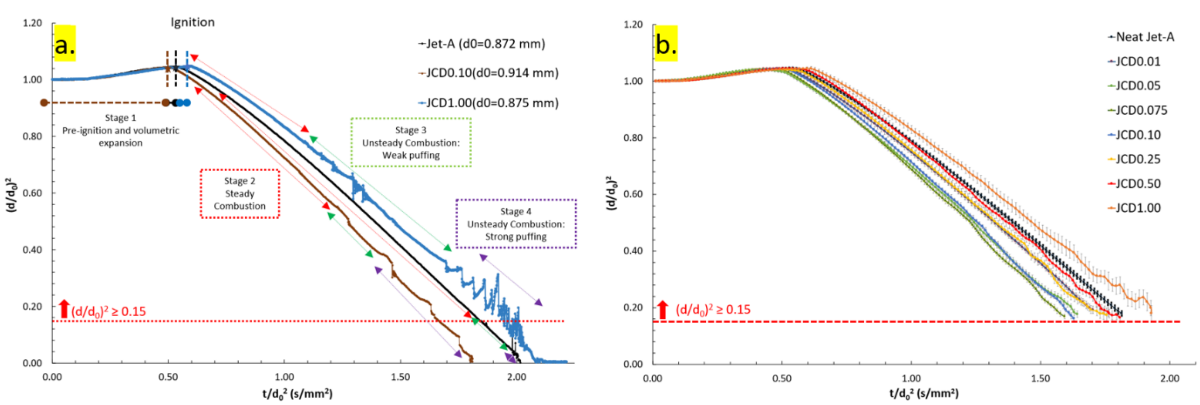

Figure 2.9 Evolution of normalized droplet size (d^2/d_0^2) over normalized time (t/d_0^2) of Jet-A based nanofuels: a) neat Jet-A, JCD0.10, JCD1.00 (representation of single experiment), b) Average d^2-plot comparison of neat Jet-A, JCD0.01, JCD0.05, JCD0.075, JCD0.10, JCD0.25, JCD0.50 and JCD1.00 [17]. Average d^2-plot is the representation of five repetitions with error bar showing the standard deviation from the mean.

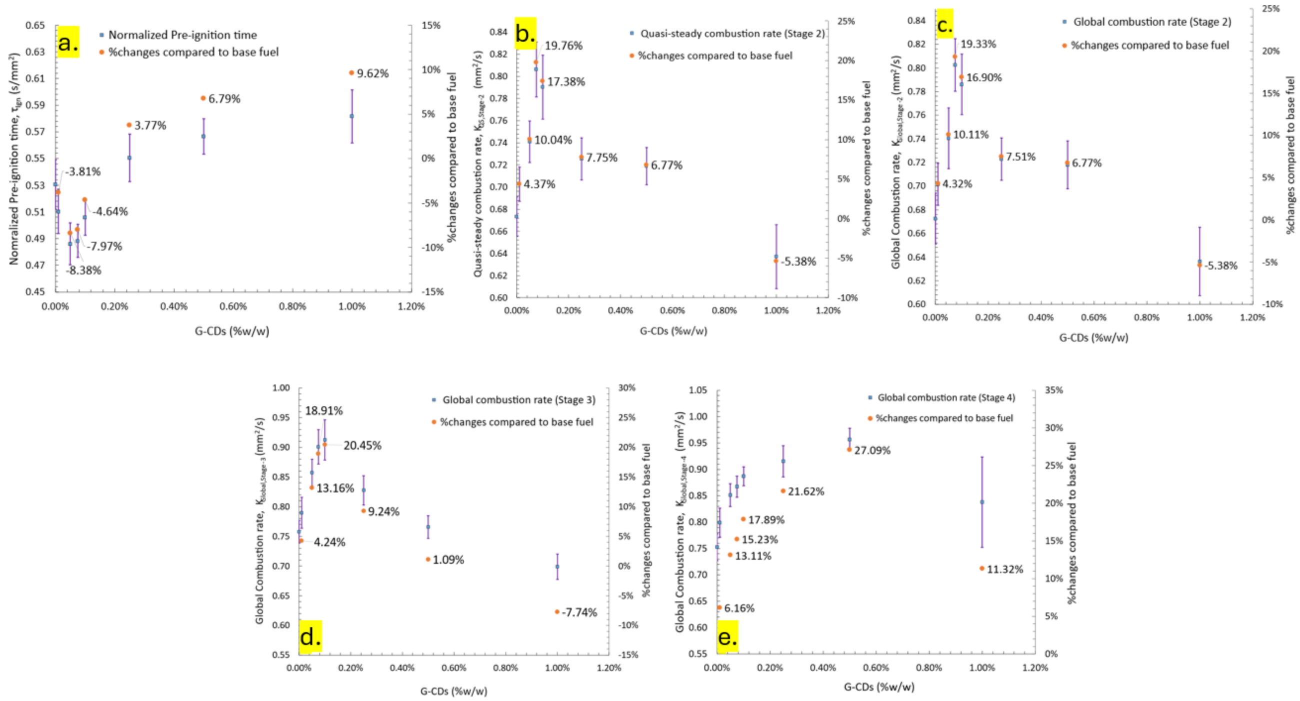

Figure 2.10 Different combustion trends of Jet-A based nanofuels and neat fuel: a) Pre-ignition time, b) Steady combustion rate at stage-2, c) Global combustion rate at stage-2, d) Global combustion rate at stage-3, e) Global combustion rate Global combustion rate [17].

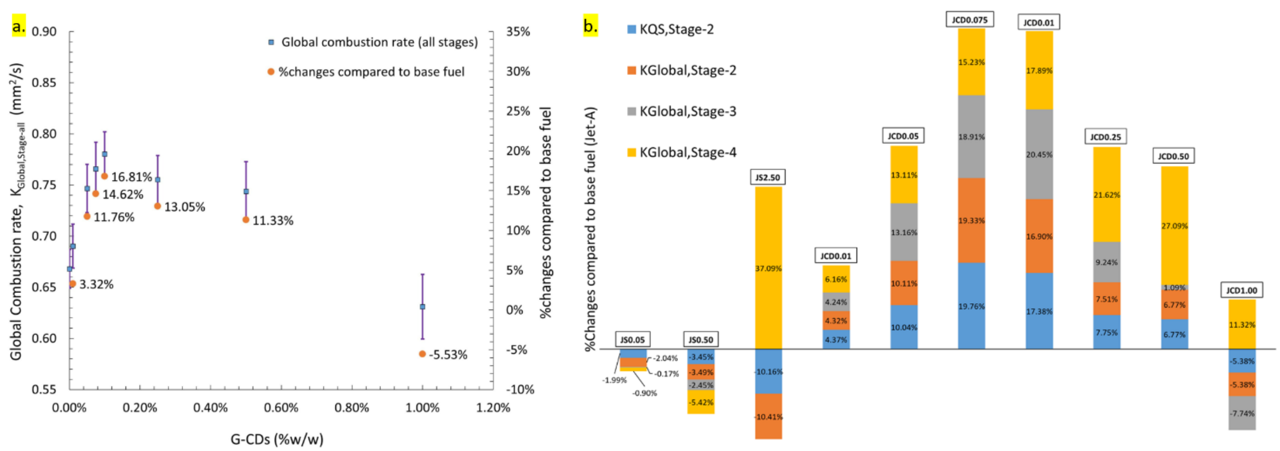

Figure 2.11 Different combustion trends of Jet-A based nanofuels and neat fuel: a) Overall global combustion rate, b) Stage wise enhancement in combustion rate compared to neat fuel [17].

Year one findings highlight G-CDs as effective combustion enhancers in nanofuels and their potential application in diesel-biodiesel blends. Optimal concentrations were 0.075%–0.10% w/w for single-component fuels and 0.05%–0.10% w/w for multi-component fuels, with low concentrations enhancing combustion efficiency and ignition delay, while higher levels caused evaporation suppression.

Chapter 3 Collaboration and Publications

3.1 Collaboration

Professor Dr. Roger M. Leblanc's group from the University of Miami (Coral, Gables, FL, USA) synthesized the gel like carbon dots (G-CDs).

3.2 Publications

All papers and posters listed here have been possible because of the work undertaken through August 31, 2024.

Journal articles:

1. Parveg, A.S. and Ratner, A., 2025. "A comprehensive review of liquid fuel droplet evaporation and combustion behavior with carbon-based nanoparticles." *Progress in energy and combustion science*, *106*, p.101198.
2. Parveg, A.S., Zhou, Y., Leblanc, R.M. and Ratner, A., 2025. "Effects of gel-like carbon dots (G-CDs) and surfactant (Span80) on the droplet combustion dynamics of liquid fuels." *Fuel*, *381*, p.133385.
3. Parveg, A.S. and Ratner, A., 2025. "Droplet-Scale Combustion Analysis of Third-Generation Biodiesel–Diesel Blends." *Energies*, *18*(7), p.1692.

Conference articles:

1. Parveg, A.S. and Ratner, A., 2024, November. Droplet Combustion Behaviors of Liquid Fuel Doped With Carbon Dots. In *ASME International Mechanical Engineering Congress and Exposition* (Vol. 88643, p. V006T08A020). American Society of Mechanical Engineers.
2. Parveg, A.S. and Ratner, A., 2023, October. Droplets Combustion Characteristics Comparison of Single Component and Multicomponent Diesel Surrogates With Petroleum-

Based Commercial Diesel Fuel. In *ASME International Mechanical Engineering Congress and Exposition* (Vol. 87646, p. V007T08A019). American Society of Mechanical Engineers.

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2. Demirbas, Ayhan. "Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods." *Progress in energy and combustion science* 31, no. 5-6 (2005): 466-487.

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