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Reducing Flammability for Bakken Crude Oil for Train Transport Final Yearly Report - Phase V

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MATC

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16. Abstract
Crude oil shipping by rail is a critical component of our energy security and has grown steadily with the Bakken oil boom. However, existing rail infrastructure is in a state of disrepair which is evidenced by several high-profile derailments of trains carrying crude oil resulting in large oil spills in recent years. This is an especially dangerous situation in the case of Bakken crude, which is of a light variety and contains significant amounts of easy to evaporate, easy to ignite, light ends, and crashes usually result in oil ignition and an intense fireball. Previous research done by Professor Albert Ratner's research group under MATC-DOT sponsorship has concluded that polymeric additives improve fire safety in diesel fuels and its blends by delaying ignition, promoting flame extinction, and suppressing splashing. There is a strong indication that the same will be true for crude oil as well. Efforts through the completion of this grant in December 31, 2022 included modification of the oil with a new class of additive, carbon dots. Of particular interest was the prospect of mixed additives (polymers and carbon dot nanomaterials) as the fire limiting agents. Through detailed testing and analysis, combustion characteristics were established for blended surrogate fuels which will aid future modeling of crude oils combustion. Also, the stability/settling characteristics were investigated with crude surrogate and bio-compatible carbon dots. This work has resulted in several published manuscripts and will help in the modeling of crude oil combustion and how to modify these properties to make crude oil transport safer.

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List of Abbreviations and Nomenclature

API = American Petroleum Institute (Gravity)
EIA = Energy Information Administration
MCF = Motor Coach Fire
MUX = Multiplexer
PBD = Polybutadiene
PANI = Polyaniline
SEL = Select (Channel select)
VGO = Vacuum Gas Oil
FSR = Flame stand-off ratio
SEM = Scanning electron microscope
CD = Carbon Dot

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Abstract

Crude oil shipping by rail is a critical component of our energy security and has grown steadily with the Bakken oil boom. However, existing rail infrastructure is in a state of disrepair which is evidenced by several high-profile derailments of trains carrying crude oil resulting in large oil spills in recent years. This is an especially dangerous situation in the case of Bakken crude, which is of a light variety and contains significant amounts of easy to evaporate, easy to ignite, light ends, and crashes usually result in oil ignition and an intense fireball. Previous research done by Professor Albert Ratner's research group under MATC-DOT sponsorship has concluded that polymeric additives improve fire safety in diesel fuels and its blends by delaying ignition, promoting flame extinction, and suppressing splashing. There is a strong indication that the same will be true for crude oil as well. Efforts through the completion of this grant in December 31, 2022 included modification of the oil with a new class of additive, carbon dots. Of particular interest was the prospect of mixed additives (polymers and carbon dot nanomaterials) as the fire limiting agents. Through detailed testing and analysis, combustion characteristics were established for blended surrogate fuels which will aid future modeling of crude oils combustion. Also, the stability/settling characteristics were investigated with crude surrogate and bio-compatible carbon dots. This work has resulted in several published manuscripts and will help in the modeling of crude oil combustion and how to modify these properties to make crude oil transport safer.

Chapter 1 Introduction

Several high-profile incidents in recent years involving oil train crashes and devastating oil fires [1] [2] [3] have raised concerns regarding the safety of oil transportation via rail. Rail transportation of crude oil is critical for the energy security of the United States: in February 2015, crude oil shipping by rail accounted for more than half of the East Coast refinery supply [4]. The latest annual data from the US Energy Information Administration (EIA) indicates that shipments out of the Midwest to other US regions via rail steadily increased from 2010 to 2015 [5]. This data directly correlates to the Bakken oil boom, which peaked in 2012. Transportation of Bakken oil via extant rail system is a major safety concern, since it is of a very light and sweet variety, with a typical API gravity of 42 [6].

There is consensus that the US rail infrastructure is in a state of neglect and will need significant overhaul to handle current and future freight congestion. This can be expected to result in long delays, which regrettably means that more crude oil freight car derailments must be planned for. The Motor Coach Fire (MCF) database identifies hot wheel wells as a common origin of fires [7]. Any derailment or crash typically leads to an oil spill in the region, with hot surfaces like wheel wells present in abundance on the site. Bakken oil, especially, contains significant amounts of light ends [6], characterized by high volatility and low ignition temperatures. In the event of a derailment and subsequent oil spill, they rapidly evaporate and catch fire.

One possible prevention method is to remove light ends from the crude before shipping it. This is already being done in Texas and California before shipping the crude (typically via pipeline). Another option is to flare them, which happens in offshore oil derricks or in remote oil fields. In North Dakota's case, the likelihood of having a light-end capturing system in operation or the creation of a new pipeline to obviate the need for shipping by rail is very low. Furthermore, flaring off light ends is tightly regulated by the EPA under the Clean Air Act, meaning this option is also very unlikely.

This report is for year 5 of a five-year investigation into a solution that can act as both a stopgap and a long-term measure to control derailment-related oil fires: polymeric additives and carbon-based carbon dots that minimize the risk of fire initiation, slow down the combustion process, and enhance its extinction. Previous work done by this research group has concluded that adding long-chain polymers to diesel and its blends suppresses mist formation and splashing [8]. Additionally, studies have shown that this additive can suppress soot formation [9], a process known to result in the formation of highly flammable hydrogen gas. Moreover, adding long-chain polymers to diesel and Jet-A droplets [10] as well as their surrogate blends [13][14][15] retards their burning rate and increases ignition delay. It is found that the addition of long-chain polymers and carbon-based nanoparticles to crude oil similarly results in less splattering, less mist generation, less soot formation, and increased ignition delay, all of which are contributing factors to better fire safety of crude during transportation. In addition, crude pipelines use polymers as drag reducing agents [11] [12], and logistical infrastructure to handle them is in place. Experiments with crude oils (Bakken crude and Pennsylvania crude) with different chain lengths polymers reveal that short chain length polymer decreases the burning rate while long chain length increases the burning rate [16]. Faster thermal degradation and increased thermal conductivity of long chain polymers contributed to the enhancement in burning rate. However, both short chain and long chain polymers showed a general increasing trend in ignition delay of the crude oils. These findings concluded that short chain length polymers are more suitable candidates as additives for crude oil transportation safety.

Work undertaken during year 5 included examining the prospects of different carbon-based additives as combustion behavior modifiers for liquid fuel, which was then formulated into a comprehensive review article [25]. The article should provide future guidelines and a generalized source of current state of the art for future researchers working on liquid fuel combustion and safety. In addition, combustion trends for different diesel-biodiesel blended fuels are also explored to assess their appropriateness as possible crude oil surrogates [27]. Also, the stability period of new class of biocompatible carbon dots with liquid fuel was also explored [28] which shows the potential as an alternative to the existing additives and can be utilized for liquid fuel transportation safety. Additionally, a tangentially related work [26] benefited from this project funding and funding was acknowledged in that paper.

The above-mentioned works have resulted in one research journal paper, one review journal paper (under review), three conference papers, two poster presentations and other manuscripts that are under development. These works are envisioned to aid in theoretical combustion modeling of complex multicomponent liquid fuels like crude oil, as well as generate interest in investigating more polymeric additives and carbon-based carbon dots for liquid fuels.

Chapter 2 Major Activities and Results

2.1 Combustion data generation and review

Ignition, combustion, and flame characteristics of different diesel-biodiesel blends droplets were investigated experimentally. Diesel-biodiesel blends can be regarded as crude surrogates and these experimental data provide a wider look into modeling the combustion behavior of crude oil and other liquid fuels. A comprehensive review was performed outlining the potentials of carbon-based nano-additives to modify the combustion characteristics of liquid fuel and current state of the art has been discussed. Previous work relating to the current project also showed the prospects of carbon dots to suppress micro-explosions [19]. So, the prospects of a mix of additives made of both polymers and carbon dots has the potential for suppressing micro-explosions, increasing ignition delay and decreasing combustion rate of crudes leading to better crude oil fire safety.

The conclusions are summarized as follows:

- B0 (neat diesel) and B100 (neat biodiesel-waste cooking oil based) fuel droplets followed the d^2-law of combustion (Figure 2.1). Blended fuel droplets deviated from the d^2-law of combustion (Figure 2.2).

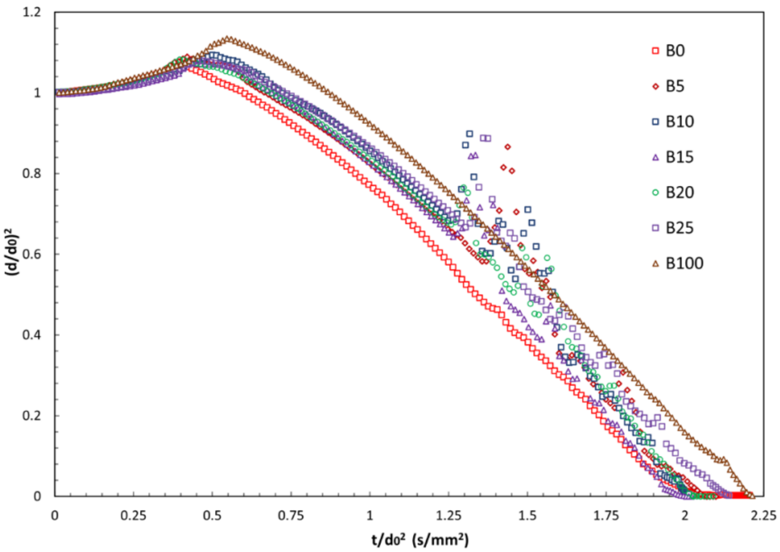

Figure 2.1 Moving average trends of normalized droplet diameter square evolution of neat diesel (B0), biodiesel (B100) and diesel-biodiesel blends (B5, B10, B15, B20, B25) different fuel droplets [27].

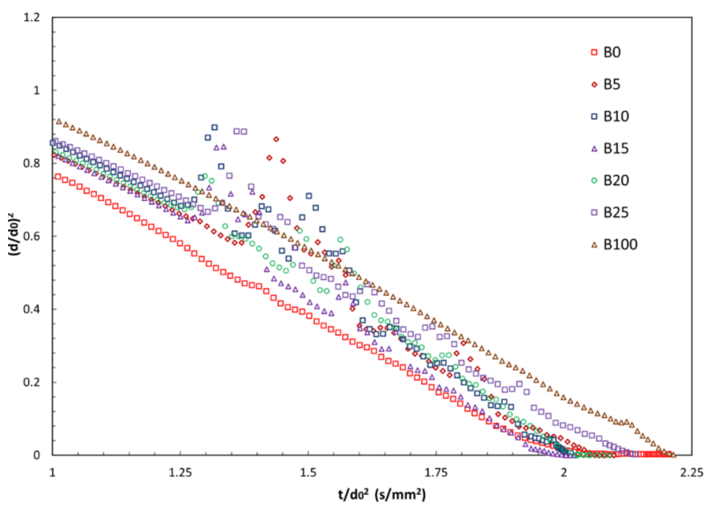

Figure 2.2 Moving average trends of normalized droplet diameter square evolution for different fuel droplets with enlarged view from $t/d_0^2 = 1.00\ s/mm^2$ to $t/d_0^2 = 2.25\ s/mm^2$ [27].

- Blended fuel droplet showed a general increasing trend in combustion rate compared to B0. The highest increase in combustion rate was observed in B15 fuel droplets which was around 7% (Figure 2.3).

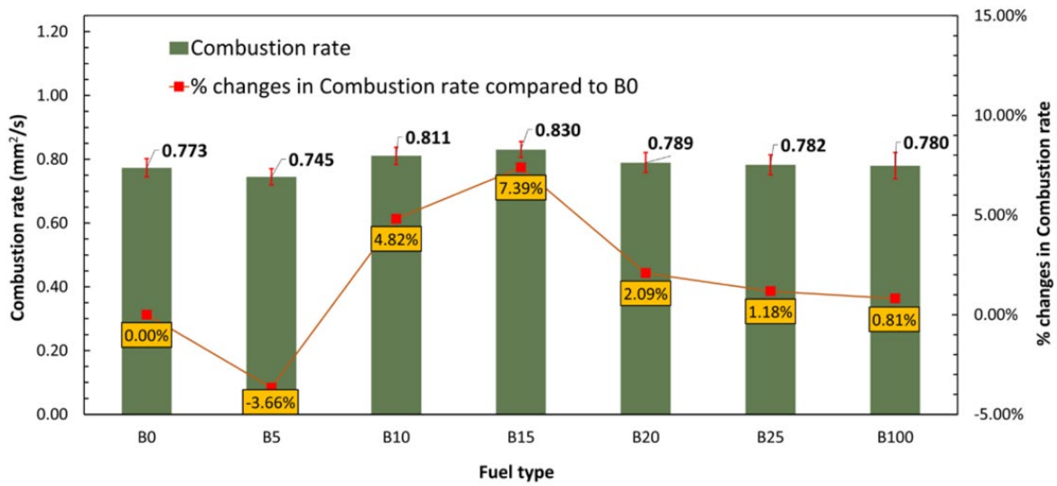

Figure 2.3 Combustion rate trends of different fuel droplets [27].

- Blended fuel droplets showed similar ignition delay compared to B0. B100 showed a significant increase (38%) in ignition delay compared to B0 (Figure 2.4). This was attributed to the higher flash point and higher surface tension of B100 compared to B0.

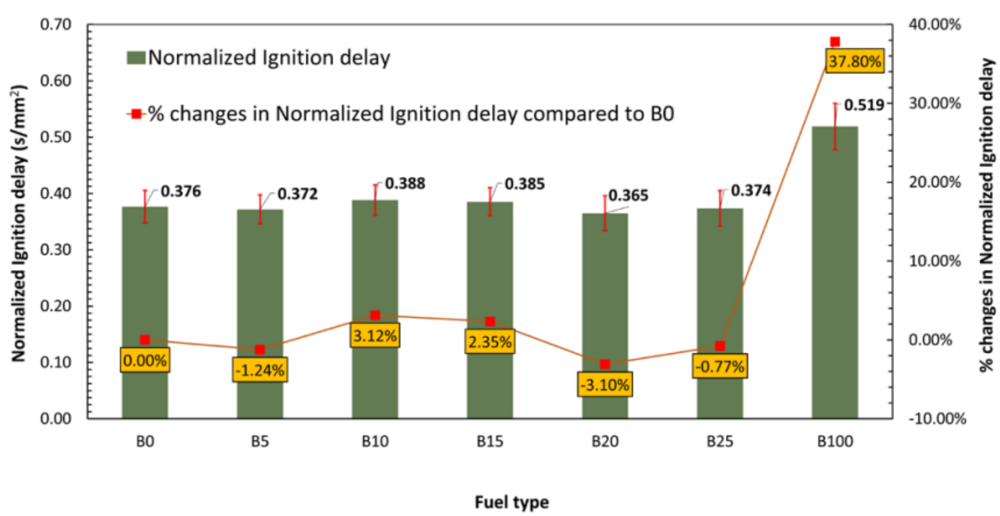

Figure 2.4 Ignition delay trends of different fuel droplets. Droplet burning time was normalized with the square of the initial equivalent diameter (d_0) [27].

- B10 and B15 fuel droplets showed a significant decrease in droplet burning time which was attributed to the increased burning rates and mass losses due to puffing and micro-explosion (Figure 2.5). The highest decrease in droplet burning time was observed for B15(8%).
- Liquid fuel droplets with carbon nano-additives generally follow the d^2-law of combustion during a significant portion of the burning period.
- The burning rate and ignition delay of liquid fuel droplets with carbon nano-additives depends mainly on the particle concentration and the thermo-physical and optical properties of the nano-additive. At a particle concentration > 0.5% w /w, the burning rate generally decreases. Generally, at a particle concentration of 0.1-1% w/w, no significant changes in ignition delay are reported, while at a particle concentration greater than 1% w/w, a significant increase in ignition delay can be expected.

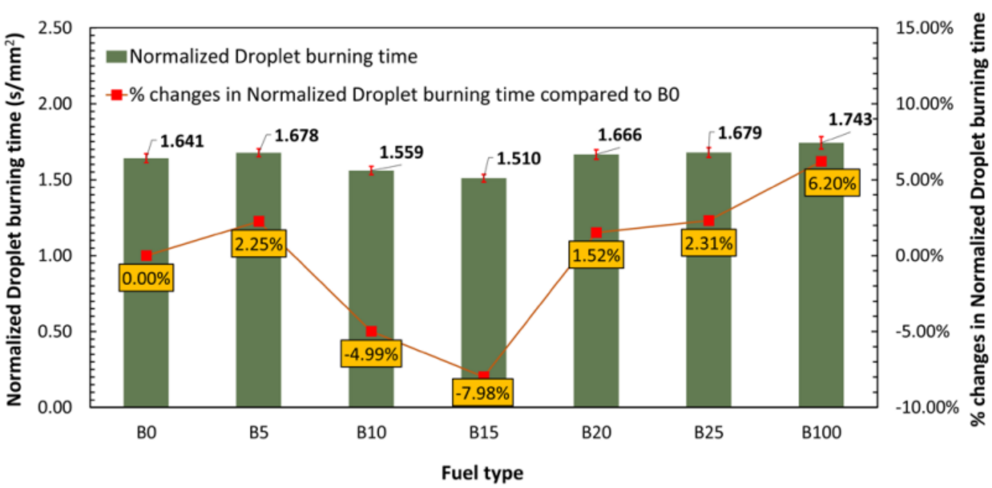

Figure 2.5 Droplet burning time trends of different fuel droplets. Droplet burning time was normalized with the square of the initial equivalent diameter (d_0) [27].

- Carbon based nano-additives can increase micro-explosion intensity and decrease micro-explosion frequency which is dependent on particle concentration.

These results will aid in future modeling of crude oil combustion and the prospects of polymer/nano-additive blends and their optimum concentrations to enhance fire safety of crude oil during shipping by rail.

2.2 Settling Characterization

Carbon dots can be used to modify different surrogate properties like viscosity, surface tension, and burning rates. The stability of such surrogate/nano-additive suspensions over time is an object of investigation.

Manual tests as well as experiments with the in-house stability period experiment setup (Figure 2.6) have been utilized to study the settling characteristics of carbon based nanofuels [22][24]. In practical application, fuel needs to be stored for a prolonged period for their operation and use. From the last four year's findings, it can be concluded that the settling experiment setup can quantitatively measure the settling and stability period [21][22][23][24]. This settling experiment setup can be utilized to investigate how the settling/stability period can be improved (with the application of surfactants or functionalized characteristics of carbon dots) for surrogates with carbon dots and polymers. The stability period of colloidal suspensions of gel like carbon dots, water, and Decane were explored revealing presence of water can destabilize colloidal suspension (Figure 2.7).

This data is expected to help in exploring the basic physics behind the settling of real-world nanofuels and nanofluids, which will further help in developing carbon dots for crude oils and their surrogates.

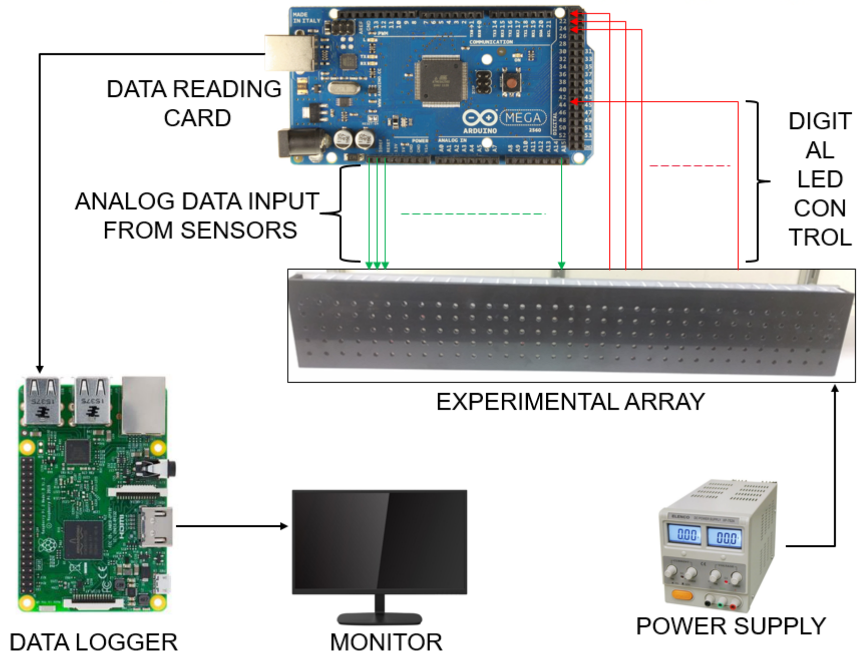

Figure 2.6 Main components of settling analysis experiment [22].

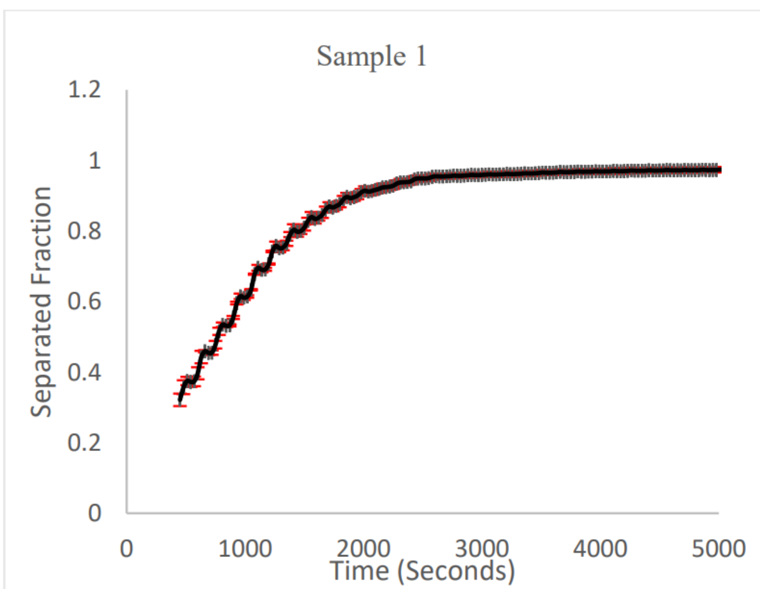

Figure 2.7 Separated Fraction vs Time curve for 3 % gel like CDs 1.5% Water 95.5% Decane Sample [28].

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.

3.2 Publications

All papers and posters listed here have been possible because of the work undertaken through December 31, 2022.

Research papers:

- Parveg, A.S.M. & Ratner, A., "A Review of the Droplet Combustion Behavior of Liquid Hydrocarbon Fuels with Carbon-Based Nano-Additives," Submitted to *Progress in Combustion Science and Technology*. (Under review).
- Parveg, A. S. M., Ordikhani-Seyedlar, R., Sharma, T., Shaw, S. K., & Ratner, A. (2022). "A Recycling Pathway for Rare Earth Metals (REMs) from E-Waste through Co-Gasification with Biomass," *Energies*, 15(23), 9141.

Conference papers:

- Parveg, A. S., & Ratner, A. (2022, October). "Combustion Characteristics of Single Isolated Fuel Droplets of Different Diesel-Biodiesel Blends Derived from Waste Vegetables Oil and Animal Fat", 2022 ASME International Mechanical Engineering Congress and Exposition (Vol. 86687, p. V006T08A009). American Society of Mechanical Engineers.
- Mollick, R., Hentges, N., Parveg, A. S., Zhou, Y., Leblanc, R. M., & Ratner, A. (2022, October). "An Experimental Investigation on the Stability of Gel-Like Carbon Dot Based Nanofluids", 2022 ASME International Mechanical Engineering Congress and Exposition (Vol. 86700, p. V008T10A019). American Society of Mechanical Engineers.
- Parveg, A. S., & Ratner, A., "Experimental Study on the Droplet Combustion Characteristics of Different Diesel-Biodiesel Blends Derived from Waste Vegetables Oil and Animal Fat", 2022 Spring Technical Meeting of the Central States Section of The Combustion Institute, May 15-17, 2022, Wayne State University, Detroit, MI.

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