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Reducing Flammability for Bakken Crude Oil for Train Transport Phase II

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2020

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Secretary for Research and Technology

MATC

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16. Abstract Various crude oil train derailments in recent years have exposed critical shortcomings in existing rail infrastructure. These incidents lead to large oil spills, and the oil finds itself in the presence of various hot surfaces on the site. 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 usually the result is an intense fireball. Previous research done by Prof Albert Ratner et al under MATC-DOT sponsorship has concluded that polymeric additives improve fire safety in diesel fuel and its blends. There is a strong indication that the same will be true for crude oil. This report covers efforts part of the larger goals of the five-year project to improve fire safety during transportation by adding long chain polymers and carbon-based nanoparticle to crude oil before shipping. This work has resulted in several journal papers and other manuscripts that are under development. This work is expected to help to model combustion characteristics of crude oil, and moreover, these results are unique. These works will also aid to evaluate splashing characteristics of crude oil and how to modify them for making crude oil transport safer.

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Table of Contents

List of Figures

List of Tables

List of Abbreviations and Nomenclature

μ = dynamic viscosity
ρ = density
σ = surface tension
L = characteristic
V_0 = Impact speed of the drop
Oh =Ohnesorge number

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

Disclaimer

Abstract

Various crude oil train derailments in recent years have exposed critical shortcomings in existing rail infrastructure. These incidents lead to large oil spills, and the oil finds itself in the presence of various hot surfaces on the site (such as wheel wells). 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 usually the result is an intense fireball. Previous research done by Prof Albert Ratner et al under MATC-DOT sponsorship has concluded that polymeric additives improve fire safety in diesel fuel and its blends by suppressing splashing, delaying ignition, and promoting flame extinction. There is a strong indication that the same will be true for crude oil. This report covers efforts thru Dec 31, 2019 that are part of the larger goals of the five-year project to improve fire safety during transportation by adding long chain polymers and carbon-based nanoparticle to crude oil before shipping. Specifics include upgrading the software for post processing of experimental droplet combustion data and then using it to analyze combustion characteristics of carbon-based nanoparticle (Acetylene black, Multi-walled carbon nanotube) and polymer additives (polybutadiene,) in various crude oil (Bakken, Texas, Colorado and Pennsylvania crudes) and biodiesel fuels, and settling characteristics. This work has resulted in several journal papers and other manuscripts that are under development. This work is expected to help to model combustion characteristics of crude oil, and moreover, these results are unique. These works will also aid to evaluate splashing characteristics of crude oil and how to modify them for making 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 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 have 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 take have 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 method to prevent this is to remove these 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 in order 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 two 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 nanoparticles 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 chained polymers to diesel and its blends suppresses mist formation and splashing [8]. Additionally, studies have shown that this additive can also 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 result in less splattering, less mist generation, less soot formation, and increased ignition delay, which are all 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.

Work undertaken during year two focused heavily on quantification of crude oil combustion properties and settling characteristics of colloidal suspension. Initially, several upgrades and modifications were made to the existing experimental setup. The post-processing techniques were also upgraded. These were used to analyze combustion properties of Acetylene black (AB) in diesel and biodiesel, which resulted in a manuscript that has been published. Also, these techniques were used to analyze combustion characteristics of carbon-based nanoparticles

(Acetylene black, Multi-walled carbon nanotube) and polymer additives (polybutadiene,) in various crude oil (Bakken, Texas, Colorado, and Pennsylvania crudes) and biodiesel fuels, and settling characteristics. Soot deposits of various crude oils were also investigated. Moreover, combustion behavior of Biodiesel-water emulsion was also investigated and published as a conference paper. These works have resulted in several published manuscripts and are expected to help model combustion characteristics of crude oil. Moreover, these results are unique. These works will also aid to evaluate splashing characteristics of crude oil and how to modify them for making crude oil transport safer.

Year two also saw the design, development and testing of a novel, low cost system to analyze the stability of solid additives in liquids. The setup developed for suspension stability analysis was used for quantification of settling properties of graphene in dodecane, which resulted in a conference publication. Also settling characteristics of carbon and Metal Oxide nanofuels were also investigated and published as a conference paper. Additional work is underway to develop mathematical models of the process.

It is expected that by the end of next year, we will complete the necessary preliminary work for identifying a splashing surrogate for the same and continue experiment investigation to modify the splashing behavior.

Chapter 2 Major Activities and Results

2.1 Combustion data generation

Combustion data was generated for various crude oil (Bakken, Texas, Colorado, and Pennsylvania crudes) colloidal suspension of carbon-based nanoparticles, and polymers. Also, evaporation data was generated for various crude oil (Bakken, Texas, Colorado, and Pennsylvania crudes) colloidal suspension of carbon-based nanoparticles. Combustion data was also generated for soy-based biodiesel and petrodiesel colloidal suspension of carbon-based nanoparticles.

These experimental data provide us a wider look into modeling the combustion behavior of crude oil and other liquid fuel.

2.1.1 Crude oil combustion

First, using the upgraded droplet combustion setup, baseline data has been generated for combustion characteristics of various US crude oil types (Bakken, Texas, Colorado, and Pennsylvania crudes). These data aid in further evaluation of potential combustion substitutes. Moreover, these data will aid to evaluate potential splashing substitutes which will be carried out on the next phase. This information needed for any attempt is made to modify these crude oil's characteristics.

Combustion data from crude oil colloidal suspensions, made using carbon-based nanoparticles (Acetylene black, Multi-walled carbon nanotube) was generated using the upgraded droplet combustion setup. Bakken, Texas, Colorado, and Pennsylvania crudes were analyzed for their combustion and soot properties. Combustion properties of various crude oils are found significantly different and might need different control strategies to increase ignition delay and decrease combustion rates. Also, soot particle sizes of different crude oils are significantly different, which has respiratory health-based ramifications for the crude oil fire control and clean-up parties. These data showed that suppression of microexplosions can be achieved in crude oil with addition of nanoparticles, leading to better crude oil fire safety. Evaporation data from crude oil colloidal suspensions, made using carbon-based nanoparticles, was also generated. These will aid in further evaluation of potential splashing and combustion substitutes. Also, Combustion data from crude oil blends with different polymers was generated showing significant improvement in crude oil fire safety parameters using polymeric additives. Combustion data was generated for droplet combustion of soy-based biodiesel and petrodiesel, at different percentages of carbon-based nanoparticle (Acetylene black). Acetylene black has been found to reduce combustion rate of soy-based biodiesel. An increase in ignition delay of soy-based biodiesel as well as a decrease in total combustion time was also observed. These data will aid for future modeling of combustion behavior of crude oil and liquid fuel and how to modify their combustion characteristics.

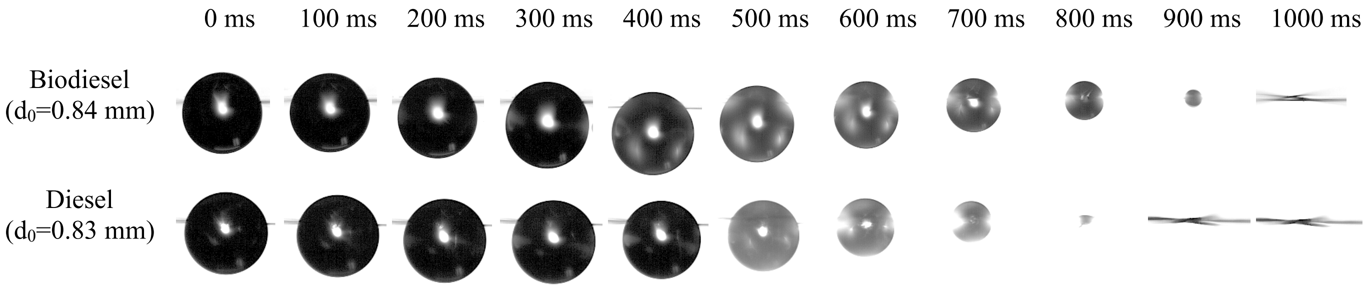


Figure 2.1 Time evolution image of a droplet during combustion for pure petrodiesel and soy-based biodiesel droplets

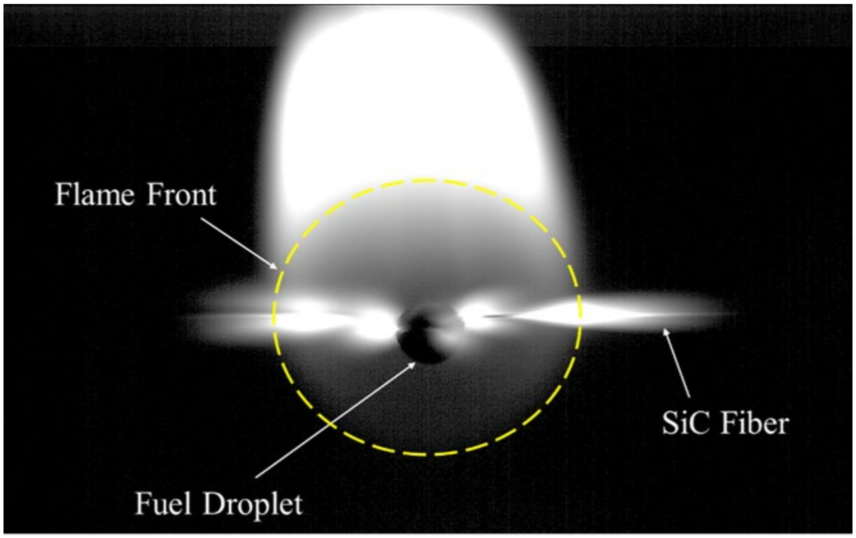


Figure 2.2 A typical image of an actual burning soy-based biodiesel droplet

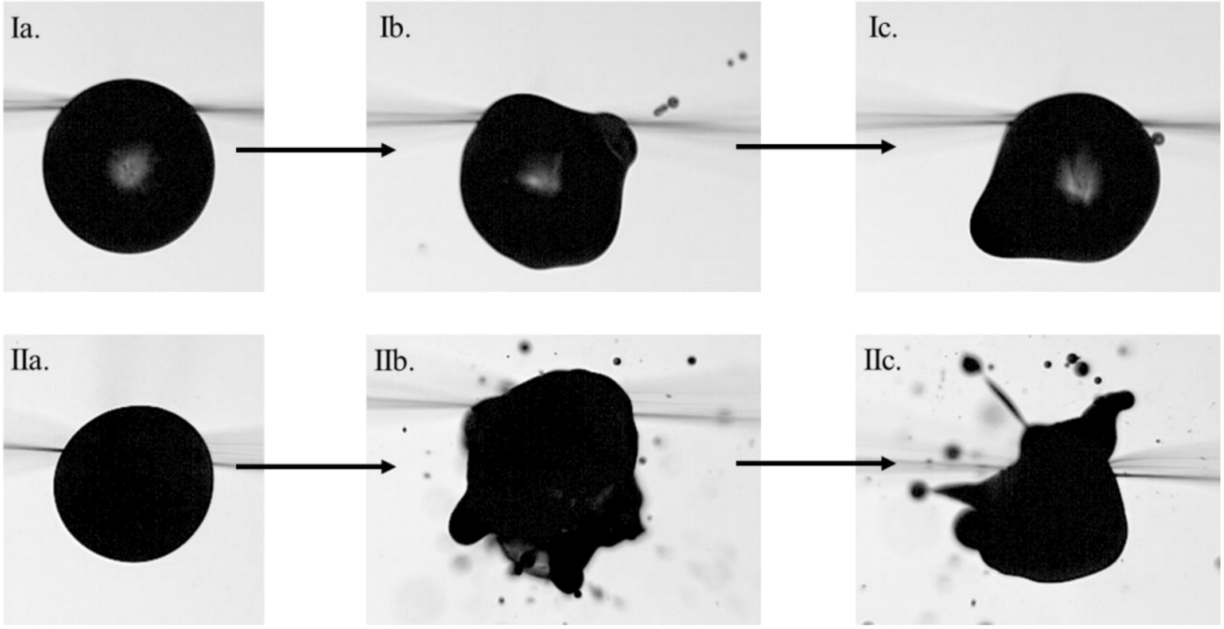


Figure 2.3 High-speed camera images showing distortion and microexplosion in Colorado (Ia, Ib, IC) and Texas (IIa, IIb, IIc)

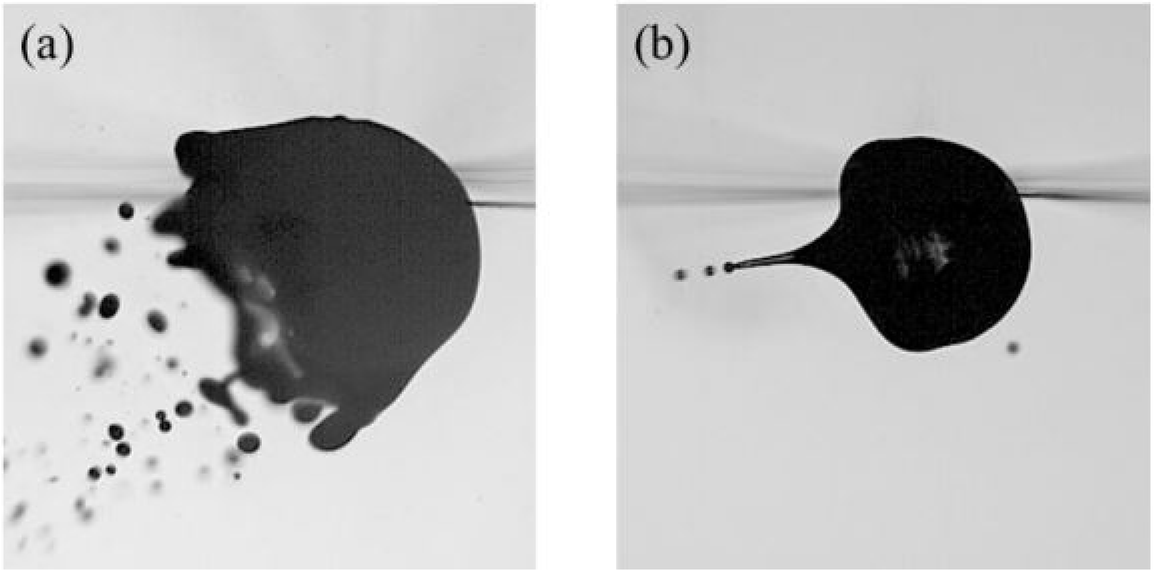


Figure 2.4 High-speed imaging of (a) Texas crude oil showing a balloon burst microexplosion and (b) Bakken crude oil showing a spitting microexplosion

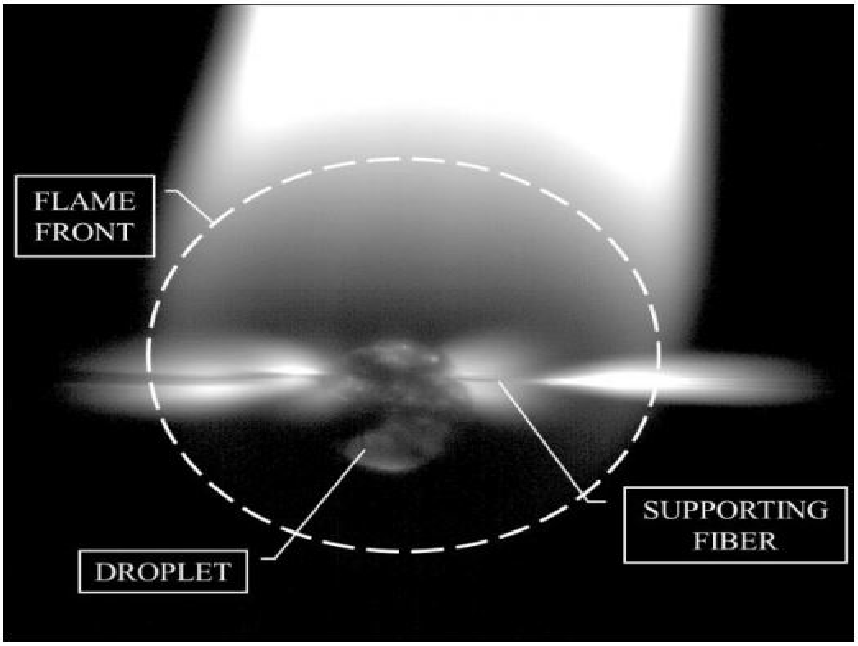


Figure 2.5 Flame structure of a Pennsylvania crude oil droplet

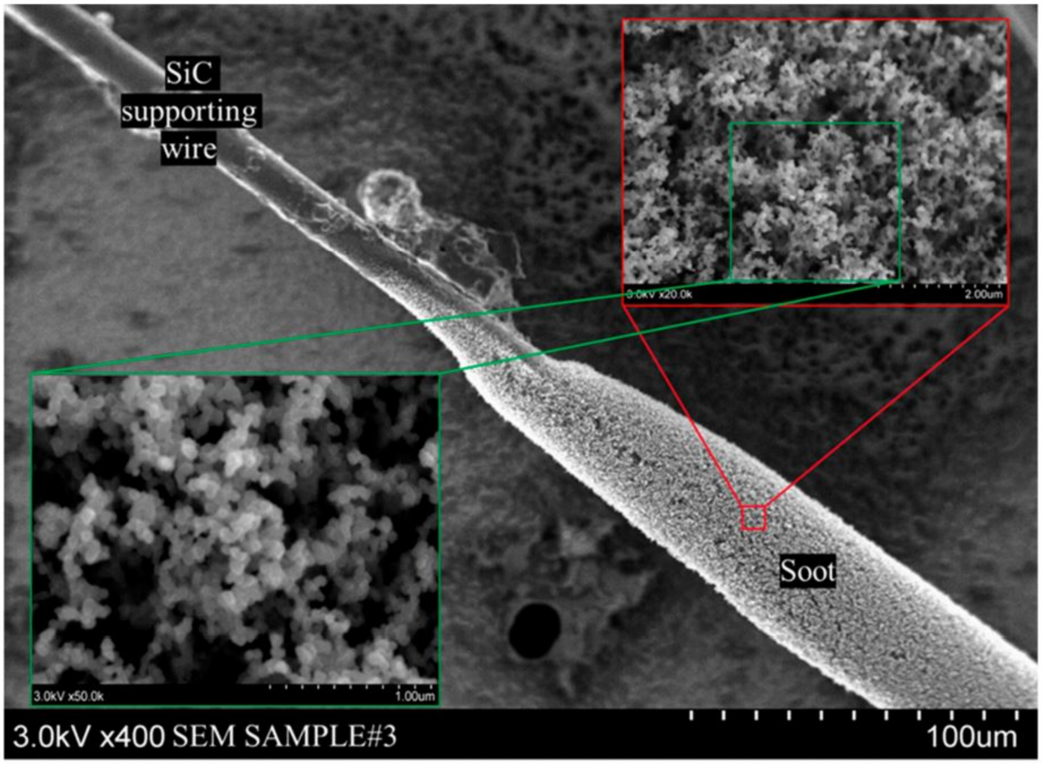


Figure 2.6 Soot sample from Colorado crude oil combustion experiment shown at various stages of magnification

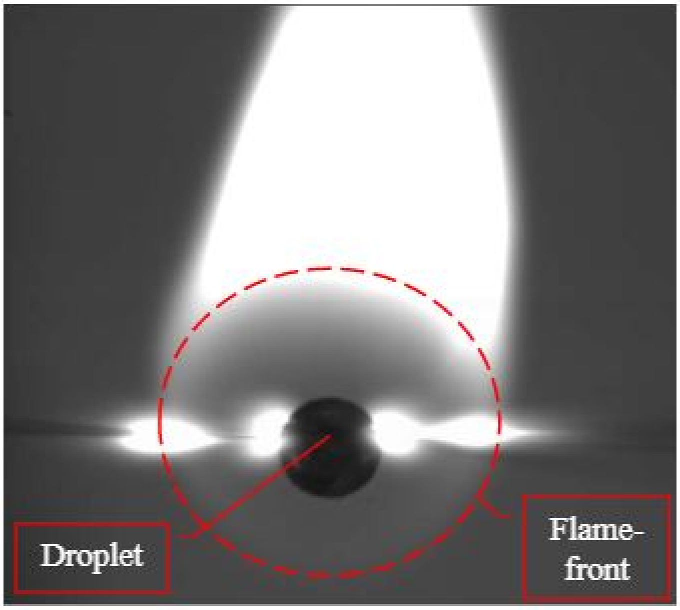


Figure 2.7 Flame structure of a 3% PBD5k-Pennsylvania crude fuel blend droplet undergoing combustion

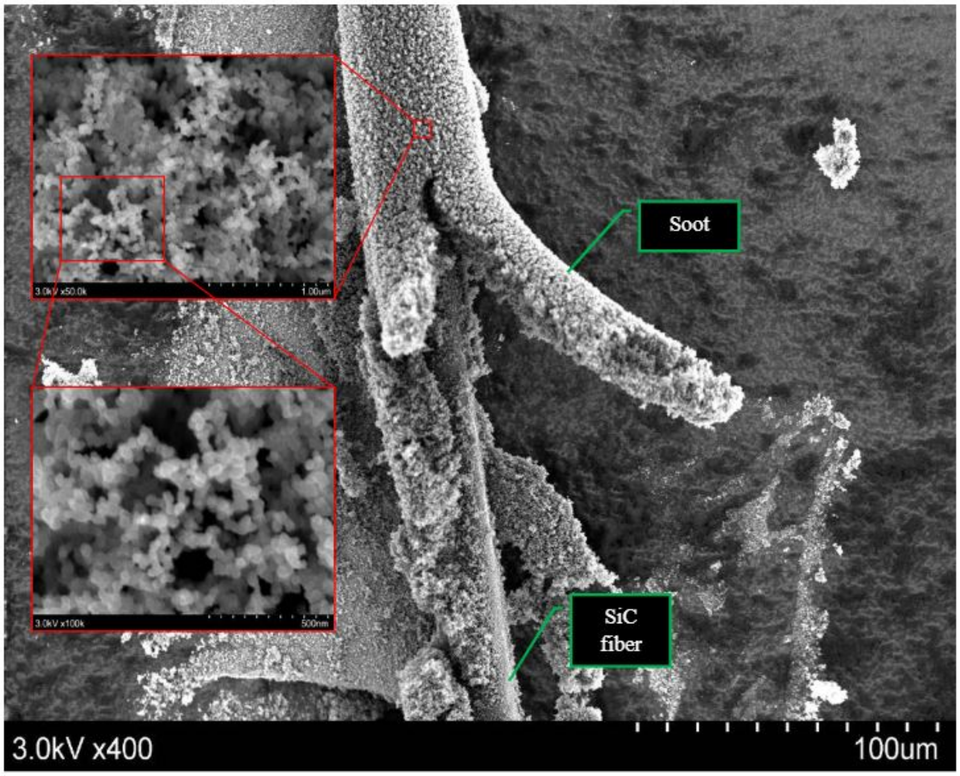


Figure 2.8 SEM images of 1% PBD5k-Bakken blend soot residue, showing soot structure at various levels of magnification. Individual soot particles can be seen

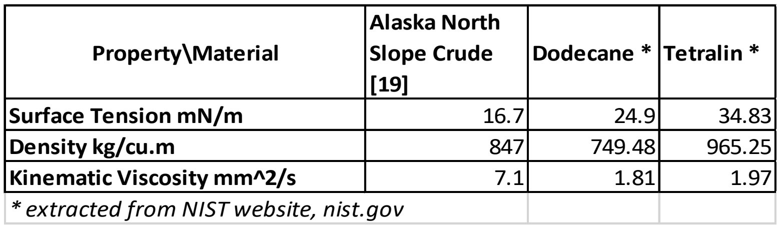
2.2 Splashing Surrogate

The Ohnesorge number (Oh) is a dimensionless parameter that relates the relevant flow and material property parameters for a liquid drop striking a solid surface.

$$Oh = \mu/\sqrt{\rho\sigma L}$$

Where μ = dynamic viscosity, ρ = density, σ = surface tension, L = characteristic dimension (usually diameter).

Table 2.1 Comparison of splashing parameters



Property\Material	Alaska North Slope Crude [19]	Dodecane *	Tetralin *
Surface Tension mN/m	16.7	24.9	34.83
Density kg/cu.m	847	749.48	965.25
Kinematic Viscosity mm^2/s	7.1	1.81	1.97
** extracted from NIST website, nist.gov*			

A surrogate blend of Dodecane and Tetralin will be used to mimic the splashing of crude oil. We need to match the Ohnesorge number of crude to that of the surrogate. For a droplet of any given diameter, a blend of 54.8% wt Dodecane and 45.2% wt Tetralin will match the density of the ANS crude in consideration. Droplets are of relevance here since turbulent breakup of crude oil mixed with dispersants results in droplets of 300µm to 1400µm size [19]. The Gambill method is used to determine kinematic viscosity of mixtures [20] and gives the kinematic viscosity of the surrogate as 5.45 mm^2/s. The surface tension of the blend would have to be manipulated by adding surfactants, which would need further experimentation.

After an initial surrogate is identified using the method outlined above, it will be fine-tuned using an experimental setup developed in an earlier project for MATC. This allows for droplets of various sizes to be imaged at high speeds as they strike a surface being maintained at a desired temperature.

Splashing experiments will be performed for Bakken crude samples and matched with the surrogate blend. The experiments will employ a solid, smooth impact surface at room temperature and at 330 °F, 450 °F, 680 °F, and 1000 °F, which are temperature cut-offs for naphtha, kerosene, diesel and VGO cuts. This will serve to establish a baseline for subsequent tests planned in the future.

2.3 Settling Characterization

Polymeric additives are used to modify different surrogate properties like viscosity, surface tension and burning rates. Stability of such surrogate-polymer suspensions over time is an object of investigation.

Manual tests have been performed to study the settling characteristics of polymeric additives in organic solvents like n-Decane and Dodecane, as well as Jet-A and diesel fuels. The technique consisted of preparing a suspension in a test tube, sealing it with a rubber stopper, and shaking it vigorously until the solution was well mixed. A note was made on when the suspension was prepared and what its constituents were, and the test tube was duly labeled and placed in a test tube stand. Periodic observations were manually made to see if the suspension was beginning to settle down and at what stage of settling it was on.

This technique is inconvenient and subjective and provides no hard data. Additionally, there are a very large number of potential polymeric additive candidates. There is moreover a large range of concentration for each of these for which they can be made into a suspension with a given solvent. Given the large number of variables and the large volume of experiments that needed to be accomplished, a system was devised by the end of year one to make the process fast and automatic, and which relied on a measurable attribute of the suspension.

Adding polymers like Polybutadiene (PBD), Polyaniline (PANI), and Graphene etc. makes clear solvents like Dodecane very opaque. It has also been observed that as the polymer settles down, the suspension starts to clear up. Therefore, if a given suspension is held in a test tube, and an LED is shined through it, how much light is transmitted through the test tube to the other side depends on what stage of settling the polymer is on. If it’s still completely mixed, no light gets through. If it’s completely settled down, most of the light gets through, and various degrees of interpolation between the two cases. This light is intercepted by a phototransistor at the other end, which generates a signal proportional to the amount of light it receives.

One experimental array has space for 33 individual test tubes and leaving three tubes for ambient light detection and calibration purposes, is able to test 30 suspensions simultaneously. At this moment, two such arrays have been constructed. Each experiment has five outputs, therefore there are 150 outputs per array. A multiplexer (MUX) system has been designed and constructed to switch between different experiments and read data from them, instead of reading data from all experiments simultaneously. The data acquisition system uses an Arduino ATMEGA 2560 and a Raspberry Pi as a data logger. A smaller version of suspension stability analyzer was designed, fabricated and instrumented. This system is more compact. It is intended to be deployed for analyzing suspension stability in a temperature-controlled environment (from 0℃ to 50℃). It is also intended to be deployed for analyzing suspension stability in a pressure-controlled environment (from 1 bar to 10 bar). This led to better insight for settling characteristics of carbon-based additives at the bottom of crude oil railcar tankers, where pressures are higher, and at different ambient temperatures. This setup can be used to test suspension stability at various climate conditions during crude oil transport.

From the experimental result, Acetylene black has also been found to form highly stable suspensions with hydrocarbon-based fuels without emulsifiers or other stabilizing agents. This has also been found to be true for crude oil. Settling characteristics of idealized spherical ceramic particles have been generated. This data is expected to help in exploring basic physics behind settling of solid particles in liquid media. Using the suspension stability analyzer, data was generated for settling characteristics for metal oxide and carbon based nanofuels with petrodiesel and biodiesel. This data is expected to help in exploring basic physics behind settling of realworld nanofuels and nanofluids, which will further help in developing nano-additives for realistic crude oils and their surrogates. Moreover, settling characteristics of metal oxide and carbon-based nanoparticles at low and high temperatures are being generated, which will help in in exploring the stability of nanoparticles in crude oil at realistic winter and summer temperature conditions during transport.

The setup developed for suspension stability analysis was used for quantification of settling properties of graphene in dodecane, which resulted in a conference publication. Also settling characteristics of carbon and Metal Oxide nanofuels were also investigated and published as a conference paper.

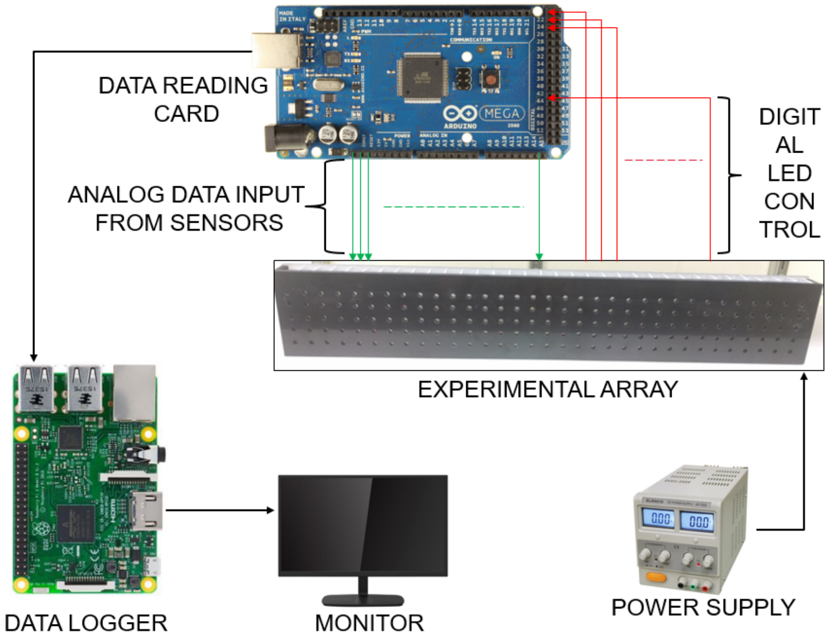


Figure 2.9 Experimental layout for suspension stability analysis

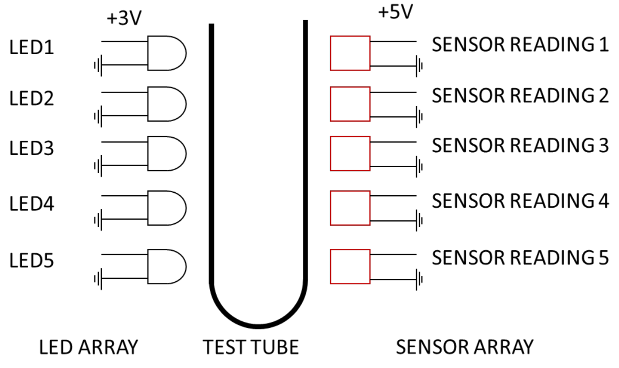
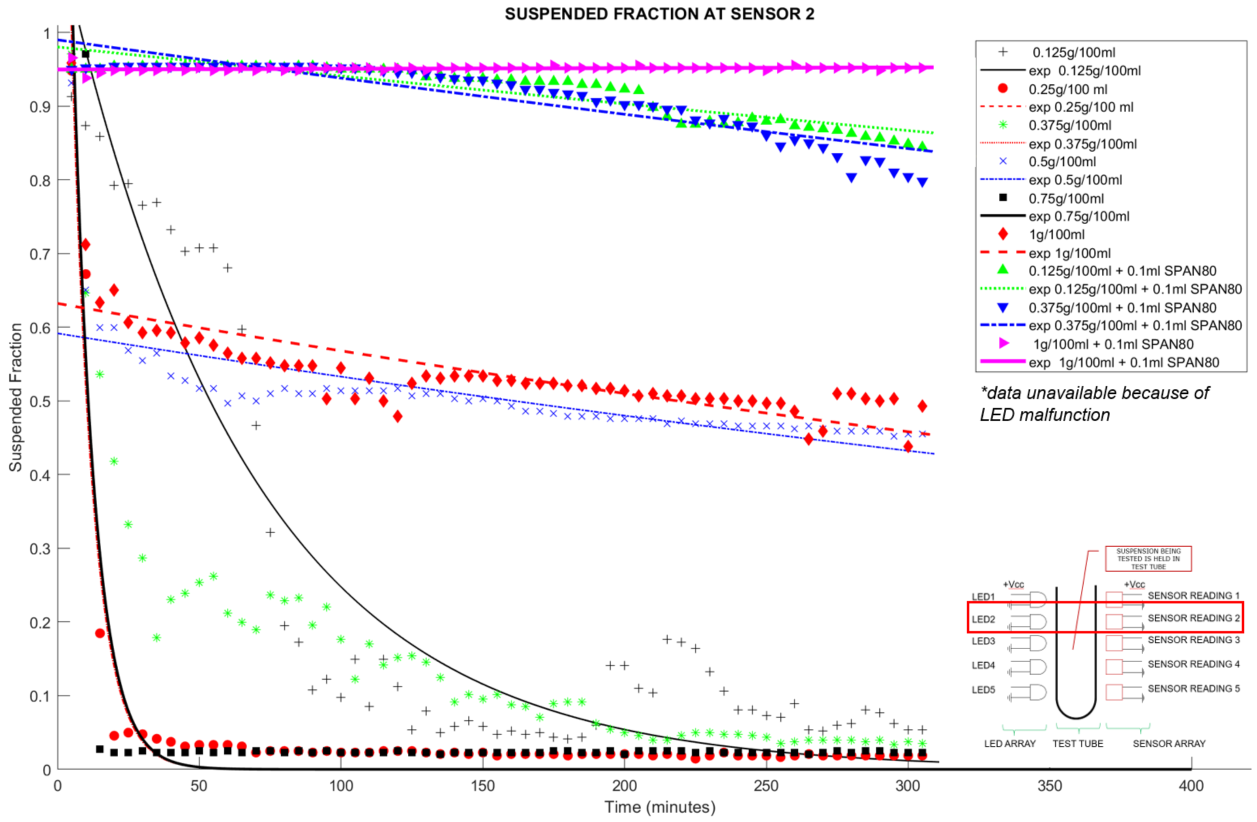


Figure 2.10 Data output from one experimental block



**data unavailable because of LED malfunction*

Figure 2.11 Example of results: settling characteristics of graphene in dodecane, mesured at Sensor 2

Additional work is underway to develop mathematical models of the process. Ongoing efforts will relate the suspension properties of standard spherical particles in distilled water, which will lead to further insight on the physical mechanics behind the process. Another variation of the suspension stability analysis setup will also lead to more insight on stability of suspensions under high pressures.

Chapter 3 Collaboration and Publications

3.1 Collaboration

The hardware for the settling has been constructed and is generating data. One of the settling arrays, along with its data acquisition and logging system, is being used by a visiting scholar. He reports to Prof Daniela Becker at Center of Technological Sciences, Santa Catarina State University, Joinville, Santa Catarina, Brazil.

Assistant Professor Mehdi Esmaeilpour (Marshall University, Mashalltown, WV, USA) is involved in post-processing of the combustion data as well as preparation of technical manuscripts.

3.2 Publications

All papers and posters listed here have been possible because of the work undertaken until December 31,2019.

Research papers submitted:

- G Singh, M Esmaeilpour, A Ratner. “The Effect of Acetylene Black on Droplet Combustion and Flame Regime of Petrodiesel and Soy Biodiesel”. Fuel 246, 108-116.
- G Singh, M Esmaeilpour, A Ratner. “Investigation of combustion properties and soot deposits of various US crude oils”. Energies 12 (12), 2368.
- G Singh, E Lopes, N Hentges, D Becker, A Ratner. “Experimental Investigation of the Settling Characteristics of Carbon and Metal Oxide Nanofuels”. Journal of Nanofluids 8 (8), 1654–1660.
- G Singh, M Esmaeilpour , A Ratner. “Effect of carbon-based nanoparticles on the ignition, combustion and flame characteristics of crude oil droplets”. Energy, 117227.
- G Singh, M Esmaeilpour, A Ratner. “Effect of polymeric additives on ignition, combustion and flame characteristics and soot deposits of crude oil droplets”. arXiv preprint arXiv:1911.00392.
- X Xing, G Singh, J Bhama, A Ratner. “Wireless Power Transfer Systems Based on LCC-Compensated Topology for Left Ventricular Assist Device (LVAD) Battery Charging Application”. Journal of Low Power Electronics 15 (2), 144-159.
- G Jenson, G Singh, J Bhama, A Ratner. “A refillable hydrogel battery: construction and characterization”. Journal of Energy Storage 23, 504-510.

Conference papers accepted:

- G Singh, S Pitts, E Lopes, A Ratner. “Settling Characteristics of Polymeric Additives in Dodecane”. Paper Number IMECE2018-88555. ASME 2018 International Mechanical Engineering Congress and Exposition. Track: Fluids Engineering. Nov 11-15, 2018.
- G Singh, M Esmaeilpour, A Ratner. “Effect of carbon nanoparticles on the droplet evaporation characteristics of crude oil”. Western States Combustion Institute Fall 2019. Meeting, Albuquerque, NM. October 14-15, 2019.
- G Singh, N Hentges, D Johnson, A Ratner. “Experimental investigation of combustion behavior of biodiesel-water emulsion”. ASME. ASME International Mechanical Engineering Congress and Exposition. November 8 – 14, 2019.
- G Singh, N Hentges, D Johnson, A Ratner. “Experimental investigation of water emulsion fuel stability”. ASME. ASME International Mechanical Engineering Congress and Exposition. November 8 – 14, 2019.

Posters accepted:

- G Singh, S Pitts, A Ratner. “Droplet Combustion Characteristics for Soy-based Biodiesel with Polymeric Additives”. 2018 Spring Technical Meeting of the Central States Section of The Combustion Institute. 2018 CSSCI Spring Technical Meeting. May 20- 22, 2018.

Presentation accepted:

- G Singh, M Esmaeilpour, A Ratner. Effect of polymer addition on burning rate of Pennsylvania crude. 11th US National Combustion Meeting. 24-27 March 2019.

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