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Reducing Flammability for Bakken Crude Oil for Train Transport - Phase I

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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 (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. Work in the second year is about continuing the work from the first year and producing results that would help accomplish the goals of a larger, five-year project to improve fire safety during transportation by adding long chain polymers to crude oil before shipping. Previous research done by Professor 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. For the second year, the experimental droplet combustion and post processing software has been refitted and upgraded, and used to analyze combustion characteristics of acetylene black nanopowder in diesel and biodiesel fuels. This work has resulted in a manuscript that has been submitted for publication. Crude oil samples from various US petroleum production sites (including Bakken) have been sources, and have been similarly analyzed for their combustion behavior. This work is expected to help identify combustion surrogates, which are necessary for their homogeneity, reproducibility, and better optical properties. Establishment of reliable surrogates will allow the research to proceed into coming years, where various additives in different concentrations will be added to such surrogates to make suspensions, in order to modify their properties in order to minimize splashing and propensity towards ignition. Stability of such suspensions will be tested using methods and techniques developed in year 1.

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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

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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 Professor 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. By the end of September 30, 2018, research efforts continued the work that would help accomplish the goals of a larger, five-year project to improve fire safety during transportation by adding long chain polymers to crude oil before shipping. The experimental droplet combustion and post processing software has been refitted and upgraded. It was used to analyze combustion characteristics of acetylene black nanopowder in diesel and biodiesel fuels. This work has resulted in a manuscript that has been submitted for publication. This work is expected to help identify combustion surrogates, which are necessary for their homogeneity, reproducibility, and better optical properties. Establishment of reliable surrogates will allow the research to proceed into coming years, where various additives in different concentrations will be added to such surrogates to make suspensions, in order to modify their properties in order to minimize splashing and propensity towards ignition. Stability of such suspensions will be tested using methods and techniques developed in year 1.

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 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 1 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 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 expected that addition of long chain polymers to crude oil will 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 1 focused heavily on quantification of crude oil combustion properties. 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 submitted for publication. Crude oil samples from various US oil sources have been obtained and work is underway to similarly quantify their combustion properties.

Year 2 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. Additional work is underway to develop mathematical models of the process.

It is expected that by the end of next year, we will finish establishing a reliable combustion surrogate for crude oil and complete the necessary preliminary work for identifying a splashing surrogate for the same.

Chapter 2 Research Approach & Methodology

2.1 Crude Oil Surrogate

One of the experimental techniques central to this project will be imaging. Crude oil does not have the optical clarity necessary for this. Additionally, crude oil is composed of thousands of chemical species, and their proportion varies with well head location, season, year of production etc. It is very hard to ensure reasonable consistency of Bakken (or any other) crude oil through the five years for which this project is planned.

For these reasons, a surrogate blend would be used to mimic the combustion performance and splashing properties of crude oil. This blend will be composed of high purity hydrocarbon compounds and will ideally be optically clear. It will also allow for high degree of homogeneity and reproducibility of exact chemical composition. Splashing and combustion behavior of crude oil droplets are governed by disparate parameters of interest, meaning different surrogates would be required for them.

Literature review has concluded there is no existing research that identifies surrogates for crude oil droplet combustion or splashing. However, crude oil can be broken down into several constituents: Light ends, Naphtha, Kerosene, Diesel, Vacuum Gas Oil (VGO), and Vacuum Residue (please see table 2.1).

Table 2.1 Assay report for Bakken Crude, compared to West Texas Intermediate (WTI) and Light Louisiana Sweet (LLS). Taken from [18]

LIGHT SWEET CRUDE ASSAY COMPARISON

		Bakken (1)	WTI	LLS
API Gravity	Degrees	> 41	40.0	35.8
Sulfur	Weight %	< 0.2	0.33	0.36
Distillation Yield:	Volume %			
Light Ends	C1-C4	3	1.5	1.8
Naphtha	C5-330 °F	30	29.8	17.2
Kerosene	330-450 °F	15	14.9	14.6
Diesel	450-680 °F	25	23.5	33.8
Vacuum Gas Oil	680-1000 °F	22	22.7	25.1
Vacuum Residue	1000+ °F	5	7.5	7.6
Total		100	100.0	100.0
Selected Properties:				
Light Naphtha Octane	(R+M)/2	n/a	69	71
Diesel Cetane		> 50	50	49
VGO Characterization (K-Factor)		~ 12	12.2	12.0

Note: (1) Properties are approximate, based on available assay information.

If we can identify surrogates for each of these constituents, a mixture made from these surrogates will behave as an appropriate surrogate for crude oil. As such, no existing research identifies surrogates for these products.

2.1.1 Combustion Surrogate

Such a surrogate will be identified via experimentation. This will involve using an experimental setup (see fig 2.2), also developed for an earlier MATC project, which allows high speed imaging of droplets as they evaporate, ignite and undergo combustion.

During testing and training for the next phase of this project, which is related to experimentally determining combustion surrogates for Bakken crude, it was felt that the droplet combustion experimental setup and the associated image post-processing software needed several improvements in the interest of better accuracy. Several key components of the droplet combustion system have been upgraded or replaced, with significant enhancement to system life and reliability. “Spotlight” image post-processing software, which was previously being used, has been replaced in favor of a better-supported, open-source ImageJ/Fiji image post-processing software after it proved to be more accurate in several tests.

The upgraded hardware and software was used to evaluate acetylene black (AB), a nanopowder, for its effects on diesel and biodiesel. It was found to be effective against preventing microexplosions which is an event that aggravates droplet burning regimes, which means AB would be potential use to ensure safer droplet combustion in crude oil.

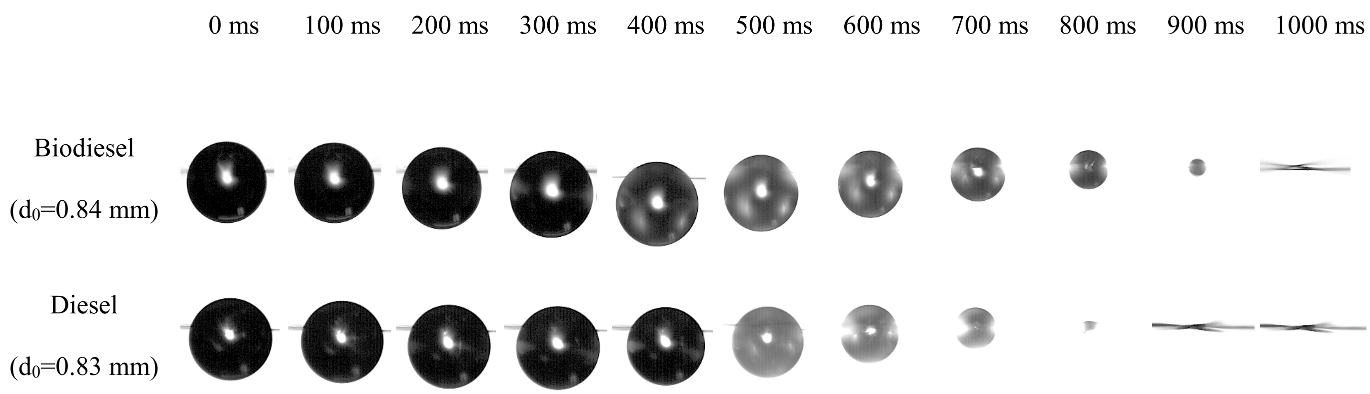

Figure 2.1 Time evolution image of a droplet during combustion for pure petrodiesel and soy-based biodiesel droplets

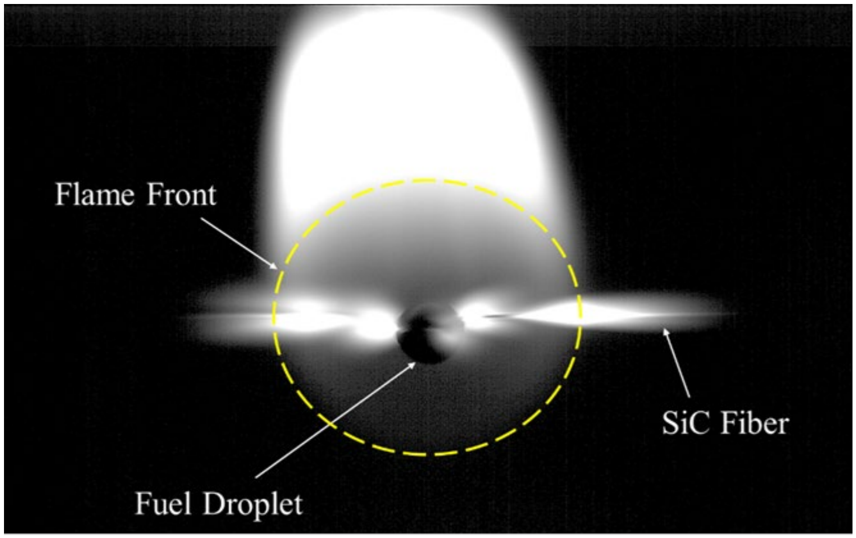

Figure 2.2 A typical image of an actual burning soy-based biodiesel droplet

Future work focuses on obtaining a reliable combustion surrogate for Bakken crude oil. Naphtha cut is further refined into gasoline and can be approximated as gasoline itself. Similarly, Kerosene/Diesel cut can be approximated as Jet-A or JP-8. Vacuum residue, which is mostly asphaltenes and coke, can be approximated with lab grade powdered charcoal, which can also be replaced with an optically clear polymer. Ethanol or methanol can serve as highly volatile and highly flammable surrogate for light ends. Ab-initio research is required for identifying appropriate VGO surrogate. High API, high molecular weight components like Tetralin, Naphthalene, Indene, and Pentacosane can act as surrogate constituents. Experimentation is needed to determine a correct proportion for these.

Gasoline surrogate as suggested by Gauthier [16] consisting of 63% iso-octane, 20% toluene, 17% n-heptane will be used. Drexel substitute [17] consisting of 43.2% n-dodecane, 26.8% iso-cetane, 15% methylcyclohexane, and 15% 1-methynaphthalene will be used as a substitute for JP-8/Jet-A.

Various crude oil samples have been obtained so far, including those from Bakken oil wells. These would be analyzed for their responses to different polymeric additives, with the aim of increasing their ignition delay and decreasing their combustion rates.

2.1.2 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 2.2 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]. Using the Gambill method to determine kinematic viscosity of mixtures [20] 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.

2.2 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 end of year 1 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 5 outputs, therefore there are 150 outputs/arrays. 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. Data acquisition system uses an Arduino ATMEGA 2560 as data acquisition system and a Raspberry Pi as a data logger.

The setup developed for suspension stability analysis was used for quantification of settling properties of graphene in dodecane, which resulted in a conference publication.

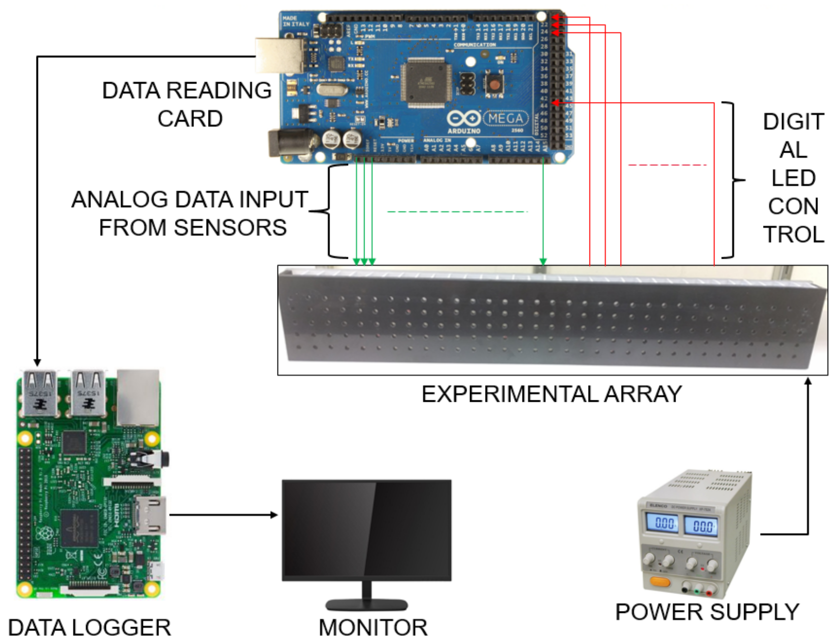

Figure 2.3 Experimental layout for suspension stability analysis.

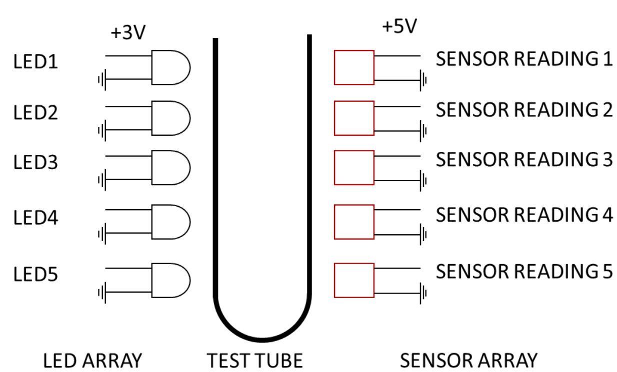

Figure 2.4 Data output from one experimental block

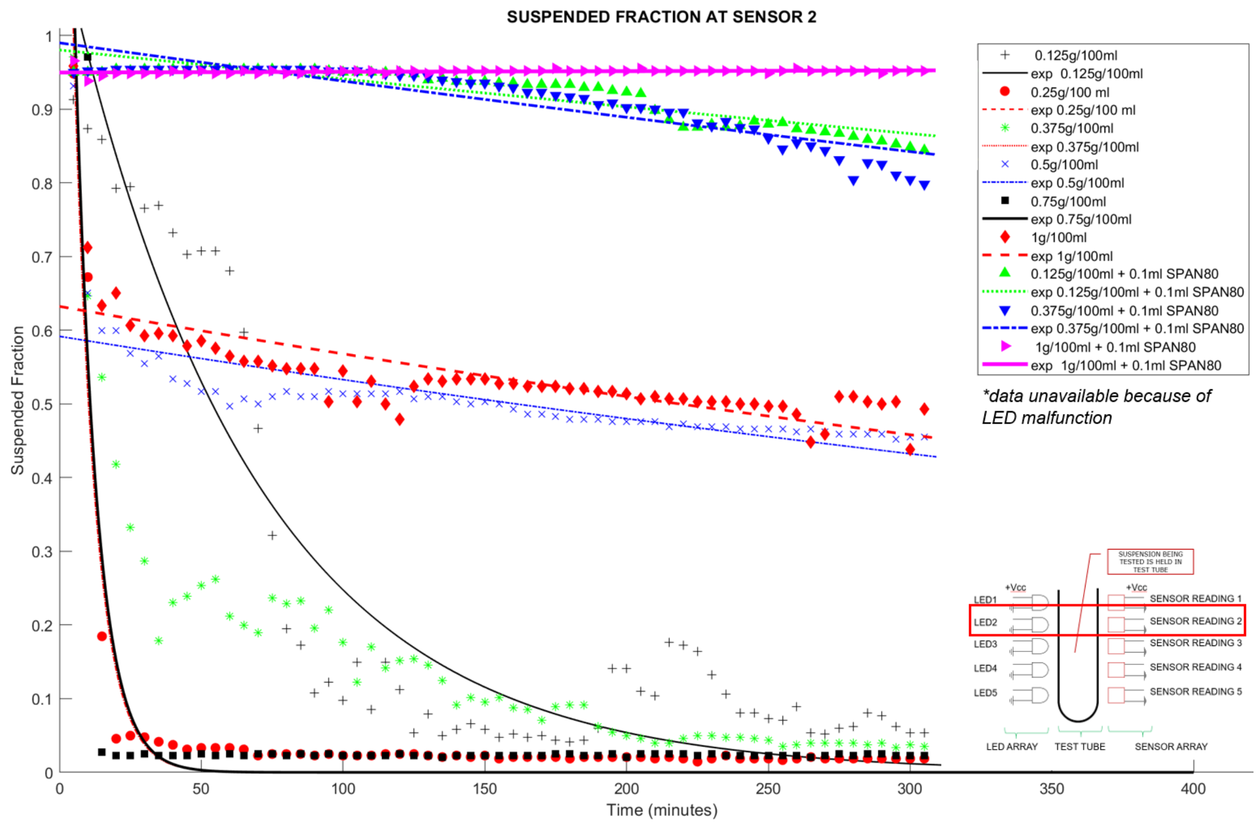

Figure 2.5 Example of results: settling characteristics of graphene in dodecane, measured at Sensor 2

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 the Center of Technological Sciences, Santa Catarina State University in Joinville, Santa Catarina, Brazil.

3.2 Publications

All papers and posters listed here have been possible because of the work undertaken until September 30, 2018.

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. Elsevier. Submitted December 2018
- 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. Electric Power Systems Research. Elsevier. Submitted November 2018
- G Jenson, G Singh, J Bhama, A Ratner. A refillable hydrogel battery: construction and characterization. Journal of Power Sources. Submitted October 2018

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.

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.

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