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

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2021

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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 the result is usually 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 as well. As of December 31, 2020, 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 and carbon-based nanoparticles 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 and settling characteristics of carbon-based nanoparticles (acetylene black, multi-walled carbon nanotube, graphene nanoparticles) in Bakken crude oil, as well as renewable jet fuel. These works have resulted in several published manuscripts and are expected to help model the combustion characteristics of crude oil. Moreover, these results are unique. These works will also help to evaluate splashing characteristics of crude oil and how to modify them to make crude oil transport safer.

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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
AB = Acetylene Black
MWNT = Multi-walled carbon nanotubes
GNP = Graphene nano particles

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 the result is usually 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 as well. This report covers efforts through December 31, 2020, which 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 nanoparticles to crude oil before shipping. Specifics include using the upgraded software for post-processing of experimental droplet combustion data to analyze combustion characteristics of carbon-based nanoparticles (acetylene black, multi-walled carbon nanotube, graphene nanoparticles) in Bakken crude oil, as well as renewable jet fuel with settling characteristics. This work has resulted in one journal paper, two conference 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 help to evaluate the splashing characteristics of crude oil and how to modify them 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 3 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-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.

Work undertaken during year 3 focused heavily on quantification of crude oil combustion properties and settling characteristics of colloidal suspension. The upgraded experimental setup and post-processing software were used to analyze the combustion properties of acetylene black (AB) and multi-walled nanotubes (MWNT) in Bakken crude, which resulted in a manuscript that has been published. These techniques were also used to analyze the combustion and settling characteristics of graphene nano particles (GNP) in renewable jet fuel and carbon quantum dot in jet fuel. Soot deposits of Bakken crude oil were also investigated. This work has resulted in one journal paper, two conference 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 help to evaluate the splashing characteristics of crude oil and how to modify them to make crude oil transport safer. It is expected that by the end of next year we will complete the necessary work for identifying a splashing surrogate and continue investigations to modify the splashing behavior.

Chapter 2 Major Activities and Results

2.1 Combustion data generation

Combustion data was generated for Bakken crude oils, renewable jet fuel, and jet fuel (Jet-A) colloidal suspension of carbon-based nanoparticles. The settling characteristics of nano fuels such as renewable jet fuel with GNP were also investigated.

These experimental data provide a wider look into modeling the combustion behavior of crude oil and other liquid fuel. First, using the upgraded droplet combustion setup, combustion data was generated for the combustion characteristics of Bakken crudes with AB and MWNT. These data aid in further evaluation of potential combustion substitutes. Moreover, these data will help evaluate potential splashing substitutes carried out in the next phase. This information is needed before any attempt is made to modify these crude oils' characteristics.

Combustion data from crude oil colloidal suspensions, made using carbon-based nanoparticles (AB, MWNT), was generated using the upgraded droplet combustion setup. Bakken crude was analyzed for its combustion properties. Also, combustion data was generated for renewable jet fuel with GNP. Combustion properties of nano fuels were found to be significantly different and might need different control strategies to increase ignition delay and decrease combustion rates. These data show that suppression of microexplosions can be achieved in crude oil with the addition of nanoparticles, leading to better crude oil fire safety. It was also found that very small amounts of nanomaterials are required to achieve a significant increase in combustion rates for crude. The ignition delay and total combustion time can be increased with the addition of nanoparticles in crude, and the addition of GNP in renewable jet fuel decreases the combustion rate, ignition delay, and total combustion time. Larger soot formations are also observed with an increase of GNP loadings. The combustion data for jet fuel (Jet-A) with carbon quantum dot will be post-processed and analyzed, and the results will be formed into a publishable manuscript. These results will aid in further evaluation of potential splashing and combustion substitutes, as well as future modeling of the combustion behavior of crude oil and liquid fuel and how to modify their combustion characteristics.

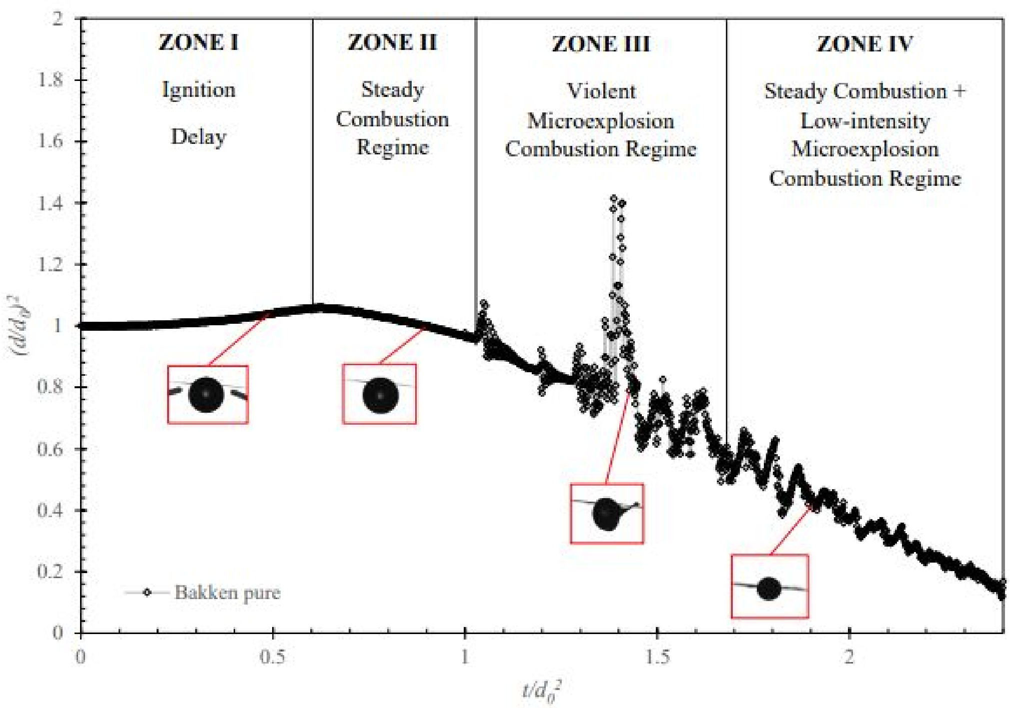


Figure 2.1 Evolution of normalized diameter $(d/d_0)^2$ with normalized time $t/d_0{}^2$ for pure Bakken crude oil

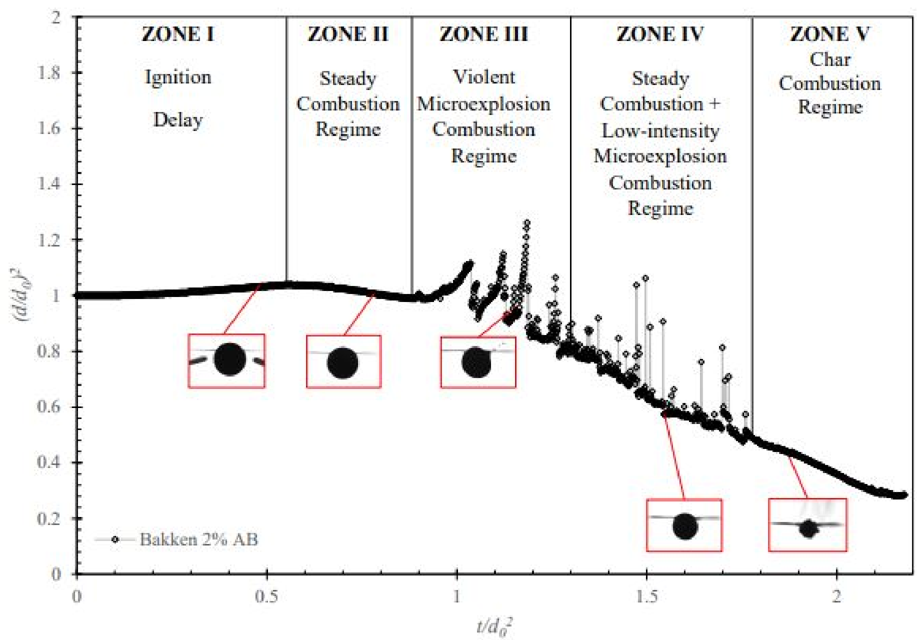


Figure 2.2 Evolution of normalized diameter $(d/d_0)^2$ with normalized time $t/d_0{}^2$ for Bakken crude oil 2% AB w/w particle loading

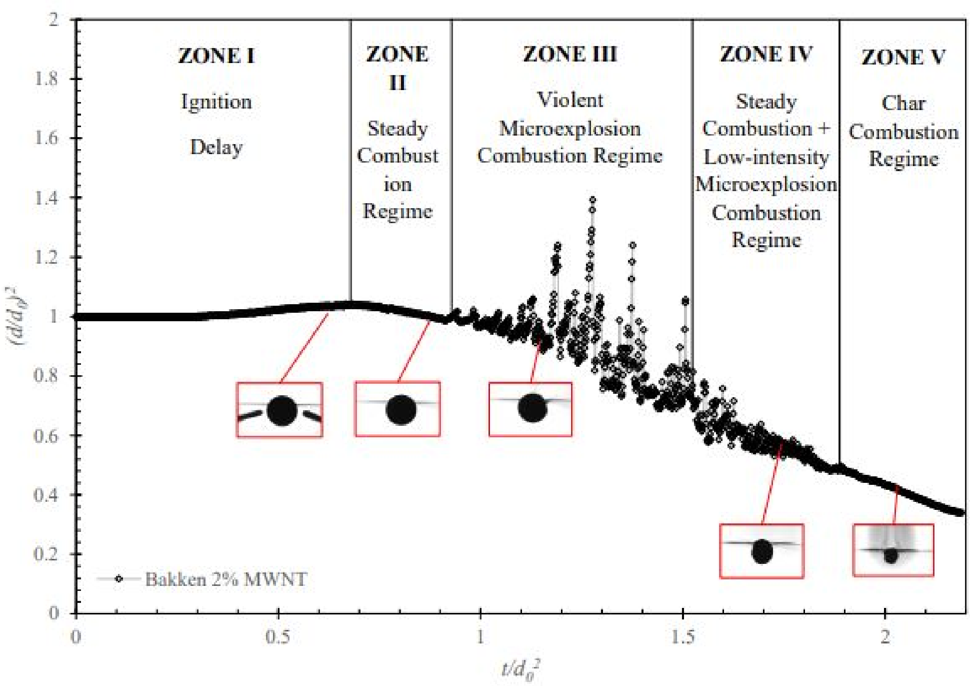


Figure 2.3 Evolution of normalized diameter $(d/d_0)^2$ with normalized time $t/d_0{}^2$ for Bakken crude oil 2% MWNT w/w particle loading

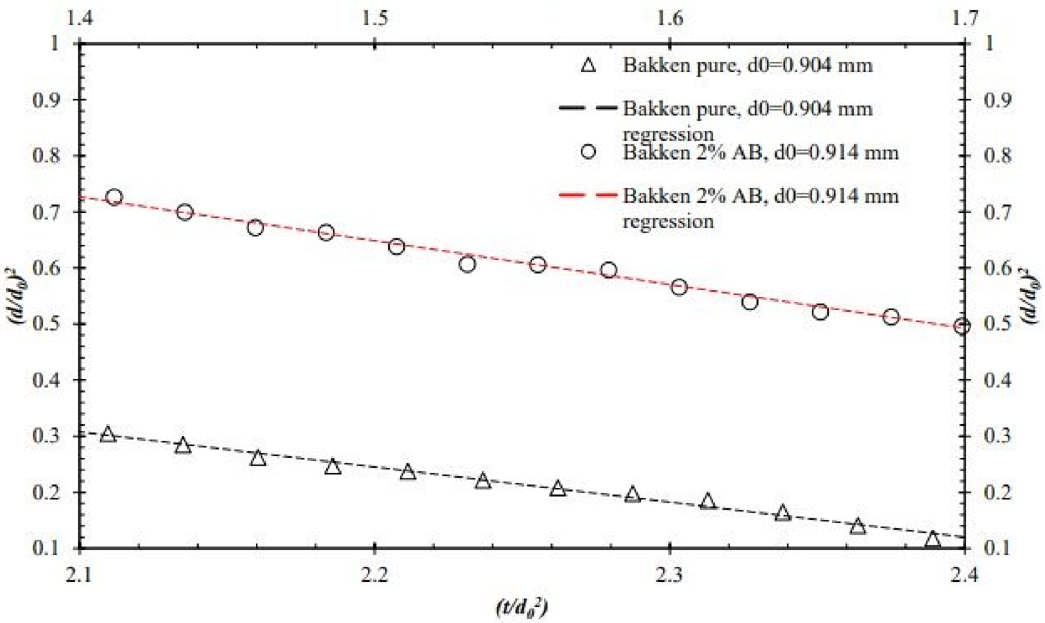


Figure 2.4 Zone IV comparison between Bakken crude and Bakken crude at 2%AB particle loadings

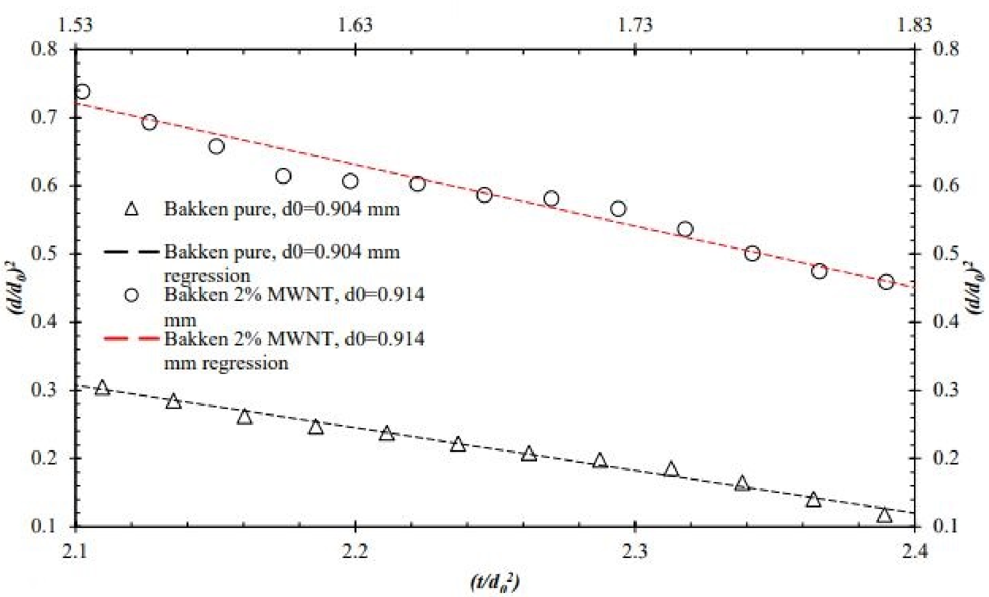


Figure 2.5 Zone IV comparison between Bakken crude and Bakken crude at 2%MWNT particle loadings

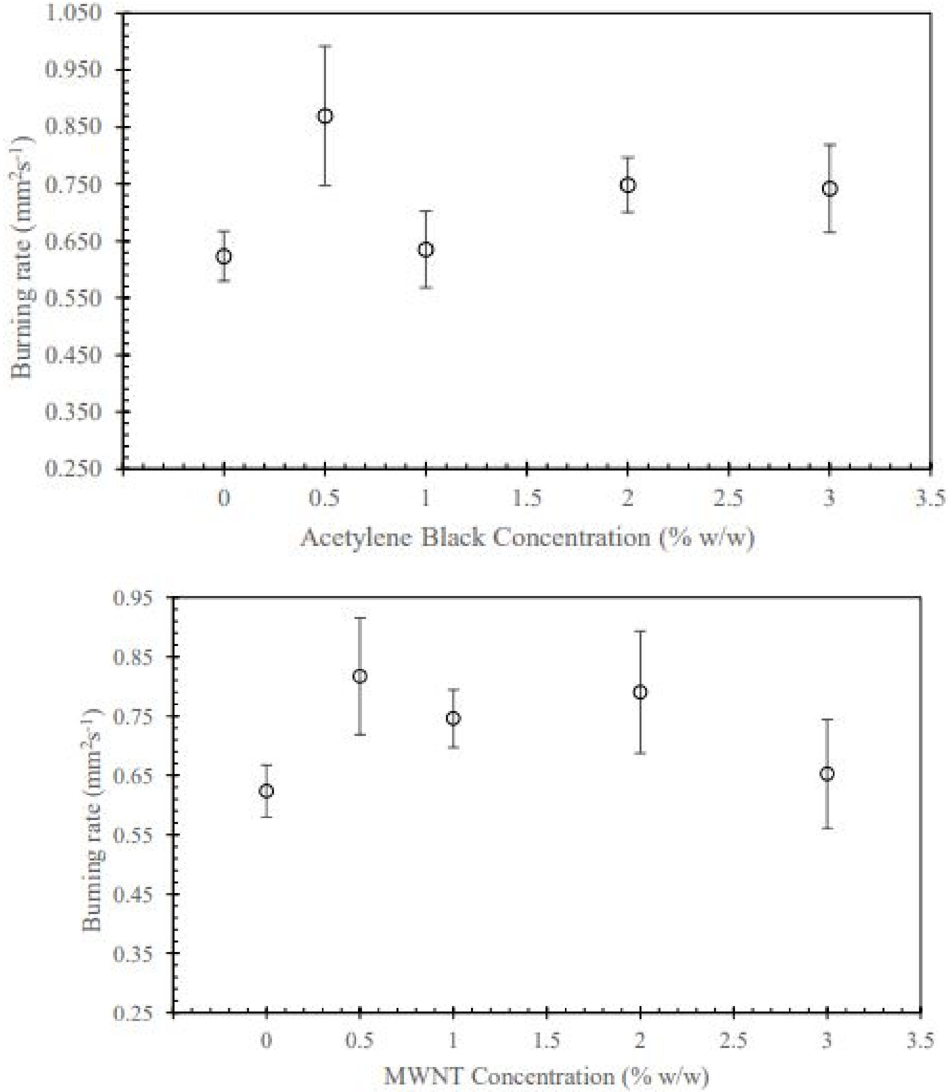
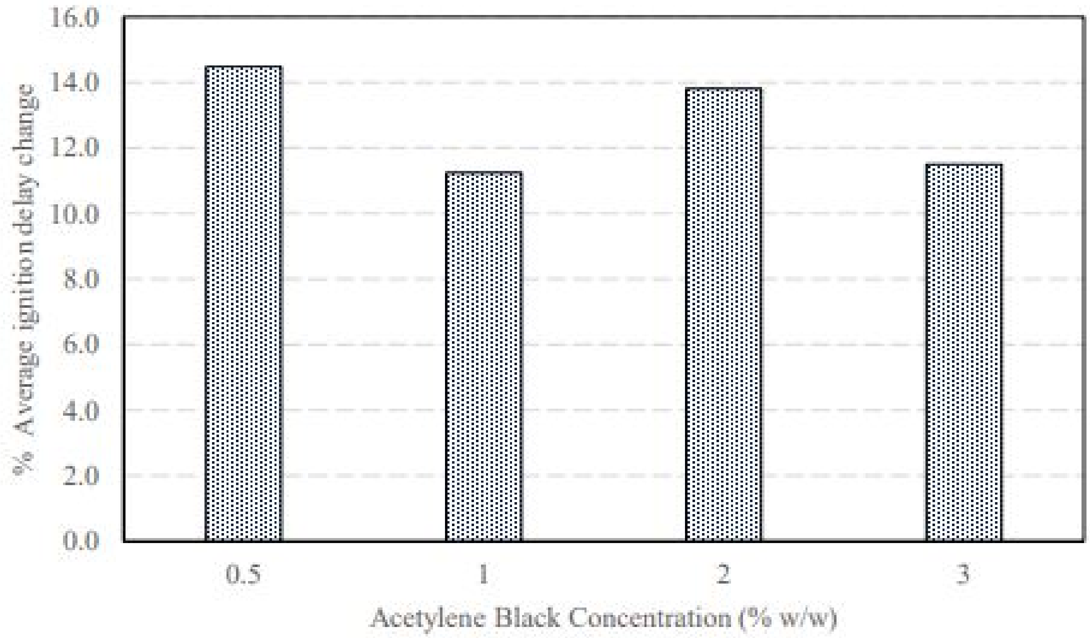


Figure 2.6 Comparison of the burning rates of Bakken crude with different mass concentrations of AB and MWNT



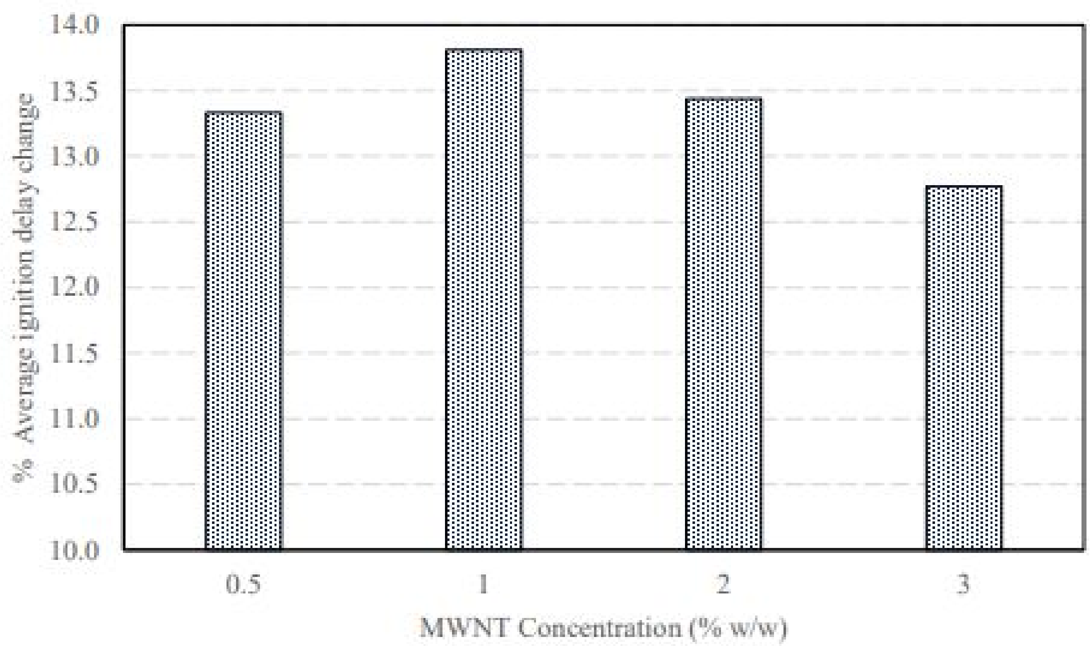


Figure 2.7 Change in average ignition delay time for Bakken crude oil at different particle loadings of AB and MWNT

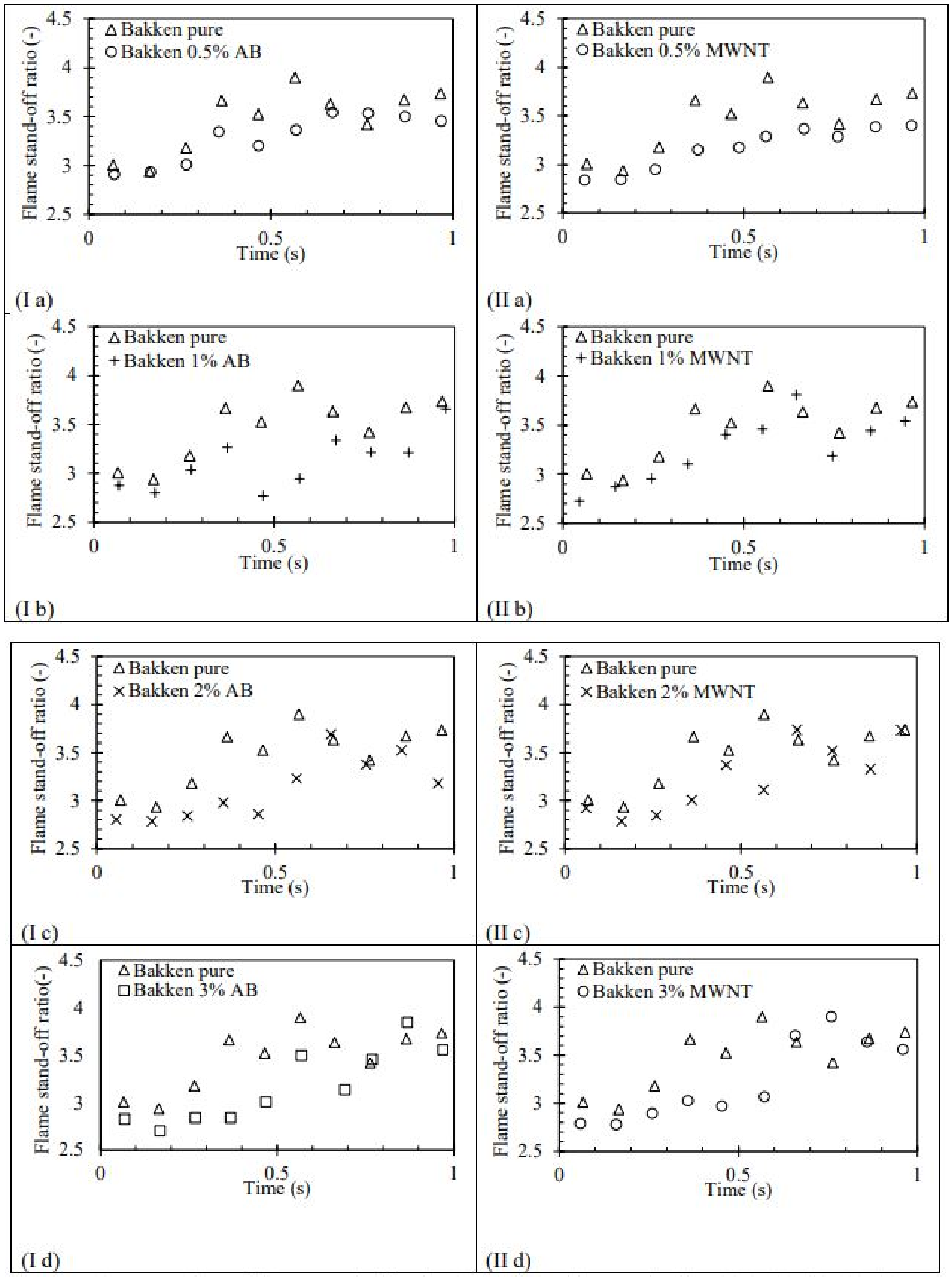


Figure 2.8 Comparison of flame stand-off ratios (FSR) for Bakken crude oil at (a) 0.5%, (b) 1%, (c) 2%, and (d) 3% w/w particle loadings of AB (I) and MNWT (II)

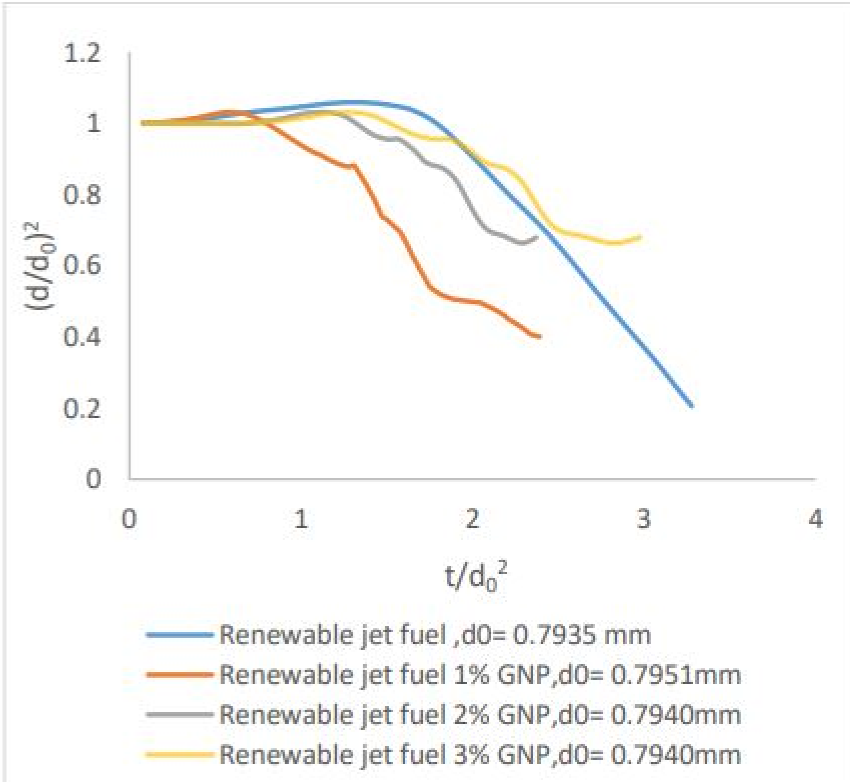


Figure 2.9 Normalized droplet area evolution for renewable jet fuel with different GNP loadings

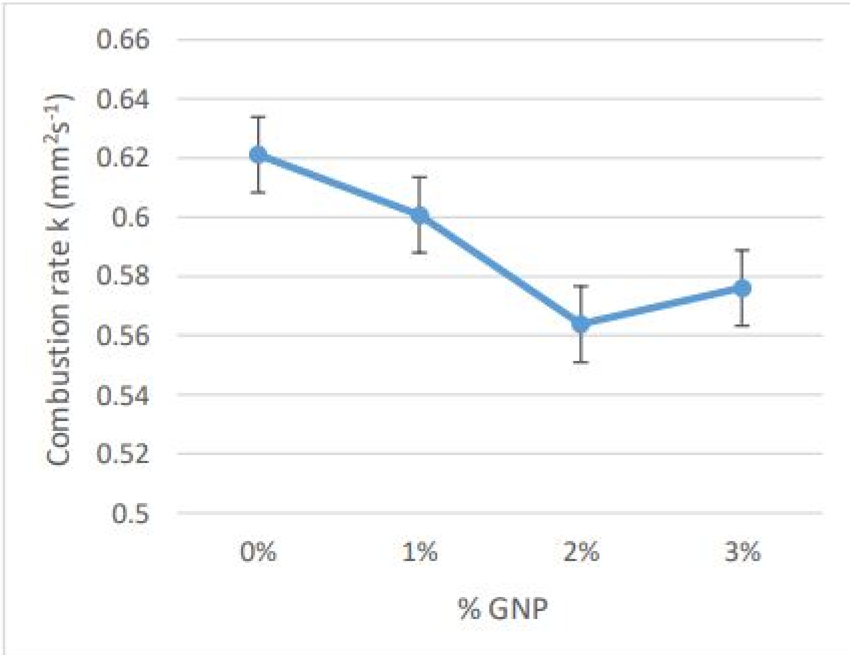


Figure 2.10 Combustion rate trends for pure renewable jet fuel and renewable jet fuel at various GNP loadings

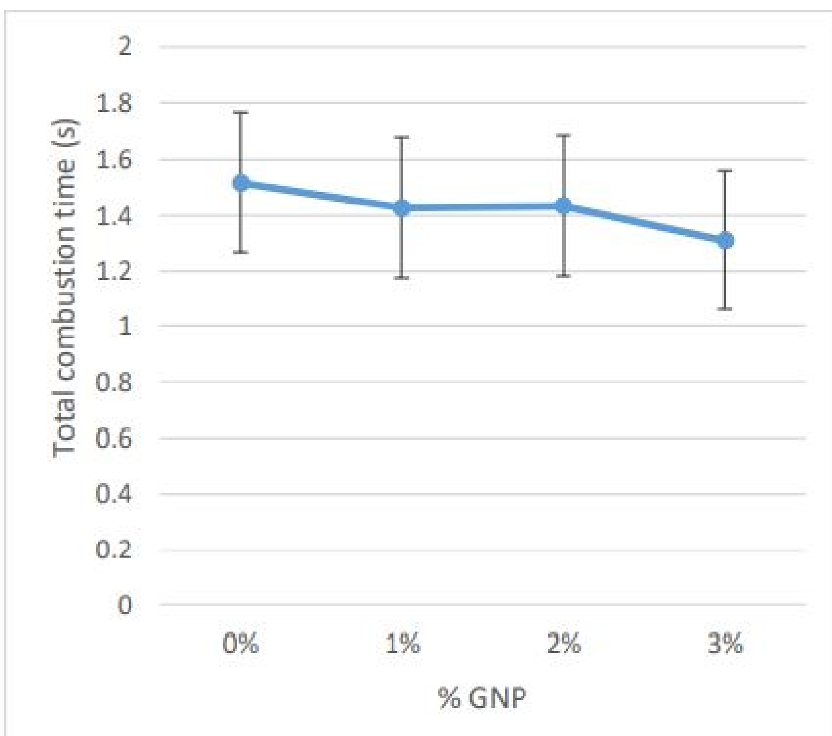


Figure 2.11 Total combustion time trends for renewable jet fuel at various GNP loadings

Figure 2.12 Soot formation at the end of the combustion process for different GNP loadings with renewable jet fuel

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, and 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 300 μm to 1400 μm in size [19]. Using the Gambill method to determine the 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 the temperature cut-offs for naphtha, kerosene, diesel, and VGO cuts, respectively. 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. The 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 made to see if the suspension was beginning to settle down and which stage of settling it was at.

This technique is inconvenient, subjective, and provides no hard data. Additionally, there is a very large number of potential polymeric additive candidates, as well as a large range of concentrations at which each can be made into a suspension with a given solvent. Given the large number of variables and the large volume of experiments needed, a system was devised by the 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 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, the amount of light that is transmitted through the test tube to the other side depends on which stage of settling the polymer is in. If it is still completely mixed, no light gets through. If it is completely settled, most of the light gets through, and there are 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, reserving 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, so 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 setup uses an Arduino ATMEGA 2560 as a data acquisition system and a Raspberry Pi as a data logger. A smaller version of the suspension stability analyzer was designed, fabricated, and instrumented. This system is more compact and 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 bars). This led to better insight into the 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.

The settling characteristics of different nanoparticles (AB, MWNT, and GNP) in renewable jet fuel were investigated. It was found that both GNP and AB settled within 11,000 seconds and that MWNT remained stable for the duration of the testing period without emulsifiers or other stabilizing agents. Also, metastable states were seen in the acetylene black suspensions, where the nanomaterial settled out at varying rates during the separation phase. These data were presented at a conference and formed into a conference paper. These data are expected to help in exploring the basic physics behind the settling of real-world nanofuels and nanofluids, which will further help in developing nano-additives for realistic crude oils and their surrogates.

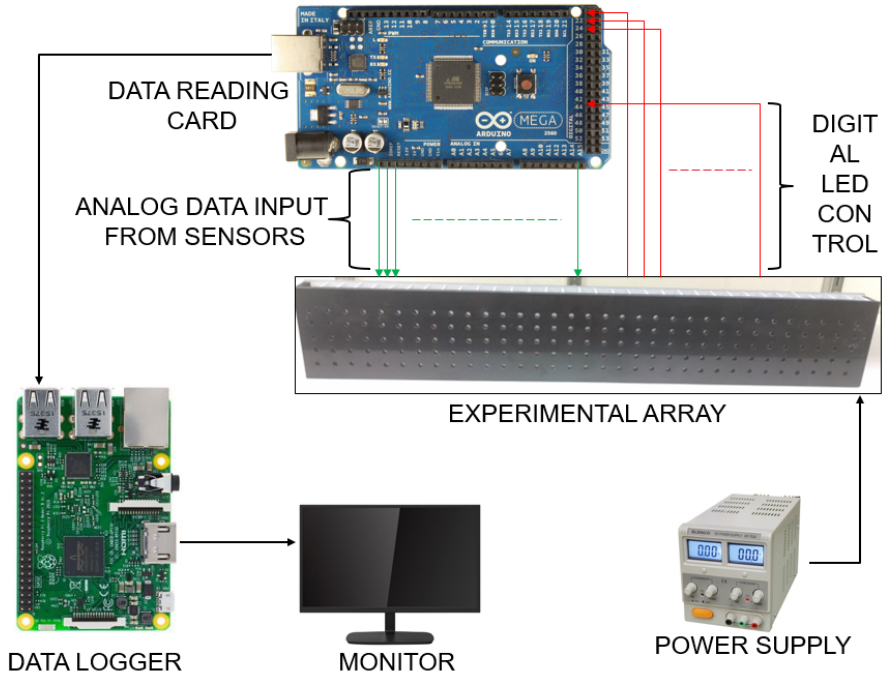


Figure 2.13 Experimental layout for suspension stability analysis

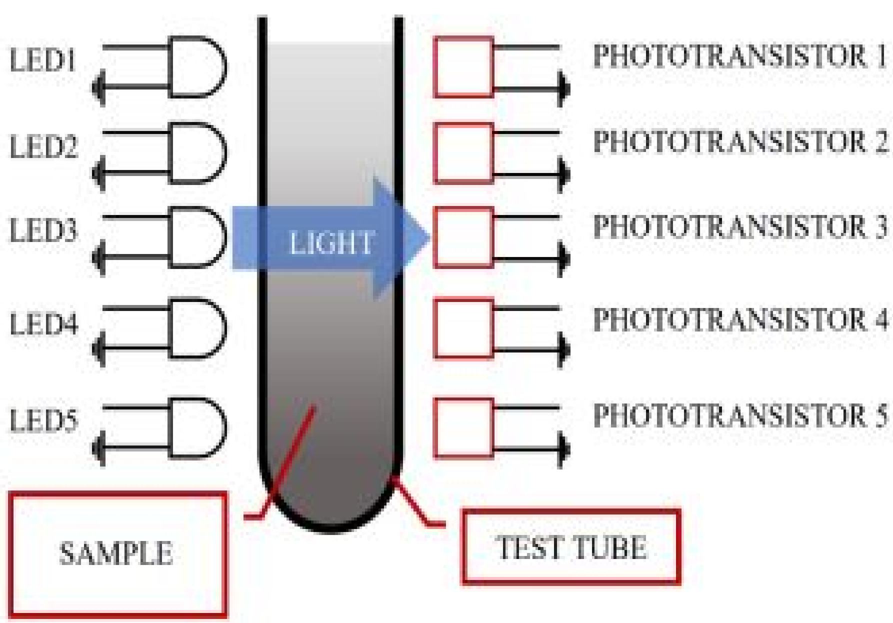


Figure 2.14 Single stability analyzer sample block

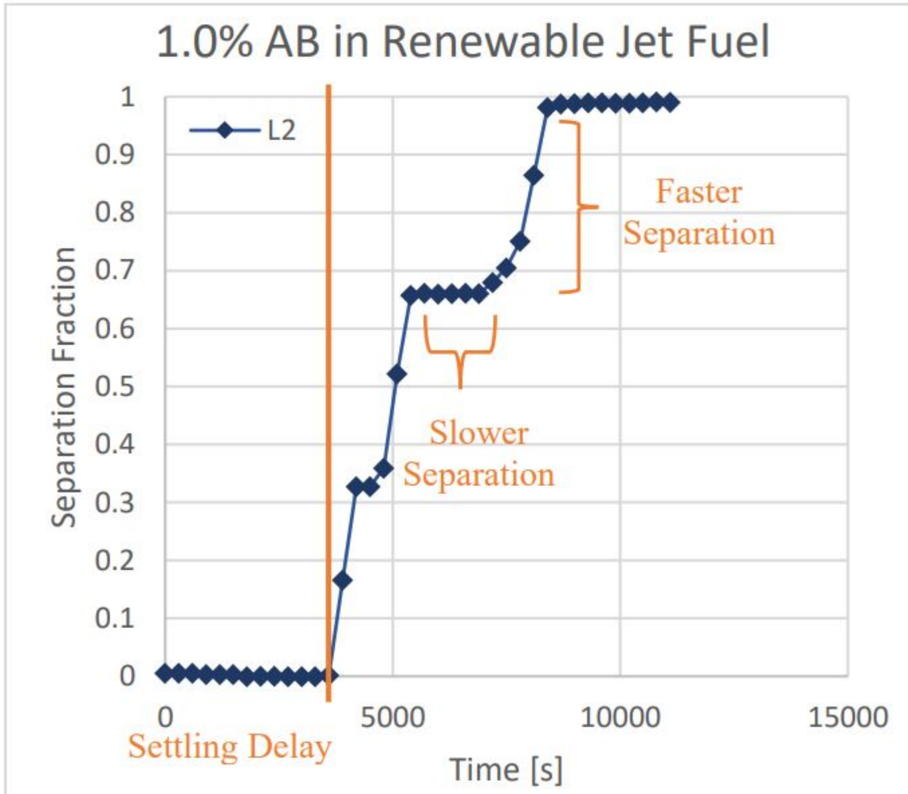


Figure 2.15 Metastable state in 1% (w/w) AB suspension

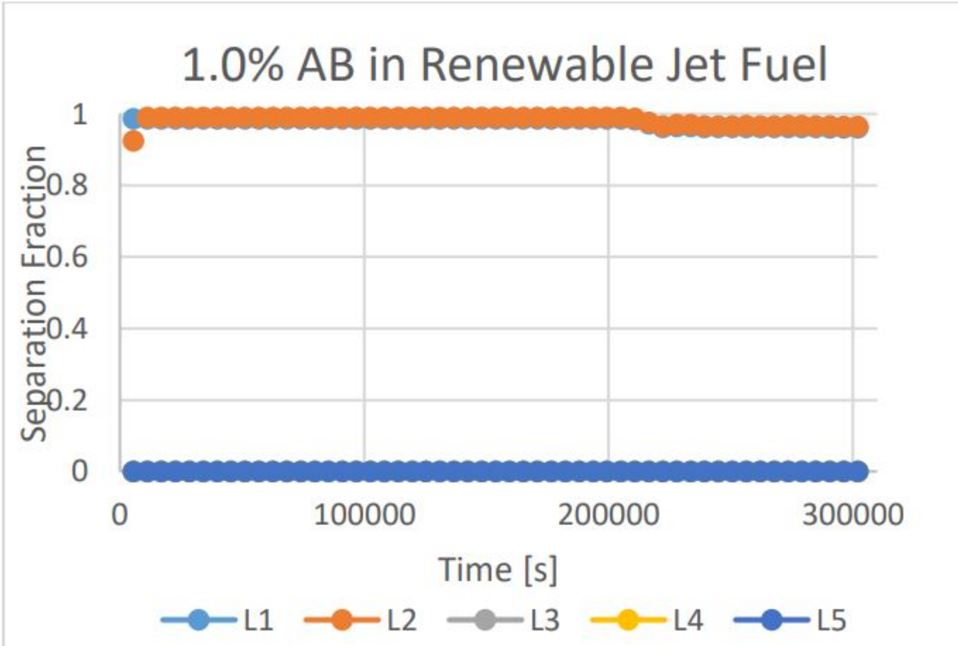


Figure 2.16 Separation characteristics of 1% AB suspension

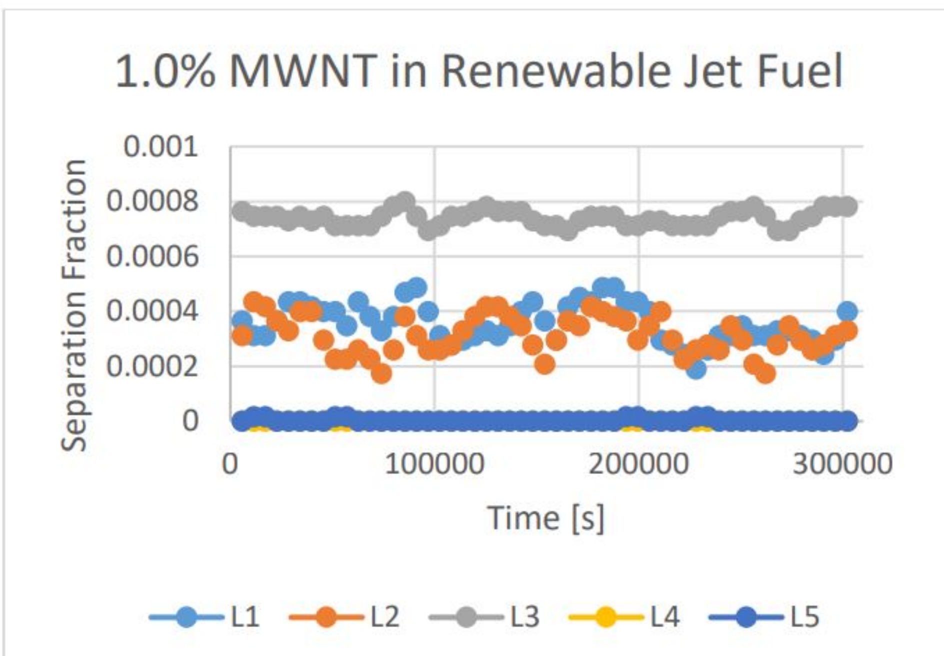


Figure 2.17 Separation characteristics of 1% MWNT suspension

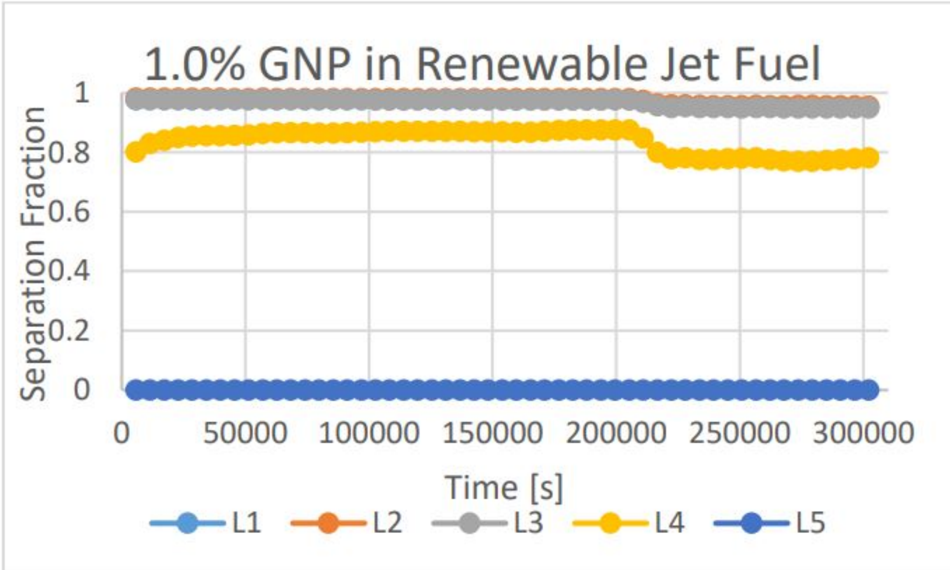


Figure 2.18 Separation characteristics of 1% GNP suspension

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 into the physical mechanics behind the process. Another variation of the suspension stability analysis setup will also lead to more insight into the 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 through December 31, 2020.

Research papers:

- G Singh, M Esmaeilpour , A Ratner. "Effect of carbon-based nanoparticles on the ignition, combustion and flame characteristics of crude oil droplets". Energy, 117227.

Conference papers:

- ASM Parveg, G Singh, A Ratner. "Experimental investigation of effect of Graphene Nano particles (GNP) on the combustion behavior of renewable jet fuel droplets". ASME IMECE 2020, Portland, Oregon, USA, 16-19 November 2020.
- N Hentges, G Singh, A Ratner. "Experimental Investigation of the Settling Characteristics of carbon-based nanoparticle in renewable jet fuel". ASME IMECE 2020, Portland, Oregon, USA, 16-19 November 2020.

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