

Evaluation of Impurities and Oxidation on the Propensity for Spontaneous Combustion of Oil and Biodiesel

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Authorization to Submit Thesis

This thesis of Brian Hanson, submitted for the degree of Master of Science with a Major in Biological Engineering and titled "Evaluation of Impurities and Oxidation on the Propensity for Spontaneous Combustion of Oil and Biodiesel," has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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Abstract

Climate change and the increasing demand for renewable energy has created a new world that is frantically looking for innovative answers to solve both. Biofuels, energy sources built from solar energy and atmospheric carbon, is regaining popularity as a potential solution. An advanced biofuel called biodiesel shows promise through its energy density, cleaner emissions, and ability to run in diesel engines without any engine modification. Biodiesel is unique because it can be made from any plant or animal oil. Since a large variety of these oils can be used to produce high-quality fuels, each biofuel has its own set of distinct properties. While all these oils can be used to create biodiesel, unsaturated oils undergo autoxidation faster than saturated oils. Autoxidation causes the plant oils to become rancid, giving the oil a foul taste and undesirable properties to the fuel. In addition, the fuel loses energy density and becomes susceptible to forming polymers which can plug fuel filters. When highly unsaturated oils are thermally insulated while drying, spontaneous combustion may occur. Spontaneous combustion is considered the result of autoxidation, an exothermic curing reaction.

Several biodiesel production facilities have recently burnt down, costing millions in damages without a known cause, with some events being attributed to spontaneous combustion. Considering the production of biofuels is increasing and many locations are hitting record high temperatures, it is significant to understand how both biofuels and plant oils spontaneously combust to safeguard future investments and establish safer operations. Using off-the-shelf components and minimal custom fabrication, a safe testing device was developed. The device provides a safe and repeatable testing method for investigating spontaneous combustion phenomena.

Using this device, a Spontaneous Combustion Severity Index (SCSI) was developed based on heat generation pattern inside the reactor in a short-term experiment. The SCSI number provided a way to quantify the likelihood of spontaneous combustion. An experiment for spontaneous combustion was designed from a combination of oils, biodiesels, and chemicals commonly encountered in biodiesel industries. The test showed that both types of feedstock and impurities in biodiesel and oil played a significant role in the likelihood of spontaneous combustion.

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Dedication

I dedicate this thesis to my family and friends for not giving up on me and encouraging me to never give up. You have supported me emotionally and financially when I needed it most. I dedicate this thesis to those facing challenges, in research and in life. To those who break the norm in the hope for a better world. Lastly, I dedicate this thesis to myself. As often as difficult as it was, I persevered and completed a task that no one in my family has done before. I often felt ashamed and broken through the many challenges that I faced and once thought of as failures, but later realized that my struggle was growth and my efforts useful.

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Chapter 1: Introduction and Scope of Research

Background

Spontaneous Combustion

Nothing seems to have a more profound effect on humanity than fire. From humanity's first fire-cooked foods to visions of the fiery depths of Hell, physically and psychologically fire has been a major factor in our existence. Fire is highly respected from its life-giving properties and feared from its destructive nature and it has been studied for millennia. Methods on how to start fires are still in development along with new technologies to mitigate and control destruction. A stronger comprehension and modern understanding of fire will only progress modern society further.

Designing an effective testing method for spontaneous combustion, by definition a random process and a subject that is little understood, was a challenge. The minimization of variables is critical in spontaneous combustion research so that variables that influence spontaneous combustion can be isolated.

Spontaneous combustion is a highly unpredictable form of fire with its effects causing severe damage and having the possibility to take lives. The National Fire Protection Association (NFPA) defines spontaneous combustion as a byproduct of spontaneous heating, a process by which a material increases in temperature without uptaking heat from its surroundings. If a material reaches its ignition temperature, spontaneous ignition or combustion occurs. An NFPA study showed between 2005 and 2009, 9% of all spontaneous combustion fires were in manufacturing, many which caused property damage (NFPA, 2011).

Spontaneous combustion is a known but unpredictable phenomenon that has puzzled humanity for centuries. For example, in 1834, a document described the spontaneous combustion of an alcoholic woman (Gavin Thurston, 1934). In addition, many studies have been conducted in coal and solid biomass spontaneous combustion, as stores of coal and barns containing hay have caught fire with no known form of ignition (Woodward, 2004) (DOE/EH, 1993). Spontaneous combustion causes thousands of fires each year, with a quarter of the fires in manufacturing beginning from oily rags (NFPA, 2011). Currently, no absorbent eliminates the potential for spontaneous combustion and can exist with any type or brand of absorbent media: mats, wipers, rags, corncob, sawdust, clay, wood chips or peat (New Pig Corporation, 2019).

Spontaneous Combustion in Biodiesel Industry

Biodiesel-coated materials can, in rare circumstances, spontaneously ignite causing damage both large and small. The mechanisms of biodiesel spontaneous combustion are not completely understood (Rob Fransham, 2014). An often overlooked possibility is spontaneous combustion from improper disposal of material used to clean up biodiesel oil spills (Van Gerpen, 2012). Yet, even with the increased understanding of spontaneous combustion people still, refer to its manifestations as random. A modern advanced biofuel plant caught fire in 2012 and was called “an act of God” and caused 15 million dollars in damages (CBC News, 2015). An investigation into the fire found that the fire started in a filter press area with no known ignition source (CTV, 2012). Another example of a fire starting near a filter press at a biodiesel facility in North Carolina. A news report stated that a fire occurred at the Piedmont Biofuels biodiesel plant in Pittsboro, N.C, after “biodiesel-ensconced filter media spontaneously combusted in the tray beneath our filter press” (Kotrba, 2013).



Figure 1.1: Winnipeg biodiesel plant fire caused by spontaneous combustion (CBC News, 2015).

Past research at the University of Idaho investigated the factors that were believed to affect the probability of spontaneous combustion. After initial experiments to re-create a spontaneous combustion in the lab, the probability of spontaneous combustion is believed to be associated with the level of rancidity of the biodiesel, the characteristics of the absorbent materials, the ease with which air could move through the material, and the ambient conditions in the storage environment (Van Gerpen, 2012). Understanding how the industry uses these absorbent materials is a factor that may increase the likelihood of spontaneous combustion. Filter presses are often used with compressed air systems to remove residual liquids. This poses a concern, as oxygen in compressed air may enhance oxidation reactions to take place. By removing excessive fuels and increasing oxygen may produce conditions closer to those needed for combustion to take place. A flooded filter-press would create a

rich environment for fuel to combust and would likely not be of much concern; however, removing most of the fuel increases the surface area of the absorbent material exposed to oxygen causing higher exothermic reactions rate. Creating safe operation and disposal procedures, utilizing any equipment or products that create high surface areas soaked in fuels like cooking oils and biodiesel, should be of utmost concern for the industry. Biodiesel and plant oils are often overlooked as dangerous liquids due to their high flashpoint and non-toxic nature. Just as there are safety procedures when handling flammable liquids like methanol, there should be plans for handling these “less dangerous” liquids.

Climate Change

Climate change has double effects on the likelihood of spontaneous combustion of biodiesel by creating a higher demand for carbon-neutral fuels like biodiesel and by setting a record high temperature. The demand for renewable fuels, that have a low impact on the climate, are in high demand and have been increasing in total volume globally. Many states in the U.S. are creating mandatory blends of biodiesel and renewable diesel. Renewable diesel has chemical properties like petroleum diesel, due to the nature of its production, and is not as much of a concern in this study for spontaneous combustion. Higher temperatures are a concern as the temperature is often known to increase reaction rates and is typically modeled using the Arrhenius equation.

Minnesota was the first to require the use of biodiesel and currently has a 20% biodiesel (B20) standard for summer months. Starting in 2019, all No. 2 diesel must contain at least 20% biodiesel between April 1 and September 30 (Minnesota Department of Agriculture, 2019). Minnesota Dept. of Agriculture is more interested in the economic prosperity and reduction in dependence on fossil fuel attributes of biodiesel. It is easy to sell biodiesel to policymakers with an added bonus of the cleaner burning emissions and near carbon-neutral fuel aspects. Many states are also falling suit with blends of 2 and 5 percent becoming more common. New York recently mandated a 5% blend in heating oil be from biodiesel (Fuels and Lubes, 2018).

Temperatures have been trending upward for the past century and are under heavy observation from many organizations using core samples, weather stations, and satellites. Using an average between 1981 and 2010, the globe has noticed a temperature increase, seen in Figure 1.2, that is causing concern for melting ice and increasing ocean levels. Spontaneous combustion reaction rates are affected by heat, increasing reaction rates as heat rises. Over the past century, global surface temperature has been trending upwards, seen in Figure 1.2 with red showing higher temperature trends, especially in the northern hemisphere.

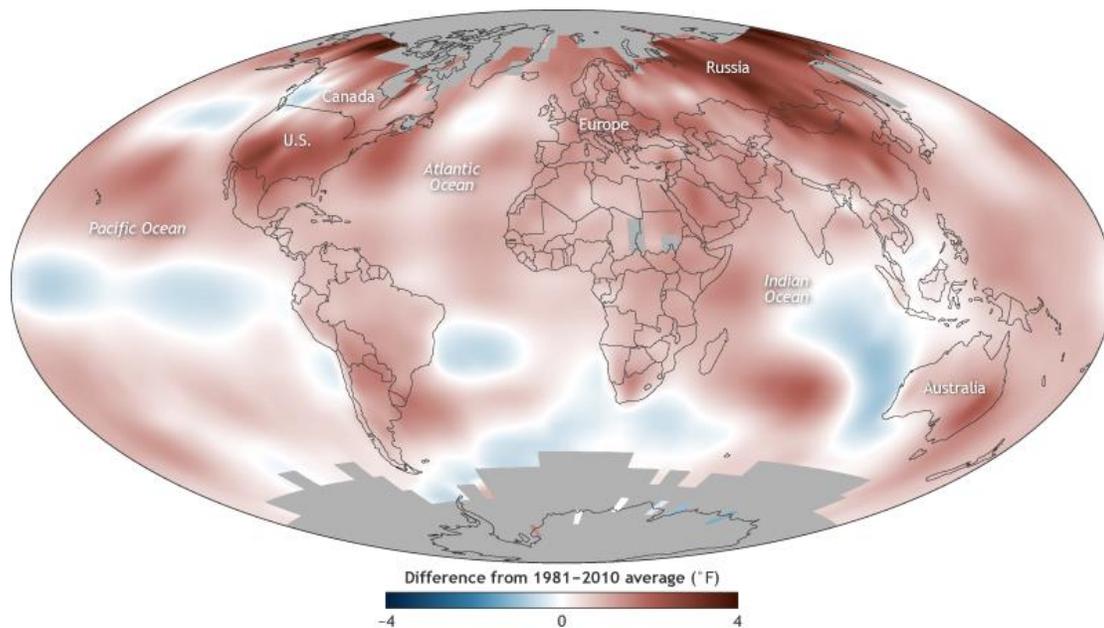


Figure 1.2: Average global temperature change between 1981 and 2010. (NOAA, 2017)

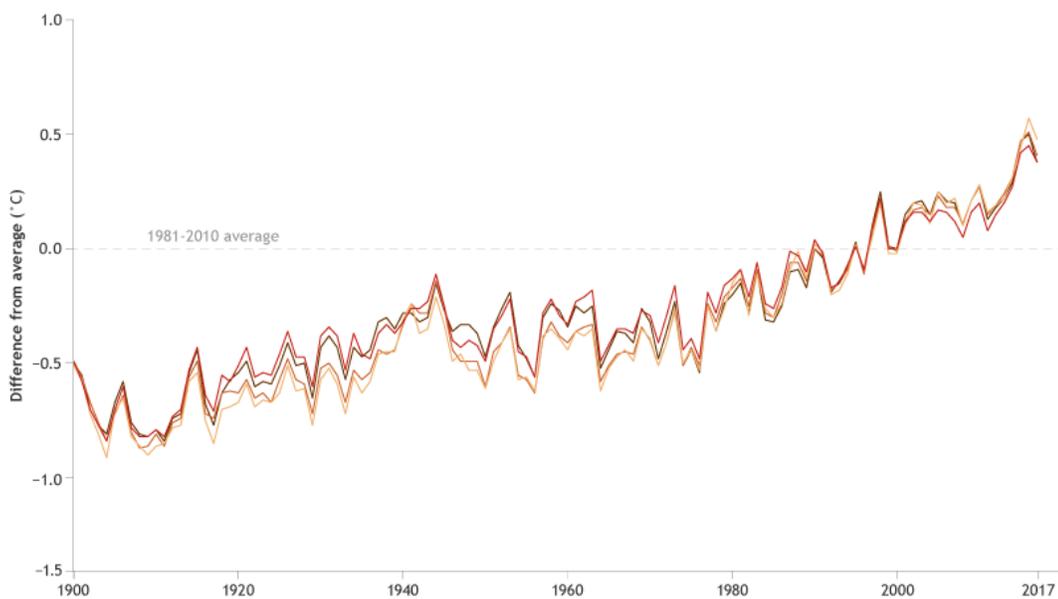


Figure 1.3: Difference in global surface temperature change from the 1981-2010 average. (NOAA, 2017)

Biodiesel

Production

Biodiesel is made using the transesterification process of plant or animal fat, composed mostly of triglycerides. Triglyceride molecule undergoes a reaction when mixed with alcohol and a catalyst. Three molecules of alcohol are consumed by one molecule of triglyceride in this reaction, turning into three alkyl esters (Biodiesel) and a molecule of glycerin. Biodiesel is chemically more uniform in composition when compared to petroleum diesel. The type of alcohol has different effects on the properties on the fuel, as well as the composition of fatty acids from the triglycerides. Biodiesel retains the fatty acid profile of the feedstock.

Waste Vegetable Oil (WVO) is a common feedstock for biodiesel and has some concerns for spontaneous combustion propensity. Composition of oils that have a higher percentage of unsaturated fats are frequently used for cooking. Typical local waste vegetable oil is comprised primarily of soy and canola oils, but are often degraded from cooking. These oils can change feedstock composition due to price, health concerns, flavors, type of restaurant, and availability in the region. Heating cooking oils to high temperatures in an oxygen-rich environment causes the oils to degrade and eventually become rancid, causing the taste to become unpleasant due to the increase of aldehydes, hydroperoxides, and epoxides. Rancidity can be caused from a multitude of factors including the degree of unsaturation of the oil, the type and concentrations of antioxidants, pro-oxidants and trace metals present, availability of oxygen, surface area, moisture content, temperature and degree of exposure to light (Kevin Robards, 1988).

Biodiesel is often produced from WVO due to its low cost and common availability as many restaurants require waste oil disposal. It's common to collect these waste vegetable oils for free, although some restaurants sell their waste oil. The United States of America currently has 124 biodiesel production facilities in operation, totaling over 2.5 billion gallons of capacity. Ten plants, adding 250 million gallons of capacity, are currently under construction (Biodiesel Magazine, 2019).

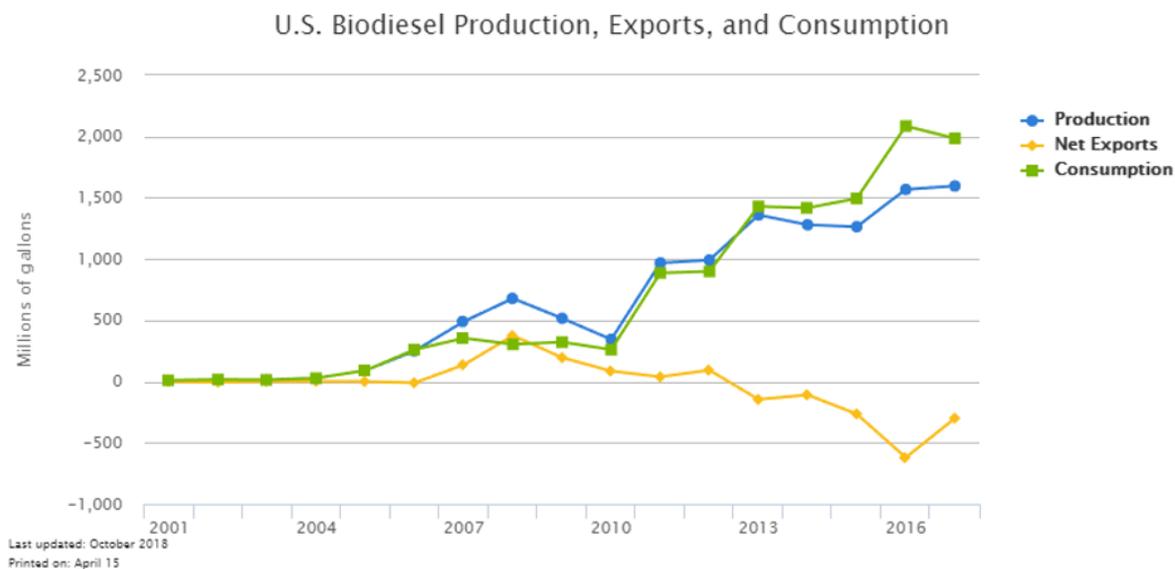


Figure 1.4: U.S. biodiesel production, exports, and consumption between 2001 and 2017 (U.S. DOE, 2019).

Figure 1.4 shows trends in U.S. biodiesel production, exports, and consumption from 2001 to 2017. Exports of biodiesel peaked in 2008 largely due to an unintended effect of a biodiesel tax credit in the European Union. Exports then dropped after that effect was eliminated. The increased production and consumption from 2011 onward are largely driven by the Renewable Fuel Standard (US-EPA, 2019). The net export of biodiesel changed from positive to negative in 2013, meaning the quantity of biodiesel imported by the U.S. exceeded quantity exported. The growth of net exports since 2013 is likely due to the continued effort of reducing greenhouse gas emissions and expanding regulations (U.S. DOE, 2019).

Global biodiesel production has also been growing. A study by the International Energy Agency (IEA) has shown a combined biodiesel and hydrotreated vegetable oil (HVO) production increase of 7% from 2016 to 2017. In 2017, a record output of nearly 39 billion liters (over 10 billion gallons) was produced. Global production is expected to grow at an average growth rate of 3% until 2023, reaching 12 billion gallons. The market expansion appears to be driven by higher mandated demand in the United States, Brazil and some ASEAN countries (International Energy Agency, 2018).

Increasing temperatures and increasing biodiesel production increase the risk of spontaneous combustion. Biodiesel production facilities located in a hot climate may be exposed to higher risk as many locations are seeing record high temperatures. Seen below in Figure 1.5, is a map using data from National Oceanic and Atmospheric Administration (NOAA) and BBI International comparing record temperatures and the location of current biodiesel plants and under construction biodiesel

plants. The map shows a large number of plants that fall in the regions that are having higher average maximum temperatures, Southern California and Texas especially. However, that doesn't mean that the other biodiesel plants are safer. The earlier example where spontaneous combustion happened at a biodiesel plant was in Canada, north of Minnesota in October.

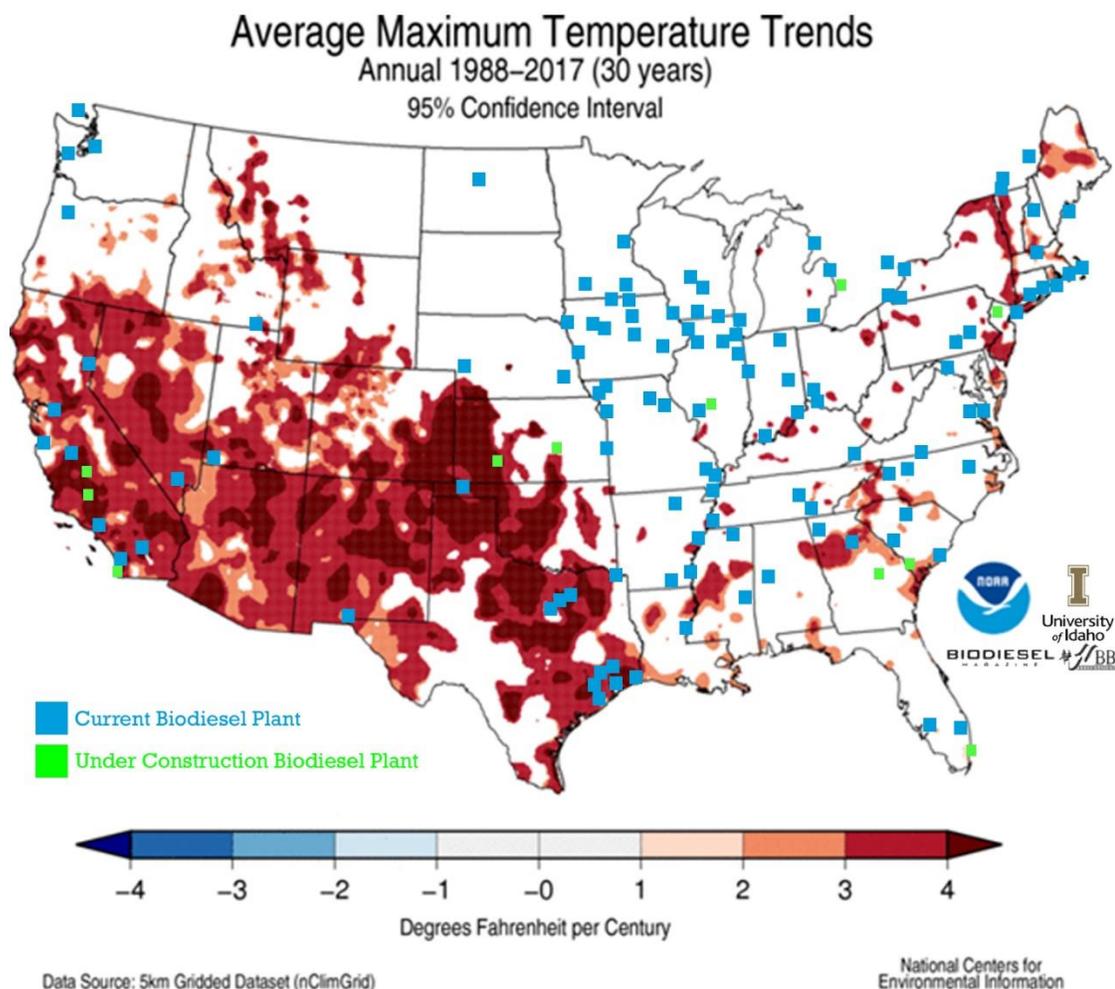


Figure 1.5: Combined average maximum temperature trend map with US biodiesel plant locations and planned location map. (NOAA, 2019) (BBI, 2019)

Biodiesel from common feedstock such as soybean, canola and other vegetable oil are quite stable. We were not able to re-create spontaneous combustion just using B100. However, the biodiesel from polyunsaturated oil such as linseed may be more susceptible to spontaneous combustion than soybean biodiesel. We found the heating rate is increased when biodiesel is contaminated with other substances to accelerate autoxidation. Some of the common impurities are briefly described below.

Drying Oils

Drying oils are classified by their iodine value, which must exceed an iodine number of 130 to be considered a drying oil. Linseed oil, also known as flaxseed oil, is a drying oil. Iodine value or number is the amount in grams of iodine consumed by 100 grams of chemical substance. Iodine is absorbed by the unsaturated carbon bonds. The higher the number of unsaturated bonds, the more iodine will be consumed. This is a normal method in determining the likelihood of oxidation. Fats and oils that are higher in unsaturated bonds are more likely to oxidize and cause chemical reactions resulting in polymers and fragmented organic groups. An example of a triglyceride is shown in Figure 1.6, which has three different unsaturated fatty acids. The top fatty acid is considered as linoleic, the middle is alpha-linolenic, and the bottom is oleic acid. The order of drying rate is alpha-linolenic is higher than linoleic which is higher than the oleic acid.

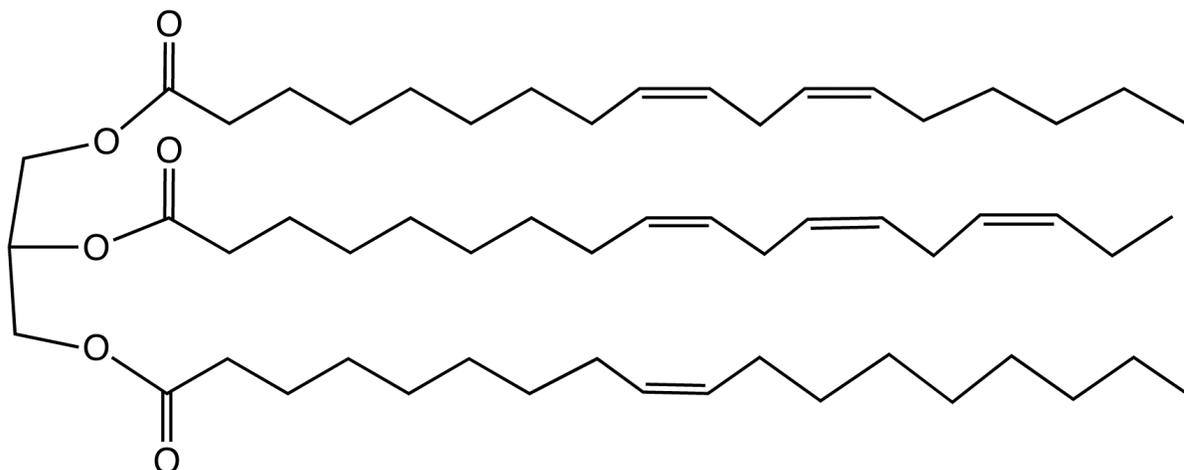


Figure 1.6: A common triglyceride found in a typical drying oil.

Fatty acids for biodiesel typically range from 16 to 18 carbons in length with varying degrees of saturation. Omega numbers dictate the location of the double bond in reference to the terminal methyl group. For example, linolenic acid is an omega-3 fatty acid as the last double bond is on carbon 15 of the 18-carbon acid. Linolenic acid is also a polyunsaturated fat meaning it has multiple double-bonded carbons. It has three double bonds at carbons 9, 12, 15. Unsaturated fats have shown better cold-weather performance for biodiesel compared to saturated fats (Anderson, 2008). Fatty acids that are heavily saturated, such as coconut oil, are more susceptible to freezing at warmer temperatures. Biodiesel has a higher cloud point than No.2 diesel and often blended between 5-20% with petroleum diesel to improve cold-weather performance. Additives help improve the cold-weather performance by preventing the fuel from freezing as easily, however, the cloud point rarely changes with additives

and may still plug fuel filters (Shrestha, et al., 2008). Cloud point is the temperature where visible crystals start forming in the fuel. The waste vegetable oil (WVO) used at the University of Idaho has a relatively high cloud point, around 10 °C, which may be caused by the saturated fats dissolved in the cooking oils from the fried food. Biodiesel does not have a standard for cloud point and pour point but is often reported.

Linseed oil, or flaxseed oil, has a very high level of polyunsaturated fats. A Canadian startup company was preparing to open a biodiesel plant to produce clean fuel, animal feed and human food from flaxseed. It plans to use 40 percent of the flaxseed for fuel and the remainder turned into a meal (Taylor, 2011). Polyunsaturated fats are also thought to be healthier than saturated fats. This health trend may cause waste vegetable oils to become more susceptible to oxidation reactions and may increase the likelihood of spontaneous combustion.

Drying Oil Reactions

Drying oils, such as linseed oil, are used to create protective polymers through natural drying processes. Plant oils, high in unsaturated fatty acids, may polymerize in the air at ambient temperatures without the need to mix other chemicals or add external sources of energy, such as light or heat. This polymerization reaction happens naturally with oxygen at room temperature but may be accelerated with heat, light, and free radicals as seen in Figure 1.8.

Drying salts, also known as siccatives, found in boiled linseed oil, increase the reactive air molecules, accelerating drying. Cobalt manganese is commonly used in boiled linseed oil to increase the drying rate. (Company, 2014) Figure 1.7 shows cobalt catalyzed oxidation reaction of two dienes, creating a hydroperoxide, then dehydrating into a crosslink. This reaction is typically associated with free radical polymerization. Iron and other metals can act as a catalyst in free radical polymerization, which speeds up the reduction of the hydroperoxide intermediates. This causes a chain reaction from addition reactions each producing additional free radicals, which cause polymerization to happen faster until all the radicals are paired up. This cross-linking is an exothermic reaction, driving off heat, free radicals, and water (MassimoLazzari, 1999).

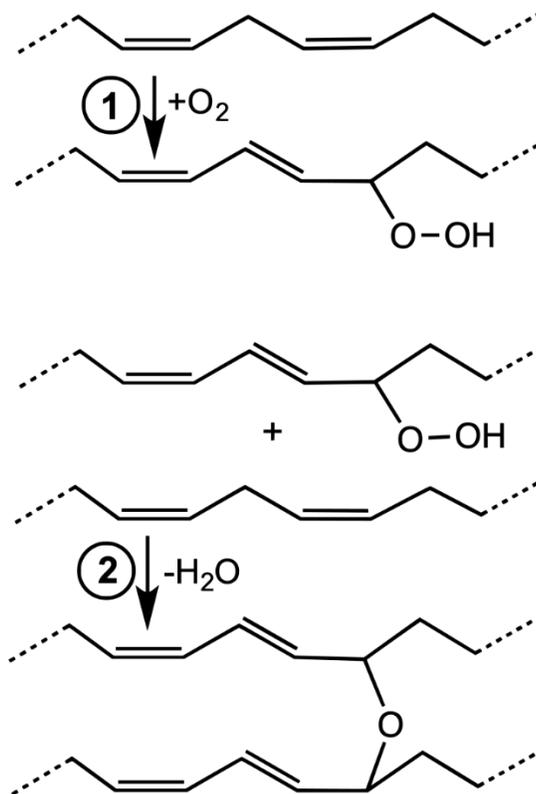


Figure 1.7: Simplified chemical reactions associated with the cobalt-catalyzed drying process. In the first step (1), the diene undergoes autoxidation to give a hydroperoxide. In the second step, the hydroperoxide combines with another unsaturated side chain to generate a crosslink. (Smokefoot, 2017)

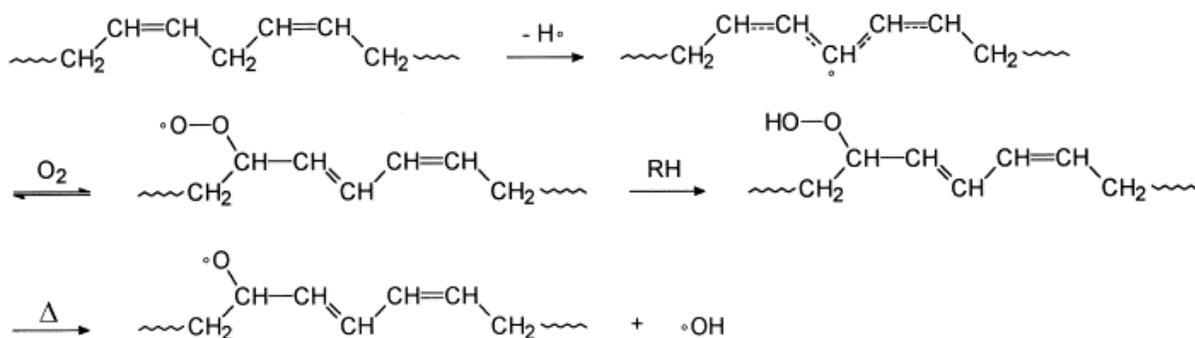


Figure 1.8 Promoted by reactive hydrogen atoms on the allylic positions of the molecules, hydroperoxide formation is easier on linoleic and linolenic components where one and two methylene groups, respectively, are situated between two unconjugated double bonds. (MassimoLazzari, 1999)

Objectives

Spontaneous combustion is affected by numerous factors such as temperature, airflow, media (substrate for absorption) use, impurities, fuel quality and so on. Additionally, the preliminary experiments with boiled linseed oil showed that spontaneous combustion may take a long time (several days) depending on the ambient temperature. All spontaneous combustion results from the exothermic auto-oxidation reactions. Common spontaneous combustion research methods are often destructive, take large quantities of time, and may consume significant amounts of fuel and absorbent material. Therefore, the objective of this research is to investigate the methods to investigate the impact of common impurities in spontaneous combustion. The specific objectives are

1. Design a quick experiment to quantify the impact of impurities on biodiesel self-heating.
2. Evaluate the effect of feedstock on spontaneous combustion
3. Evaluate the effect of rancidity on spontaneous combustion
4. Compare the likelihood of spontaneous combustion between vegetable oil and biodiesel
5. Evaluate the effect of impurities like a catalyst on spontaneous combustion.

Chapter 2: Methodology

Designing the System

Fuel Preparation

The fuels and impurities under investigation include only those commonly found in a biodiesel production facility. A common fuel feedstock is waste vegetable oil (WVO). Restaurants dispose of their waste cooking oils after they degrade from use. These oils are often mixtures of the lowest cost of cooking oils that meet the needs of the consumers' demand. Soybean oil and canola oil are commonly used due to their lower cost and healthy ratings. Soybean oil and canola oil are considered semi-drying oils due to their iodine number normally being around or below 130. Iodine number is a method used to define the number of unsaturated bonds of an oil. A higher iodine number indicates more unsaturated bonds. Oils with the highest iodine values dry most quickly and form the hardest films (Abraham, 1996). Linseed oil, also known as flaxseed oil, is a very unsaturated fuel with a high percentage of 18:3 molecules in its fatty acid profile. Linseed oil typically has an iodine number around 188. Fuels made from common waste vegetable oils and linseed oil will be observed in this experiment due to their availability and potential to spontaneously combust. The container that linseed oil came in had a warning on the side about oily rags likely to spontaneously combust. This oil is occasionally used as a feedstock for biodiesel production and appears to be a strong candidate as a fuel that would likely spontaneously combust. Fuel made from linseed oil may act like a reference point, serving as a worst-case-scenario fuel, that could be compared to other fuels.

Biodiesel (BD) was prepared using WVO collected from the University of Idaho dining services and linseed oil was purchased from a local hardware store. Linseed oil comes as furniture stain in both raw and boiled forms. Boiled linseed oil has been heat-treated with an additive to increase drying rates. The drying agent additive, known as a siccative, in the boiled linseed oil was cobalt manganese. Only raw linseed oil was used in the production of fuel. The fatty acid profiles of these two oils determined at the University of Idaho using a Gas Chromatograph are shown in Table 2.1. It should be noted the high level of 18:3 (3 double bonds on an 18-carbon chain) in linseed oil compared to the waste vegetable oil. Due to the biodiesel production process of transesterification, the fuel fatty acid profile should maintain the composition of the oil fatty acid profile.

Table 2.1: Fatty Acid Profiles of WVO and Linseed Oil

Sample ID	16:0	18:0	18:1	18:2	18:3	20:1	22:1
Waste Veg Oil	9.3	2.5	62.9	21.4	1.4	1.2	-
Raw Linseed Oil	5.5	4.2	22.7	15.7	51.7	-	-

The fuels were produced using methanol and sodium methylate in a constantly stirred reactor. The molar ratio used was 6:1 alcohol to oil and 0.5% catalyst (sodium methylate) to oil by mass. The reaction was done by an 80-20 method, in this method, the reaction was run twice using 80% of the methanol and catalyst in the first reaction followed by glycerol separation and then using remaining 20% of the methanol and catalyst for an additional hour of reaction time to completion. The fuel was water washed until meeting ASTM standard levels of soap, then dried and filtered through magnesium silicate. Once the quality was determined, half of each fuel was turned rancid by heating the fuels above 120 °C while percolating air into the fuel. The fuel was tested using a Rancimat test to determine the level of rancidity. The final biodiesel fuels and their rancid samples are shown in Figure 2.1, where the fuel changes color from an amber color to a light yellow after going rancid.

Table 2.2: Induction time results using Metrohm 873 biodiesel rancimat at 120 °C according to EN 16568.

Rancimat Results	WVO		Linseed Oil		WVO BD		Linseed BD	
	Fresh	Rancid	Fresh	Rancid	Fresh	Rancid	Fresh	Rancid
Induction Time (hr.)	2.05	0.26	0.73	0.18	1.86	0.06	1.70	0.03

While WVO is unlikely to pass ASTM standards for oxidative stability (>3 hr.) due to being degraded through use in cooking, the induction time was significantly higher for WVO oil and WVO BD than that of the fuel that was turned rancid. Antioxidants are typically added at the end of the manufacturing of biodiesel before shipping to increase the fuel's shelf life by increasing its induction time above three hours to meet ASTM D6751 standards. Antioxidants were not tested in this experimental design as the experiment is looking at biodiesel in the manufacturing process and what would likely be found in a filter press or cleaned in a spill in a biodiesel plant. Therefore, biodiesel tested will not pass ASTM D6751 standards, and the experiment must account for potentially unreacted fuel and known impurities that may be found in a filter press. Rancid fuels and oil are of interest due to their susceptibility for polymerization in fuel tanks from their partially oxidized structure. In a biodiesel plant that has been shut down for an extended period of time, a filter press may contain a significant amount of rancid fuels and oils. Alcohols and residual catalysts may also be found in a filter press and will need to be observed as well.



Figure 2.1: Rancid and Fresh versions of prepared biodiesel for testing. From left to right: Linseed Biodiesel, Rancid Linseed Biodiesel, Biodiesel from WVO and Rancid Biodiesel from WVO. The rancid biodiesel had a lighter color than the fresh biodiesel.

Preliminary Reactor Design

Research began with a home-made reactor that was designed for spontaneous combustion. The reactor consisted of an aluminum angle iron bar that held four aluminum reactor tubes. Each tube had holes for temperature probes, insulating reactor sleeves, 1" NPT threaded pipe for airflow entering from the bottom of the reactor, and electric pipe heating sleeves. The temperature of the inlet air was controlled using a pulse modulated PID controlled attached to a computer running LabVIEW®. The reactor used a T-type thermocouple to measure the core temperature filled with sawdust soaked in fuel and impurities. A USB-based 8-channel thermocouple input device with 24-bit resolution from measurement computing (mccdaq.com) was used as a signal conditioning unit. The LabVIEW program was written to read and log temperature from eight thermocouples simultaneously every 30 seconds. The air-flow was controlled using a manual control valve.

The lab compressed air was used as it was readily accessible and is easy to measure and control through utilizing flow meters. The air distribution system comprised of a simple laser cut box to house the fabricated metal compressed air manifold, a pressure regulator, and four controllable flow

valves. This system was then plugged into an auxiliary air compressor. To control the heating, electric heating bands were wrapped around the 1" NPT steel threaded pipes which were sized down to fit a 1/4" hose. These electric bands were connected to a power distribution system that was measured by a LabVIEW program on a computer. LabVIEW utilized thermocouples data to pulse width modulate the electric heater power output.

Reactor Redesign

The first test of the reactors initially appeared to work. After half-filling a reactor with sawdust mixed with boiled linseed oil and running the compressed air at 5 L/min @ 80 °C, one of the reactors started to smoke after 2 hours. The controlled heated air system was working but noticed some issues with the reactor design. As one reactor started to rise sharply in temperature, the other reactors closest to the hot reactor started heating as well. This was due to the fact that all four reactors were attached together with an aluminum bar (Figure 2.2).

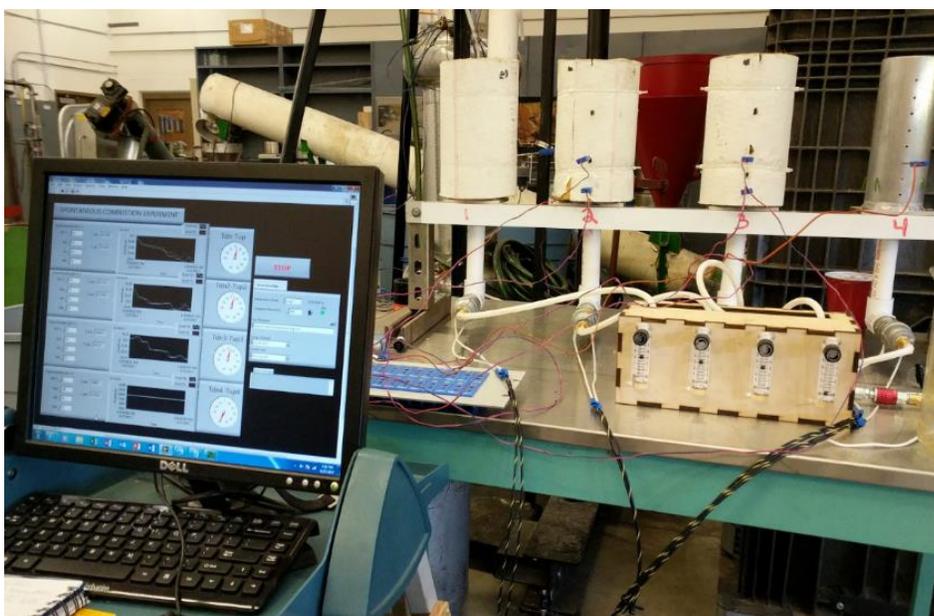


Figure 2.2: Aluminum tube reactors mounted on an aluminum frame with plastic intake.

Aluminum is a lightweight and strong material that is easy to fabricate and low cost but has a melting point around 660 °C which was proved inadequate to withstand repeated cycles of high temperature when the fuel spontaneously combusted. Repeated spontaneous combustion resulted in a catastrophic meltdown of the reactor (Figure 2.3).



Figure 2.3: Melted aluminum reactor on a glowing bed of smoldering sawdust.

With the compressed air flow valve wide open and the reactor was well insulated, the aluminum reactor could not withstand the heat.

Taking the lessons from the aluminum meltdown and connected reactor heat transfer, the reactors were re-built individually using steel tube nearly identical to the original aluminum reactor tubes size. The tubes used in the reactor was 11 Gauge (0.120" wall thickness) steel with 3 in. internal diameter. The reactor was 9" tall with thermocouple holes drilled at 1", 3", 5", and 7" from the bottom plate that was welded on. Two rods welded into the tube, 2 in. from the bottom plate of the reactor, support a pair of steel screen meshes seen in Figure 2.4. The large mesh screen supports the fine mesh screen which increases the life span of the fine mesh screen.

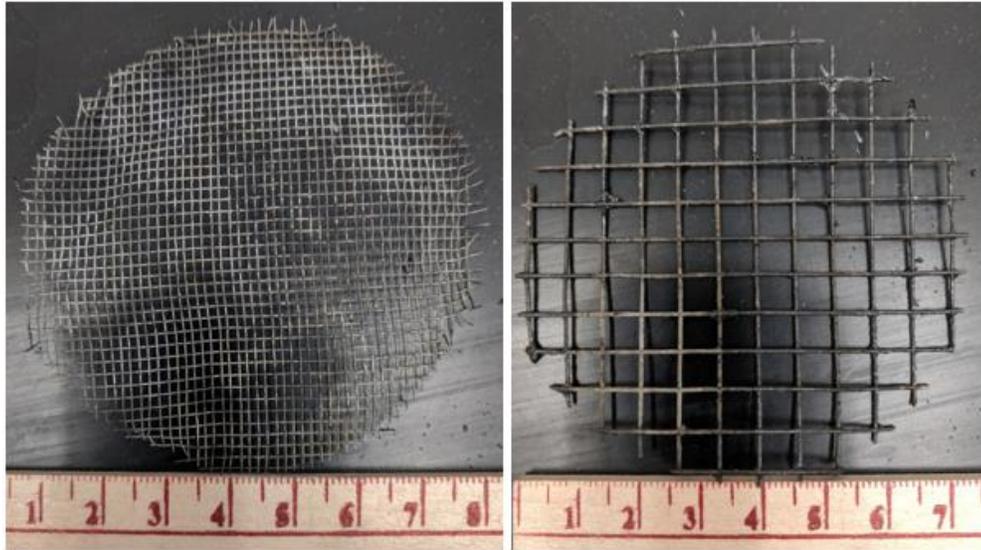


Figure 2.4: Two-stage structural screen system used to separate the lower air chamber from the testing fuel in the reactor. Measurements shown are in cm.

The individual reactors are supported by three legs for stability. The legs were 0.25 in square rods mounted at about 30 degrees. The legs had small metal rectangles made out of 0.25" thick, 1" steel flat bar to improve stability. The small legs reduce temperatures from the reactors to the supporting surface through convection to the surrounding air, increasing safety and reducing the likelihood of damaging its supporting surface.

The original PVC air ducts were replaced with galvanized 1" NPT steel pipe and fittings to carry the heated air into the reactor. The heating system warms the pipe through conduction using electric mica band heaters. Steel wool was packed inside the pipe to improve heat transfer helping the reactors reach testing temperature quickly. The final design of the prototype reactor is shown in Figure 2.5. The packing of steel wool is shown in Figure 2.6 with the 160 W mica band heater surrounding the pipe and secured with a stainless steel hose clamp. As compressed air enters the heating system, it gathers heat and fills the empty chamber below the screen mesh. This temperature is measured and recorded as air temperature and used to control the heating system. The air temperature was also used to determine the health of the reactor by observing heating rates and stability.

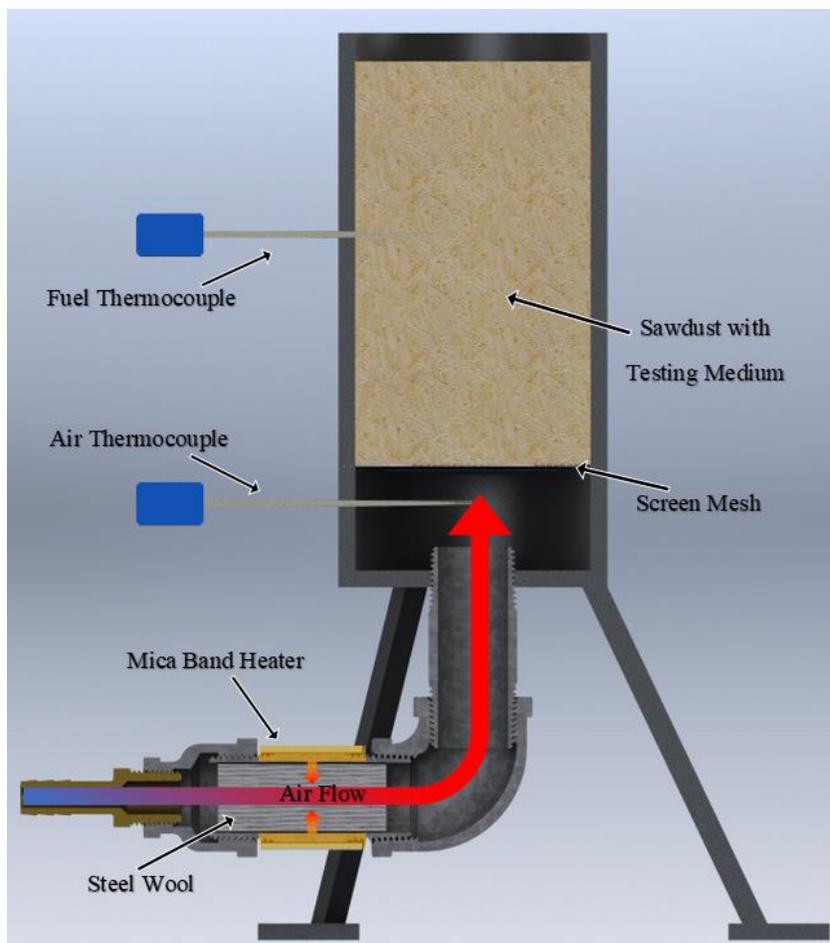


Figure 2.5: Cutaway model of the prototype reactor



Figure 2.6: Steel wool stuffed steel pipe wrapped in a 160W mica band heater.

The warm air passes through the sawdust media soaked in the fuel of interest. The warm air heats the media to a set point. The insulated jacket around the reactor core helps reduce heat loss from walls. Most of the heat loss is through the open top, while some heat is lost to the remaining exposed metal on the legs, bottom, and intake pipe.

Stress test of the steel reactor

Setting up a similar test that eliminated the aluminum reactors, the durability of the new steel reactors was tested. Loaded with sawdust, boiled linseed oil, and with the air valves wide-open, the fuel was ignited. The thermocouples measured temperatures reaching a maximum possible temperature which was above 600 °C. The duration of the test lasted for about 10 minutes until all of the fuel was consumed. No apparent damage was observed. Flow rates were also compared using the height of the flames after ignition. Ash was vacuumed out after cooling to room temperature.

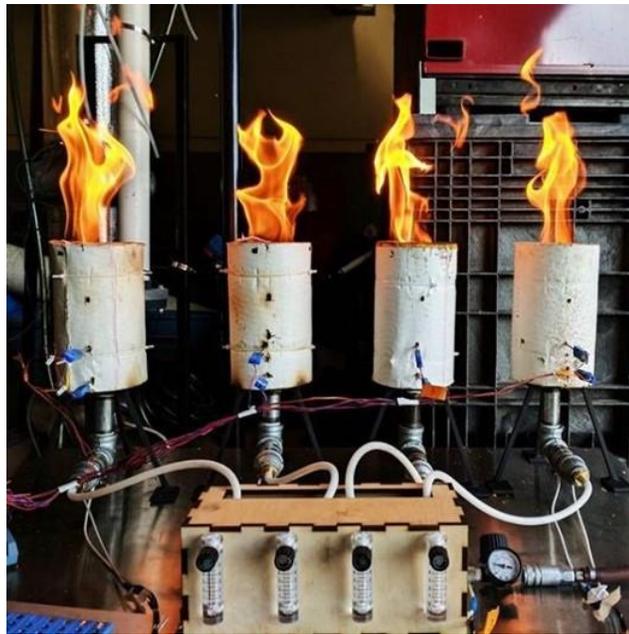


Figure 2.7: Thermal stress testing new steel reactors with >5 L/min air flow through ignited sawdust soaked in boiled linseed oil simulating a worst-case scenario.

The inlet air temperature was set to 80 °C to be near real-world conditions. According to Stephan Boltzmann's equation, direct sunlight (750 W/m^2) can heat a black body to temperatures 66 °C above its ambient temperature. On a summer day at 34 °C ambient temperature, theoretically, a black body can reach up to 100 °C, assuming no loss to the environment due to conduction or convection. However, due to convective and conductive heat loss, the actual temperature is going to be less than

the theoretical maximum. In this experiment, 80 °C was considered a representative temperature likely to occur inside a trash can under the sun.

Heating the air quickly to the desired temperature causes reactions to take place quicker, reducing the total test time to a couple of hours for some mixtures, creating safer operating conditions by having someone more likely to be present when the reactions occur. It can be dangerous to leave the reactors unattended during testing as the open top and flammable materials may cause an accident if not careful. Limiting the inlet air flow to 80 °C also helped prevent melting of the inlet air hose. Separate experiment with higher than 80 °C significantly decreased the time for spontaneous combustion.



Figure 2.8: Planned worst-case scenario testing in a laboratory hood. Max pressure and max airflow were forced through heavily oil-saturated sawdust and ignited. No damages were observed to hood or equipment.



Figure 2.9: Potentially dangerous sparks leaving an ignited reactor under airflows greater than 5 L/min.

To improve the safety of the system, the reactors were placed in a metal lab hood to ventilate smoke and vapors and reduce contact with flammable materials or people. To reduce the chance of large glowing sparks (Figure 2.9) from flying up the lab hood ventilation system, spark arrestors (Figure 2.10) were installed. Under normal testing conditions, no flames were present during tests. Spark arrestors and low airflow prevented the formation of an open flame. Reactants would smolder until the fuel ran out.



Figure 2.10: Spark arrestors installed on two reactors. The left reactor is under spontaneous combustion at 5 L/min airflow, but no flame was present.

Due to the nature of sawdust being varying size and shape, a method to provide consistent airflow was critical. Porosity and density of mass changes between each test that uses the sawdust. Pressurized air from a continuously ran air compressor would provide the air for the test



Figure 2.11: Dia-Vac continuous use air compressor to ensure consistent air supply.



Figure 2.12: Compressed air manifold (left) and airflow metering valves (right).

Pressurized air is controlled using a regulator installed before the manifold (Figure 2.12). The manifold splits the air to four controllable flow valves. The air volume was kept constant by a flow valve. To ensure dry air, despite changing atmospheric conditions of the laboratory over the changing weather during testing, a large column full of oven dried A4 molecular sieves were used (Figure 2.13).



Figure 2.13: A4 molecular sieve air dryer to remove atmospheric water.

T-Type thermocouples were used to measure temperature. The thermocouples are composed of copper and constantan, a copper-nickel alloy, and protected by a stainless steel sheath. Copper being the weakest material, melts at a temperature nearly twice as the hottest recorded temperature. The thermocouples were sufficiently durable to handle the high temperatures of combustion over many tests, but are not recommended by the manufacturer Omega. Omega suggests a maximum operating limit of 350 °C and suggests K-Type thermocouples for higher temperatures, but come at the loss of accuracy compared to T-Type thermocouples. (Engineering, 2019) T-Type thermocouples from Omega have an accuracy rating of +/- 1 °C.



Figure 2.14: Sawdust weighed on a digital scale for each reaction (left). After mixing test chemicals in the sawdust, it is added to the reactor by pouring in the top.

A digital scale was used to measure the chemicals that were going to be performed during each test. A large beaker was tared and filled with $70 \pm .05$ g of sawdust. The sawdust was dried in an oven at 103 °C for at least 24 hours. Before testing, the sawdust would be set out to cool to room temperature before mixing in chemicals. Chemicals were carefully added to the sawdust, measured by the scale, and then mixed until uniform by hand using latex gloves. The contents would then be added to the reactor as soon as possible, to reduce the time between the additions of other chemicals in the other reactors. A light rocking back and forth would cause the sawdust to settle to a height about one inch from the top of the reactors. The airflow would then be adjusted using the flow valves to the set airflow rate.

Issues

During testing, several issues arose and were dealt with as soon as possible. Output performance was monitored using computer software and would show signs of premature failure in the heating system. This became evident in some of the tests which showed poor heating performance and erratic results. Ash also would build up and was difficult to remove with the vacuum cleaner, a T-pipe with a drain plug might be a better design than the elbow which allowed ash, and in one case oil (Figure 2.17), to

plug the steel wool heating core. This increased the demand on the heater and in turn cause excessive heat transfer into the barbed hose fitting. This caused the hose to melt and fail (Figure 2.16). A better-designed air delivery system would greatly improve the stability of the test reactors.



Figure 2.15: Excessive ash buildup in the bottom of the reactor reduced airflow and reactor performance. Thermal coloring of the steel wool shows cooler temperatures farthest from the mica heating band indicating effective heat transfer to air.

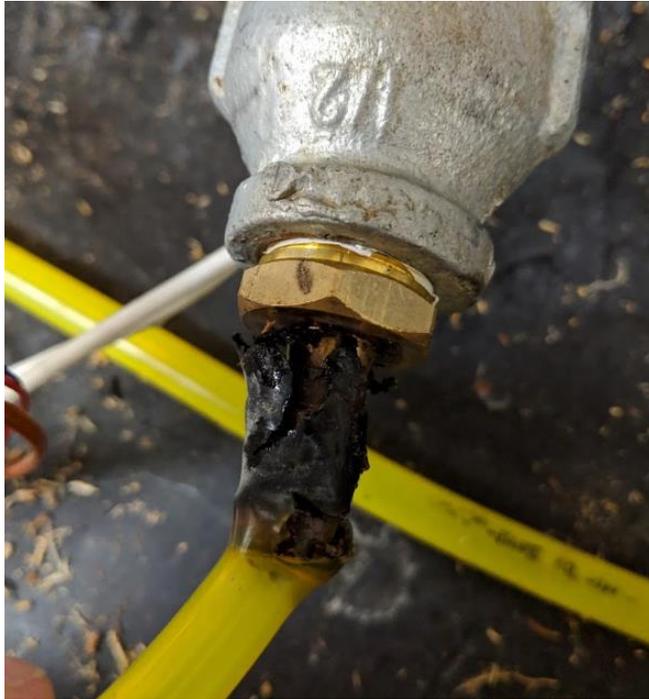


Figure 2.16: Poor reactor performance increases demand from the heating band, resulting in a hotter operating system that damages the flexible air hoses.



Figure 2.17: Excessive oils dripped down into the heating core, causing a polymer to form which greatly restricted airflow and reactor performance.

After observing data, runs that were affected by issues that caused the reactor to behave differently than normal were rerun after fixing the issues. The data shown in Appendix A are color-coded for the reactor that was used and the date is displayed next to the data in case of variation due to time the experiment was performed. Normal operation was shown by a consistent and stable air temperature of the reactor which is shown often as a dashed line in the data in Appendix A that stabilizes around 80 °C.

Determining parameters

To validate that the new reactors were running consistently and safely, some preliminary experiments were run to create parameters to test experimental design factors. Quantities of chemicals, temperatures, and airflow rates were determined through a series of tests.

Oil to Sawdust ratio

The first test determines the effect the mixture of boiled linseed oil to sawdust ratio has on the reactions (Figure 2.18). 25% oil to sawdust mixture had some thermal activity and surpassed the 80 °C reactor setpoint but didn't fully combust. 50% oil to sawdust ratio had significant heating. A mixture between 50% and 100% oil/sawdust ratio, by mass, appeared to have reached the highest temperature the quickest. This would be optimal for testing as it required the least amount of sample with a potential to spontaneously combust. 200% oil/sawdust or 150 g of oil to 75 g sawdust was very excessive and was beyond the saturation limit of the sawdust. The residual oil was left in the mixing beaker which also drained down the heating system, plugging the steel wool heater core (Figure 2.17). From a range of oil to sawdust tested, a 50% mixture of oil to sawdust appeared to give consistent results in subsequent tests and was used for this experiment. The sawdust was stored in an oven at 103 °C for at least 24 hours before removing it to cool to room temperature and use immediately. The sawdust was a common filter media used for biodiesel purification. It also works great as an absorbent to clean up spills. The sawdust was shaved aspen cellulose and had a wide variety of particle sizes. The sawdust was mixed well before distributing evenly for each mixture, avoiding high quantities of dust to ensure similar packing performance in the reactors.

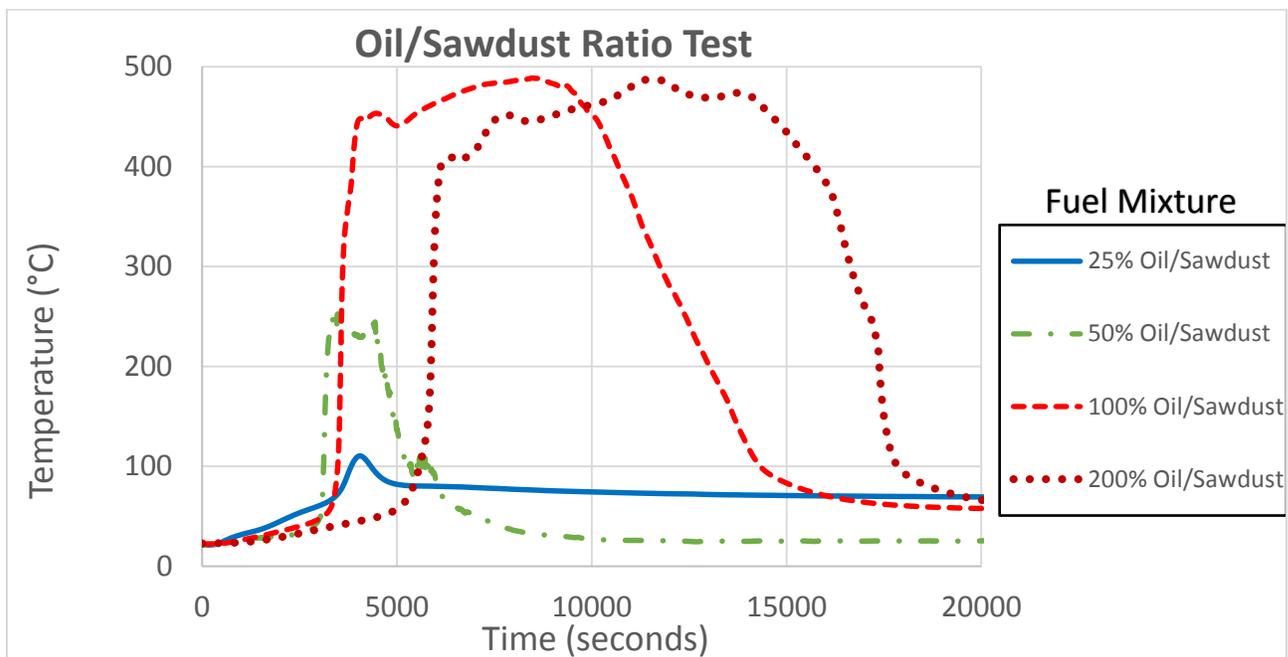


Figure 2.18: Mass-based mixtures of boiled linseed oil to sawdust, i.e. 50% = 37.5 g oil. 75 g of sawdust at 80 °C and 5 L/min

Inlet air airflow

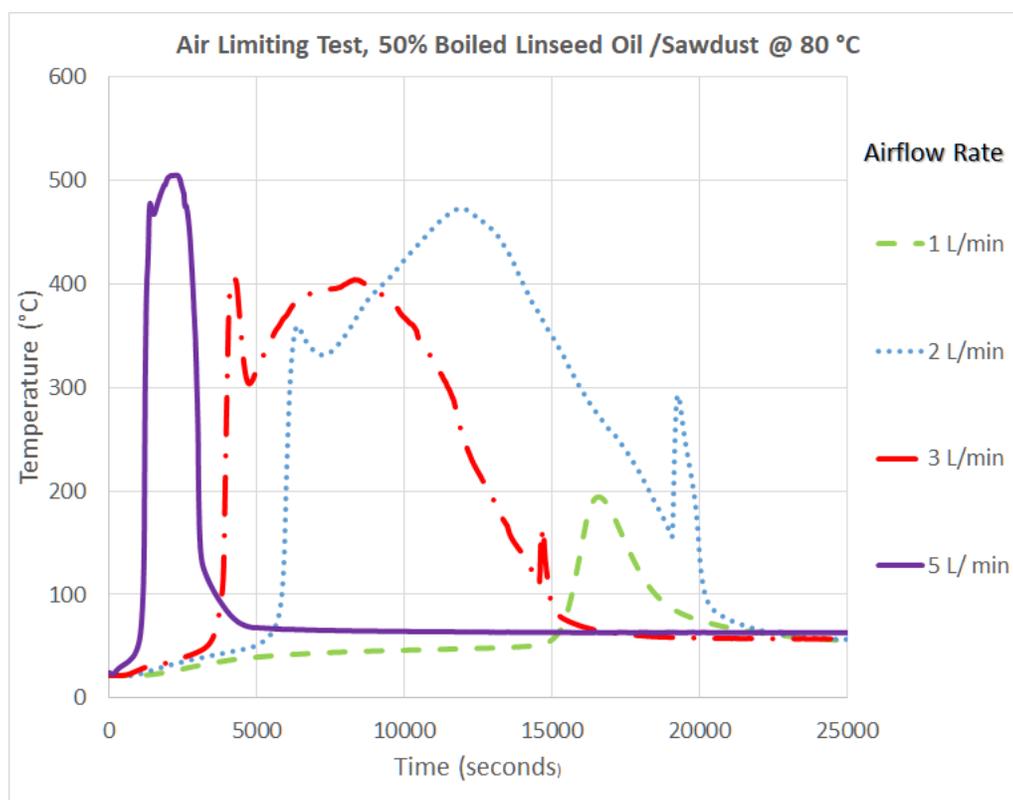


Figure 2.19: Varying amounts of airflow, 50% boiled linseed to 75 g of sawdust at 80 °C

Air limiting test verified that increased airflows reduce time to combustion. 1 L/min of airflow was not enough to cause spontaneous combustion with the same parameters used in the other tests that had higher flow rates. To increase reaction rates, while maintaining measurable air flows using this system, the airflow was maintained at 5 L/min for the final experiment.

Antioxidants

Antioxidants inhibit autoxidation. Antioxidants are typically used as an additive in fuels to prevent oxidation and polymerization that can cause fouling in fuel filters. Adding antioxidants to boiled linseed oil slowed drying reaction rates with increasing amounts of antioxidants. Increasing the amount of antioxidant to 0.2% of the total mass of boiled linseed oil, spontaneous combustion didn't happen in the duration of the test as seen in Figure 2.21. These results infer that oxidation is critical to the self-heating nature of spontaneous combustion of boiled linseed oil. Free radical polymerization may have also been reduced by the antioxidants as well.



Figure 2.20: Increasing amount of Ethanox 4760R, in boiled linseed oil with the leftmost not containing any antioxidant followed by 0.06%, 0.12% and 0.2% of antioxidants by mass.

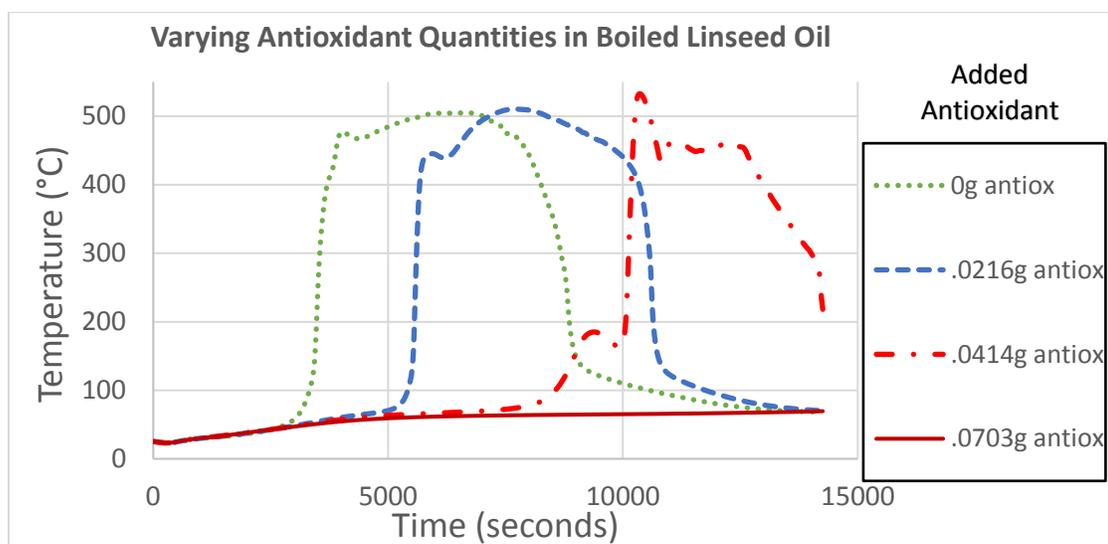


Figure 2.21: Varying amounts of antioxidant added to boiled linseed oil, .0703 g of added antioxidant prevented spontaneous combustion.

Chapter 3: Experimental Results and Discussion

Thermal Runaway

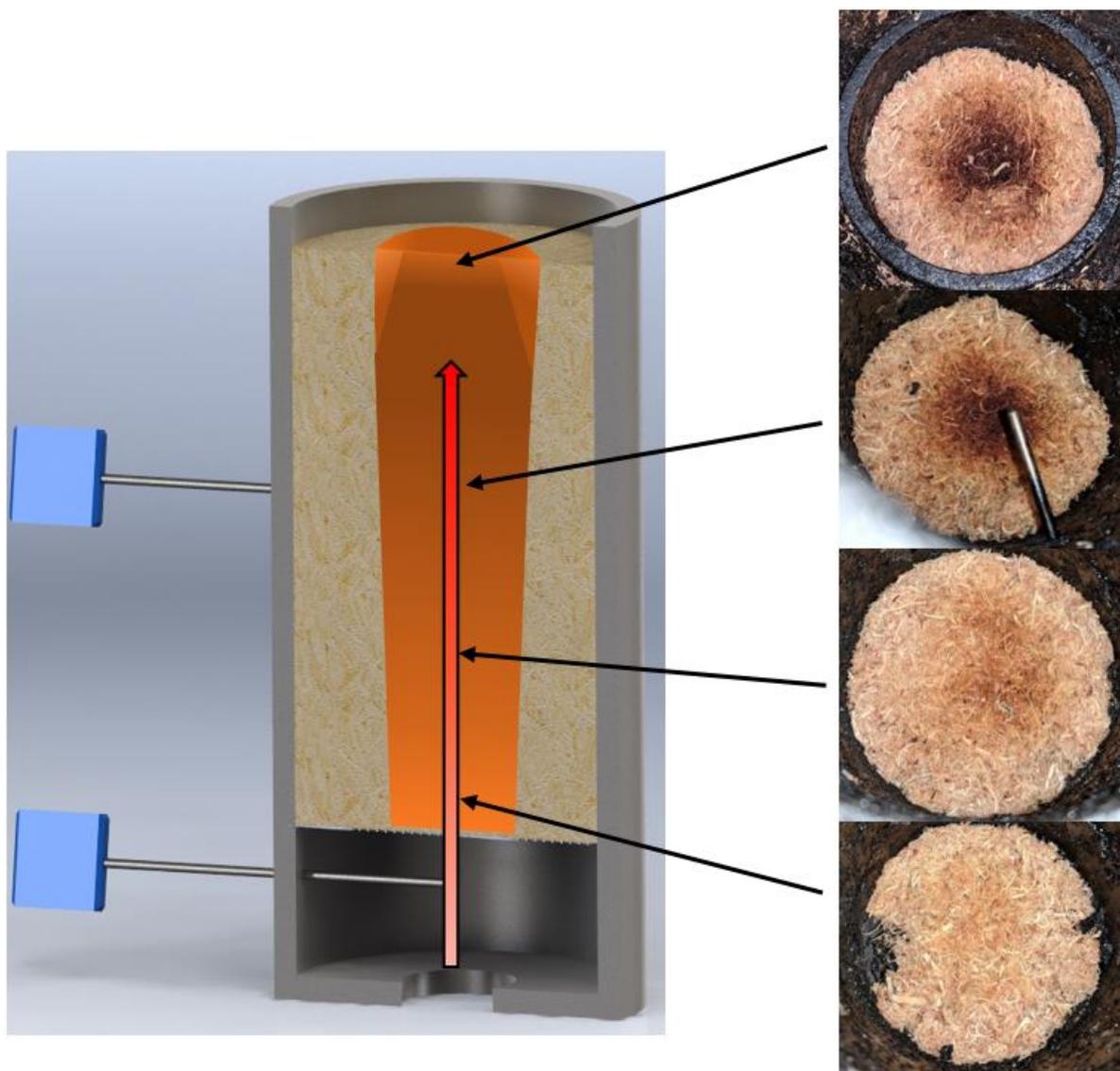


Figure 3.1: Cutaway model of the inside of the reactor, filled with linseed oil soaked sawdust showing the path of heat with the real photo shown on the right. [1 L/min air]

Running 35 g of boiled linseed oil at 1 L/min airflow rate, a near combustion heating event took place with the reactor air set point at 80 °C (Figure 2.19). Photographing from the top of the reactor, sawdust media was removed with a vacuum, shown in Figure 3.1. A picture was taken at the top, 5" from the screen, 3" from the screen, and near the bottom screen. The discolored sawdust, due to pyrolytic reactions, shows the movement of heat through the reactor. The darkest areas indicate the hottest temperature, and a temperature of 194 °C was recorded. It was observed that heat rose and

increased through the reactor, staying hottest at the core of the media. Energy loss through the walls and likely reduced airflow prevented the fuel media from pyrolyzing near the edges of the reactor. The top of the reactor showed lighter colored pyrolyzed sawdust between the center and the edge, indicating greater heat loss near the top as the reactor was open to ambient air. The red arrow at the core of the reactor simulates the incoming heated air gathering heat as it rises through the media, concentrating the most heat near the top of the reactor. The orange gradient simulates the observed color change of the sawdust media due to pyrolysis. Nearly no color change was observed at the bottom near the screen. Although in direct contact with the incoming heated air, the bottom screen may have drawn heat away through conduction, preventing pyrolysis or combustion.

The movement of heat through the reactor appears to be a cumulative effect, as the heat of reaction carries the heat of subsequent reactions. As the heat increases, reaction rates appear to increase, causing significant temperature change throughout the reactor. Natural convection is likely taking place due to buoyancy forces, alongside the forced convection from the heated compressed air.

The fuel media had a smoky, caramel smell, especially in the darkest regions. Apparently, the physical changes to the sawdust are caused by thermal degradation, however, reactive species from the degrading oils and degrading sawdust may also cause exothermic reactions. Acids are known to degrade cellulose, and when tested in the lab with concentrated acid being poured on the sawdust, the sawdust turned to a black sticky liquid that released steam. Temperatures observed of the acid-soaked sawdust exceeded 100 °C and smelled of burnt sugar. Experiments with a non-cellulosic mixture would need to be used to test the effects of acidic volatiles, which are likely created from degrading oils. The Rancimat test used to test the quality of the fuel measures the reactive species from degrading oils and fuels. Further experiments showed that a basic catalyst, sodium methylate, used for making biodiesel reduced the heating effect and may have neutralized some of the acidic volatiles. A filter press would likely capture any remaining catalyst left over from the reaction and may reduce the likelihood of spontaneous combustion.

Spontaneous Combustion Severity Index

Complicated data can make analysis difficult. Systems with high amounts of known variables and potentially higher quantities of unknown variables cause confusion and lack of confidence when collected data is messy. Strong statistics are critical to interpreting meaningful results from data. Organizing data in uniform patterns, such as Latin squares, can simplify statistical methods and produce strong evidence over multiple factors. Assuming my reactors would perform similarly, and my limited time to run my experiments, I utilized a 2^4 factorial design through three completely randomized replications. The factorial table of the 16 mixtures is shown below in Table 3.1. A total of 48 experiments were run with the data shown in Appendix A. The data consists of multiple tests stacked on the same graph based on the mixture. The temperature of the air and the temperature of the fuel, measured from the middle of the reactor, was plotted. The air temperature was set to stay consistent at 80 °C. The fuel temperature, sawdust soaked with the mixture, was also recorded and used for statistical analysis.

Table 3.1: 2^4 factorial design of mixtures

Mixture	Fuel	Type	Catalyst	Quality
I	Oil	WVO	No	Rancid
a	Biodiesel	WVO	No	Rancid
b	Oil	Linseed	No	Rancid
ab	Biodiesel	Linseed	No	Rancid
c	Oil	WVO	Yes	Rancid
ac	Biodiesel	WVO	Yes	Rancid
bc	Oil	Linseed	Yes	Rancid
abc	Biodiesel	Linseed	Yes	Rancid
d	Oil	WVO	No	Fresh
ad	Biodiesel	WVO	No	Fresh
bd	Oil	Linseed	No	Fresh
abd	Biodiesel	Linseed	No	Fresh
cd	Oil	WVO	Yes	Fresh
acd	Biodiesel	WVO	Yes	Fresh
bcd	Oil	Linseed	Yes	Fresh
abcd	Biodiesel	Linseed	Yes	Fresh

Testing Consistency

With minimal knowledge about what would happen with the testing system, experimentation led to a stronger understanding. Using a systematic approach, each test was conducted similar, but with inherent variations. Sixteen runs using four similar reactors, operating at similar set points for temperature and airflow, were randomized completely. Uncertain about drying rates for any mixtures, twenty-four-hour runs were used. Determining the set points were done using runs of boiled linseed oil. Testing reactor consistency, bone-dry sawdust (BDS), was filled in each reactor. $70 \pm .05$ g of BDS was loaded in each reactor, lightly compacted by gentle shaking, then set to run at $80\text{ }^{\circ}\text{C}$ at 5 L/min airflow for at least 48 hours. This test was conducted to determine if there was variation in the media temperature through a couple of day and night cycles along with the consistency of the heating controller. Results from the test are shown below in Table 3.2 after a 59-hour-long test.

Table 3.2: Temperature variation over 59 hours running bone-dry sawdust (BDS). Maximum and Minimum temperatures were recorded for each reactor for both the BDS and air. The difference between temperatures is color-coded based on variation as higher yellow and lower green.

	Reactor 1		Reactor 2		Reactor 3		Reactor 4	
	BDS	Air	BDS	Air	BDS	Air	BDS	Air
Max	65.87	80.49	69.31	80.26	60.35	80.70	61.30	80.24
Min	65.30	79.46	68.80	79.70	59.92	79.35	60.65	79.78
Diff.	0.57	1.03	0.51	0.57	0.43	1.35	0.65	0.47

The difference in temperature changed very little between the reactors, maintaining a difference less than $\pm 1\text{ }^{\circ}\text{C}$ for the BDS. The reactors were brought up to temperature nearly as fast as possible and after stabilizing near 10,000 seconds, measurements in variation were shown in Table 3.2. The test ran for 213,750 seconds (59.3 hours) measured at 30-second intervals. The results of this test show the reactors are fairly stable at maintaining temperatures over extended periods of time without much effect from daily temperature fluctuations or activity in the laboratory. Air temperature, the controlling factor, had on average more fluctuation than the sawdust, with sawdust more stable from the larger thermal mass. Reactor 3 had a small, harmonic-like variation, that caused rapid oscillations of temperature and was later refined by tuning of the controller parameters in the fine adjustment settings.

Table 3.3: BDS temperature variation and average temperature. Conditional formatting shows reactor 3, in green, as the coolest and reactor 2, in red, as the hottest.

	Reactor 1	Reactor 2	Reactor 3	Reactor 4
	BDS	BDS	BDS	BDS
Max	65.87	69.31	60.35	61.30
Min	65.30	68.80	59.92	60.65
AVG.	65.62	69.06	60.16	60.99

The average temperature of the BDS in each reactor was nearly 9 °C difference between the reactors with reactor 2 having the highest average temperature and reactor 3 having the coolest as seen in Table 3.3. This one run is not enough to show trends in the behavior of each reactor. Due to the nature of the sawdust having shape, density, porosity, compaction, and chemical composition to name a few of the variables, creating similar results is difficult and may nullify max temperature as a possible element in determining the reactivity of the reactants. Multiple tests, alternating the same set of sawdust randomly in the reactors, while maintaining similar bulk density may uncover temperature bias for each reactor. However, observing the results in Figure 3.2, similar patterns emerge in the behavior of the BDS. The sawdust was placed in the reactors after coming out of the 103 °C oven and cooling for a short time. The reactors take about one hour to reach stable operating temperatures, while the sawdust takes about three hours to reach stable temperatures. Fast reacting mixtures may be difficult to determine if reactions take place during initial reactor heating and may require lower temperature set points to delayed reactions.

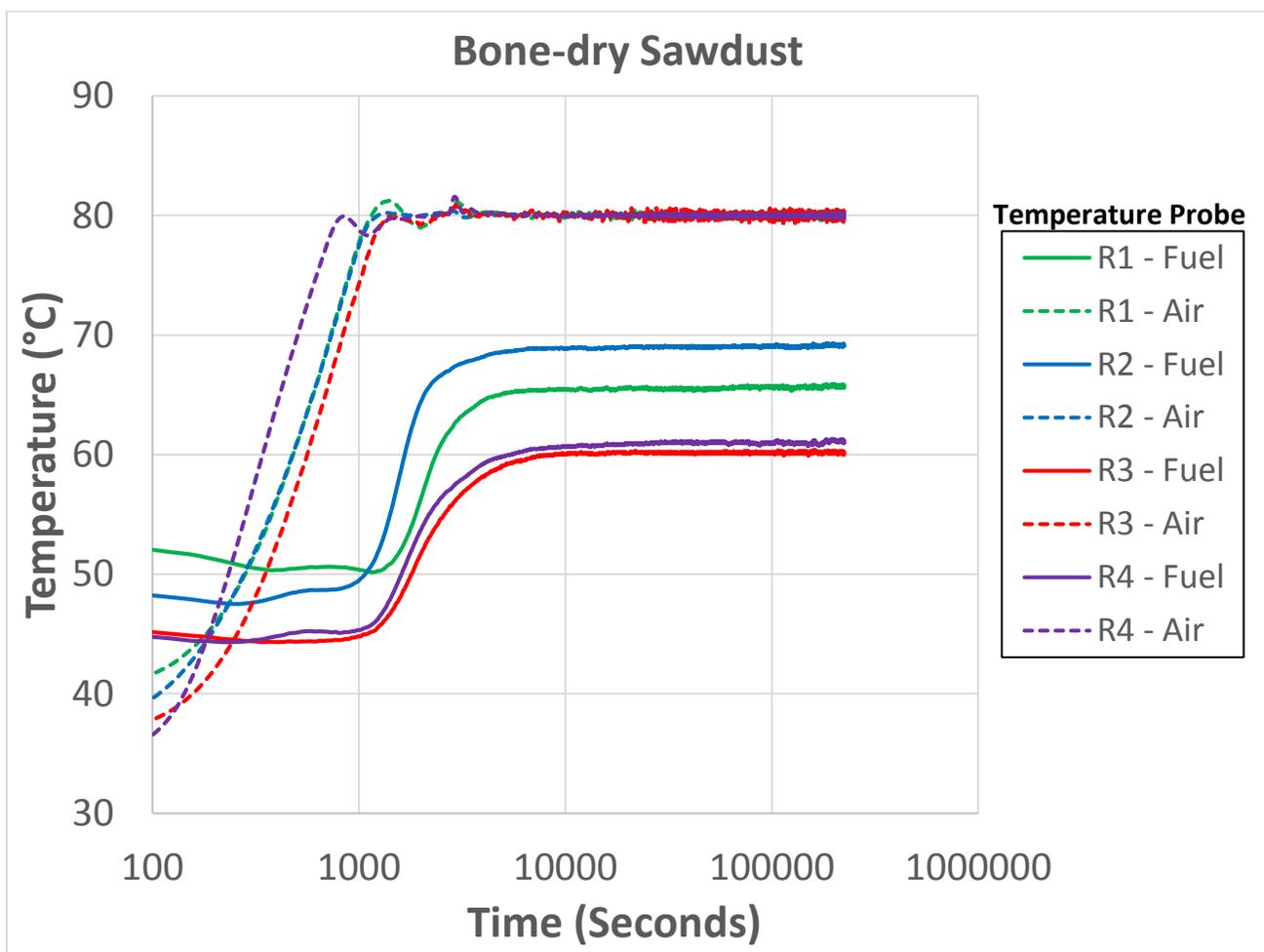


Figure 3.2: BDS recorded temperatures of the four reactors. 5 L/min airflow at 10 psi at 80 °C air temperature.

Interesting notes from the BDS test show cooling effects for the first five minutes as the air temperature matches the pre-warmed sawdust. A shallow dip in BDS temperatures around 1000 seconds matches when the air temperature drops to meet the setpoint. Reactor 4 reached 80 °C air temperature the quickest but was one of the slowest to reach a stable temperature. The variation in BDS temperature in four reactors may be due to the variation in heat loss due to nonuniform conductive properties of reactor wall, sawdust, insulation, airflow over the exterior of the reactors.



Figure 3.3: Thermal image of reactors during operation. Heat loss is seen in the legs of the reactors and through the holes for thermocouples. Reactor 4 has four holes for extra temperature measurement locations

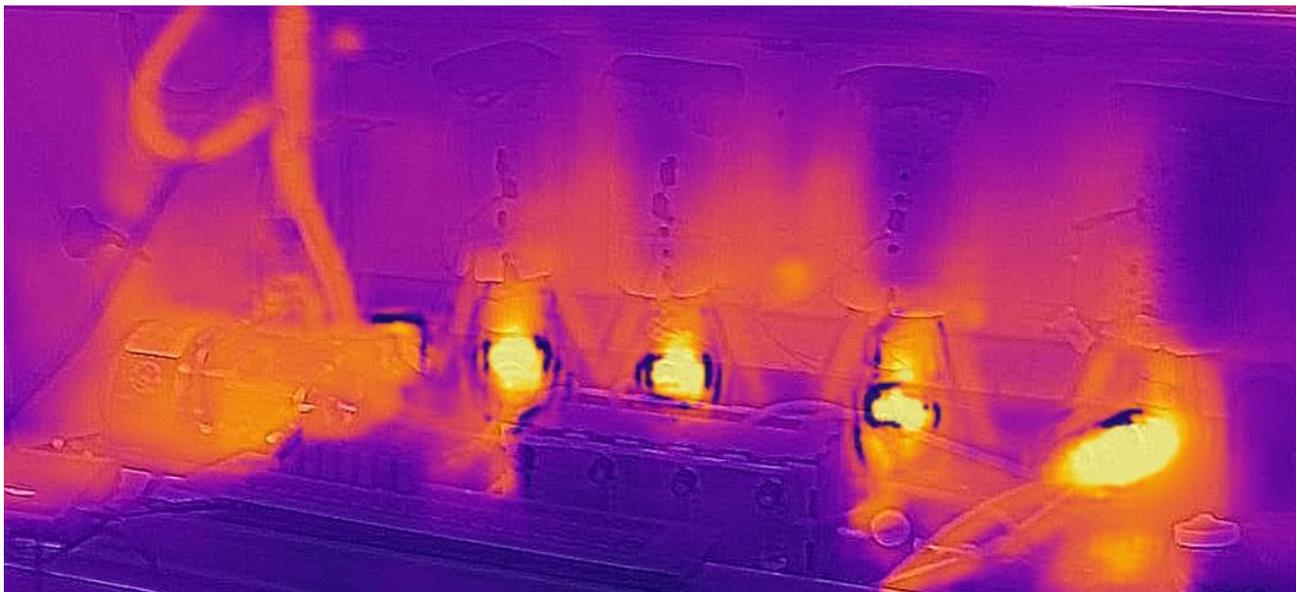


Figure 3.4: Thermal image during Initial heating of reactors. All reactors are currently at room temperature with heaters at 100% power.



Figure 3.5: Thermal image of the experimental setup during operation. Reactors are numbered from left to right, 1 to 4 respectively. Reactor 1 and 2 were slightly closer together in position and in close proximity to the compressor.

These thermal images show the heat flow out of the reactors and other factors that may affect the thermal values measured during the tests. Testing would be optimized if the reactors were sealed from external sources of wind and heat. Better insulation will provide more consistent results.

Testing Parameters

The experiment ran an 80 °C setpoint for 24 hours, a 2⁴ factorial was created and replicated 3 times to determine mixtures placement and run order. Each test used the same quantity 70 ± .05 g of BDS, hand-mixed uniformly with 35 ± .05 g of the predetermined mixture from the factorial table. 5 ± .05 g of 25% sodium methylate in methanol was added to the mixture that was YES for catalyst. It should be noted that catalyst is a term used for biodiesel catalyst, and not something deliberately added to

increase the rate of reaction for spontaneous combustion. It was unknown the effects the caustic catalyst would have, if any, on the propensity for spontaneous combustion to happen in biofuels.

Spontaneous Combustion Severity Index (SCSI)

After reviewing the data from the experiment, it was observed that a crossing-point temperature was never met under the tested parameters. A crossing-point temperature is when the temperature of an initially colder measured species meets and exceeds the oven temperature set point. The crossing-point method is useful as the kinetic parameters of the testing material and oven are not needed, however, due to the lower temperatures of the experiments performed, the crossing-point method could not be used. Therefore, a new method needed to be created to help decipher the data. Looking at the resulting graphs from the data, which are all shown in Appendix A, multiple patterns were observed. A small rise in temperature was observed in the BDS mixed with linseed fuels, after three hours when the fuel temperature started to level out. Consistent shapes appeared between different runs in different reactors with the same mixtures. Some of the heat rise recorded was greater than other mixtures and some heat rose sooner than other mixtures. Fresh fuels appeared to take longer to have a thermal event when compared to rancid fuels, which heated very quickly in comparison. Linseed oils and fuels showed higher changes in temperature when compared to WVO oils and fuels. Mixtures with added catalyst appeared to not have as much thermal change when compared to mixtures without catalyst added, much like the catalyst retarded the reaction rates. This new method, which is being called Spontaneous Combustion Severity Index (SCSI), was designed to be a unitless value that took in account the setpoint temperature of the oven along with the time the fuel reaches its maximum temperature. Set time and temperature at that set time were introduced to reduce variations between reactors and solely look at the factors being tested, assuming the reactors had little effect on the SCSI value.

SCSI is calculated using the equation 1. SCSI is used to simplify a complex relation of a material and its likelihood to spontaneously combust.

$$SCSI = \frac{Max\ Temp. - Temp.\ at\ Set\ Time}{Oven\ Set\ Point\ Temp.} * \frac{Set\ Time}{Max\ Temp.\ Time} \quad [1]$$

Running an analysis of variance over the SI80 (Spontaneous Combustion Severity Index 80 °C) values, an ANOVA table (Figure 3.6) was created along with an interaction plot (Figure 3.7) and the main effects plot (Figure 3.8) using Minitab software. The ANOVA table shows a high R-sq value along with significant effects from each of the four factors, along with most of the 2-way interactions. The reactors appear to have no significant effect on the SI80 value, so it appears it was safe to assume they were similar. The difference between oil and biodiesel appear to be slight in the effect on SI80

values, with biodiesel slightly more likely to have higher SI80 values. A higher SI80 value, the more likely the mixture is to self-heat and potentially spontaneously combust. SI80 values are calculated using Eq. [1] and shown in Table A.1 in Appendix A.

Factor Information

Factor	Type	Levels	Values
Fuel	Fixed	2	Oil, Biodiesel
Type	Fixed	2	WVO, Linseed
Catalyst	Fixed	2	No, Yes
Quality	Fixed	2	Rancid, Fresh
Reactor	Fixed	4	1, 2, 3, 4

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Fuel	1	0.000096	0.000096	12.26	0.001
Type	1	0.000815	0.000815	104.59	0.000
Catalyst	1	0.000298	0.000298	38.21	0.000
Quality	1	0.000413	0.000413	53.04	0.000
Reactor	3	0.000032	0.000011	1.35	0.273
Fuel*Type	1	0.000034	0.000034	4.38	0.044
Fuel*Catalyst	1	0.000001	0.000001	0.08	0.778
Fuel*Quality	1	0.000037	0.000037	4.74	0.036
Type*Catalyst	1	0.000194	0.000194	24.95	0.000
Type*Quality	1	0.000463	0.000463	59.38	0.000
Catalyst*Quality	1	0.000138	0.000138	17.66	0.000
Error	34	0.000265	0.000008		
Lack-of-Fit	20	0.000208	0.000010	2.54	0.039
Pure Error	14	0.000057	0.000004		
Total	47	0.003169			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0027921	91.64%	88.44%	83.33%

Figure 3.6-ANOVA table of SI80 (Severity Index 80 °C) of the experiment

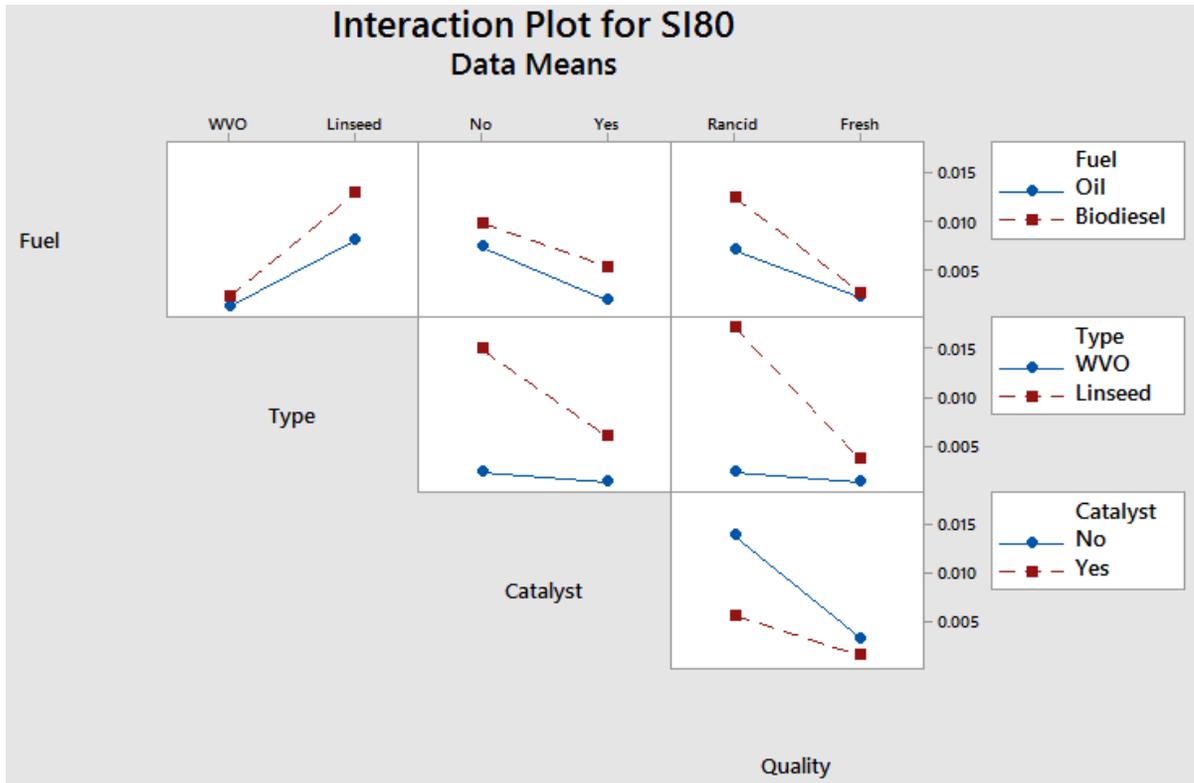


Figure 3.7 - SI80 interaction plot of the experiment

Factors and interactions

Interaction plots visually show variation between factors, with parallel lines showing little to no interaction. A brief explanation of the factors follows. A higher SI80 value, the more likely the mixture is to self-heat and potentially spontaneously combust.

Catalyst: Virtually no effect between the type of fuel, oil or biodiesel, however, adding catalyst reduced the SI80 value of both. Adding catalyst to linseed fuel reduced the SI80 value significantly. Linseed is likely to self-heat versus WVO, so adding the basic catalyst appears to have reduced the propensity for spontaneous combustion. Comparison between Figure A.3 and Figure A.7 in Appendix A.

Type: Linseed fuels, both oil and biodiesel, were more affected by the addition of catalyst and the quality of fuel. Rancid linseed fuels were the highest values recorded, which can easily be seen in the graphs Figure A.3 and Figure A.4 in Appendix A.

Quality: Rancid fuels were more likely to have a higher SI80 than fresh fuels. This was mostly caused by the rate at which the fuels would heat. Quicker to heat fuels are more dangerous if temperatures rise to critical levels for shorter periods of time. Highly unsaturated fuels are more

susceptible to going rancid quicker, as observed in Table 2.2 and heat quicker between Figure A.4 and Figure A.12 in Appendix A.

Fuel: Oil and biodiesel both can be found in a filter press. Biodiesel, a smaller molecule, appears to have a higher SI80 value compared to oil. Catalyst affects both oil and biodiesel similarly as the fuel and oil have the nearly identical quantity of unsaturated bonds as the fatty acid profile of the oil becomes the fatty acid profile of the biodiesel.

The main effects overall can be seen below in the main effects plot for SI80, Figure 3.8. Looking only at the individual factors, the higher the mean of SI80, potentially the higher the propensity for spontaneous combustion. Lower values such as oil, WVO, catalyst added, and fresh fuel factors are likely to reduce the potential for fires. Higher values such as biodiesel, linseed, and rancid fuel factors are more likely to create higher SI80 values and are more likely to potentially spontaneously combust.

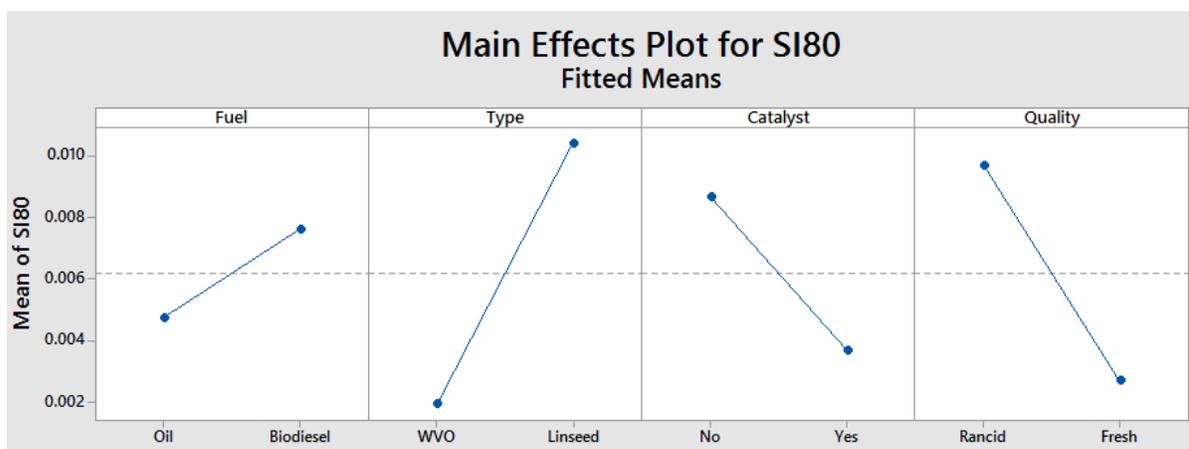


Figure 3.8 - Main effects plot for SI80 of the experiment

Conclusions

The results gathered in the temperature graphs and using the SI80 method to perform statistics on the results have developed a way to understand the conditions necessary to cause spontaneous combustion using chemicals likely found in a biodiesel plant. Saturation of the fatty acid is critical to the likelihood of fuel spontaneously combusting, shown between linseed and WVO mixtures. Fuels with higher levels of 18:3 fatty acids should be treated with care when used and disposed of. The addition of basic catalyst appears to reduce the likelihood of spontaneous combustion by potentially neutralizing the acids released by the decomposing fuel, but further testing is required to develop a stronger understanding. Biodiesel is slightly more likely to spontaneously combust when compared to oil, likely due to oils absorbing higher amounts of energy when compared to the smaller biodiesel molecules. Rancid fuels and oils were more likely to heat quicker than fresh fuels and oils and had more of an effect with highly unsaturated oils. Sawdust and other absorbent materials should be disposed of properly to reduce the chance for fires, especially rancid unsaturated fuels. Antioxidants and basic chemicals may be used to prevent spontaneous combustion by adding them to adsorbents and filter media but may create other issues such as costs and environmental hazards.

Chapter 4: Future Work

Using the information gathered from this research, a few unanswered questions emerged. How do other materials, such as rust, affect the propensity for spontaneous combustion? Is there a critical reactor set point temperature where reactions will happen nearly 100% of the time by increasing inlet air temperature? What if there wasn't enough fuel to sawdust ratio to get accurate results? What if the temperature probes measuring the fuel temperature were placed in different locations? Are there other feedstocks, high in unsaturated fats, that should be measured? Does sawdust have an effect on the likelihood of spontaneous combustion? Could this test run different media, such as ion exchange beads or magnesium silicate? How repeatable are these results if manufactured and tested elsewhere? These questions open many opportunities to increase understanding and provide valuable research.

As for curiosity to answer above questions, the reactor was modified with a water-cooled air intake nozzle, fitted with 3 fuel temperature probes, and was filled with the most susceptible to spontaneous combustion fuel, rancid linseed biodiesel. Running the test for less than 2 hours at 100% fuel/sawdust (70 g fuel/ 70 g sawdust) at 100 °C at 5 L/min airflow at 20 psi produced the first crossing point temperature and complete spontaneous combustion (Figure 4.1). These results are encouraging interest to research more on this topic in the future.

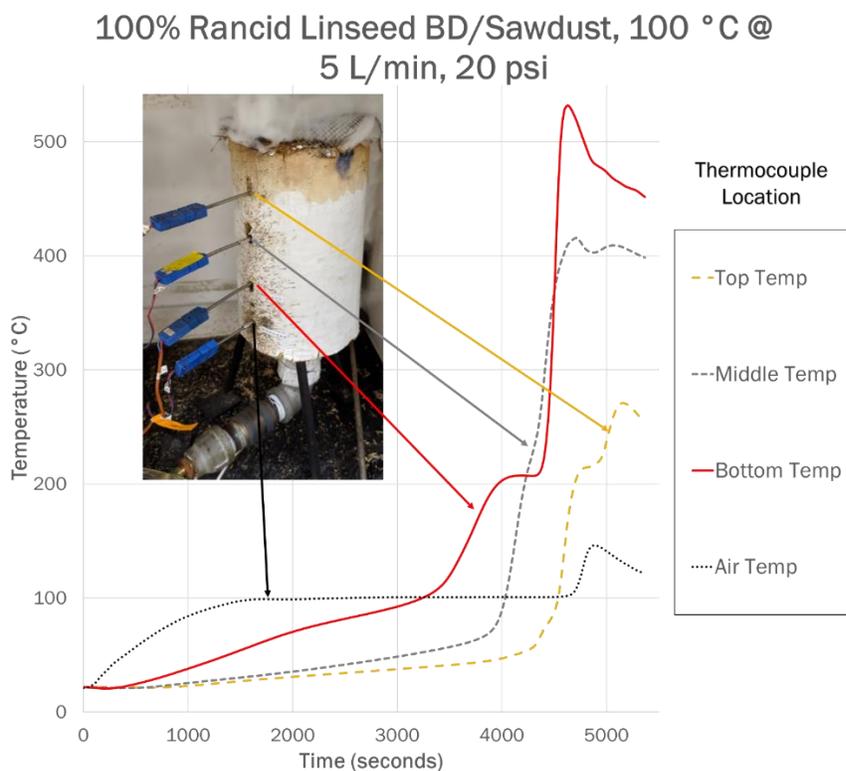


Figure 4.1: Spontaneous combustion of rancid linseed biodiesel.

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Appendix A - Experimental Results

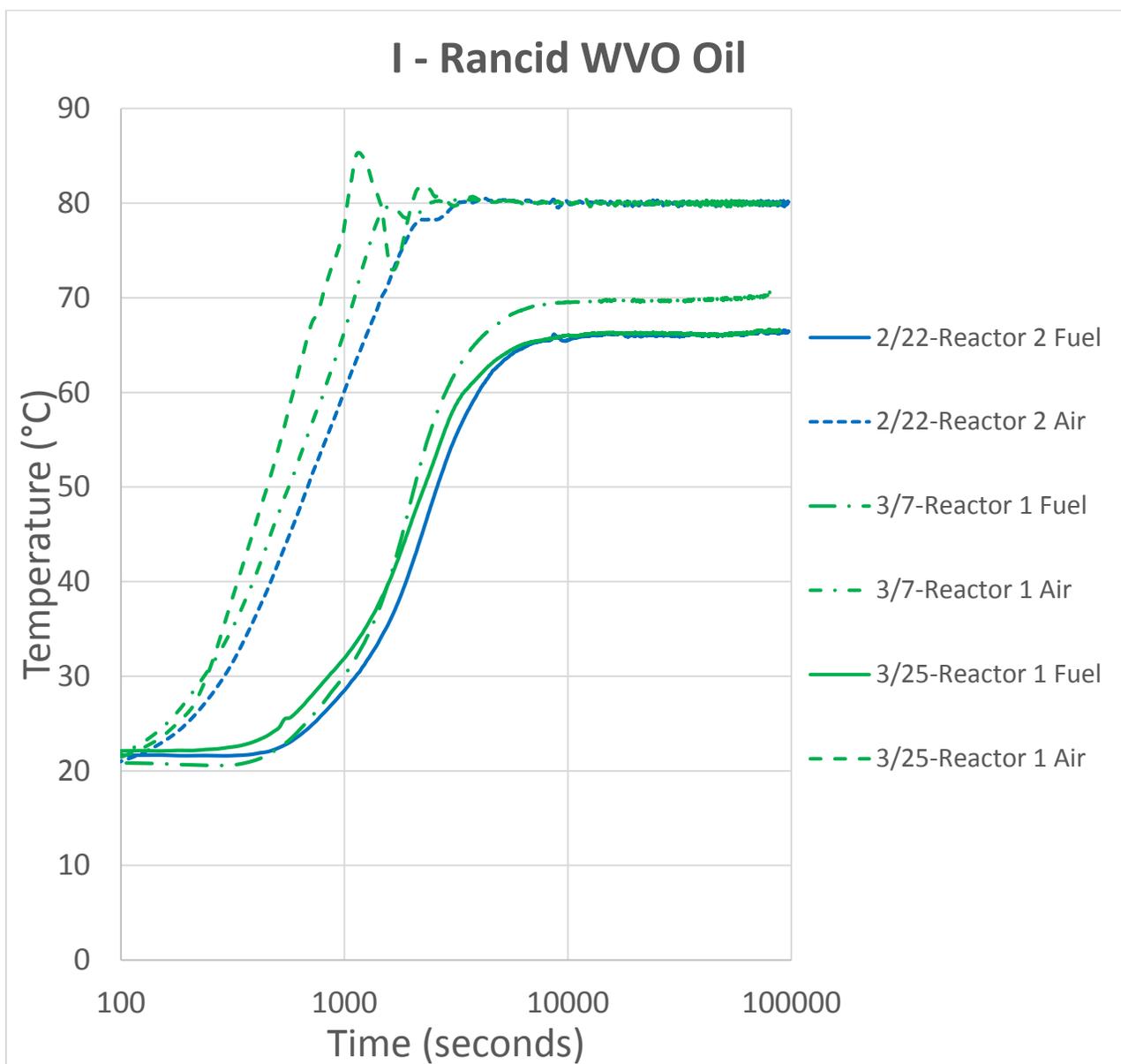


Figure A.1: I - Rancid WVO Oil

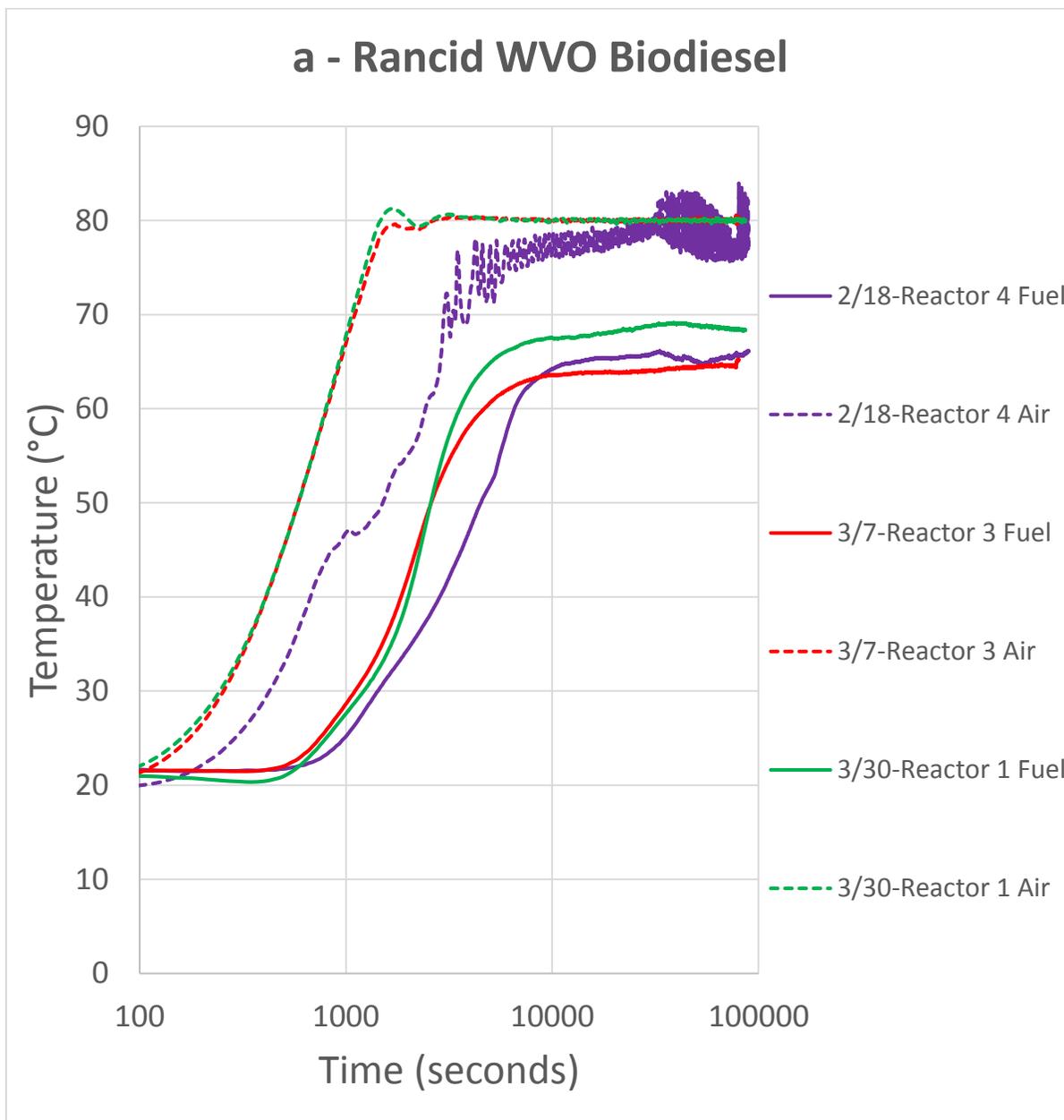


Figure A.2: a - Rancid WVO Biodiesel

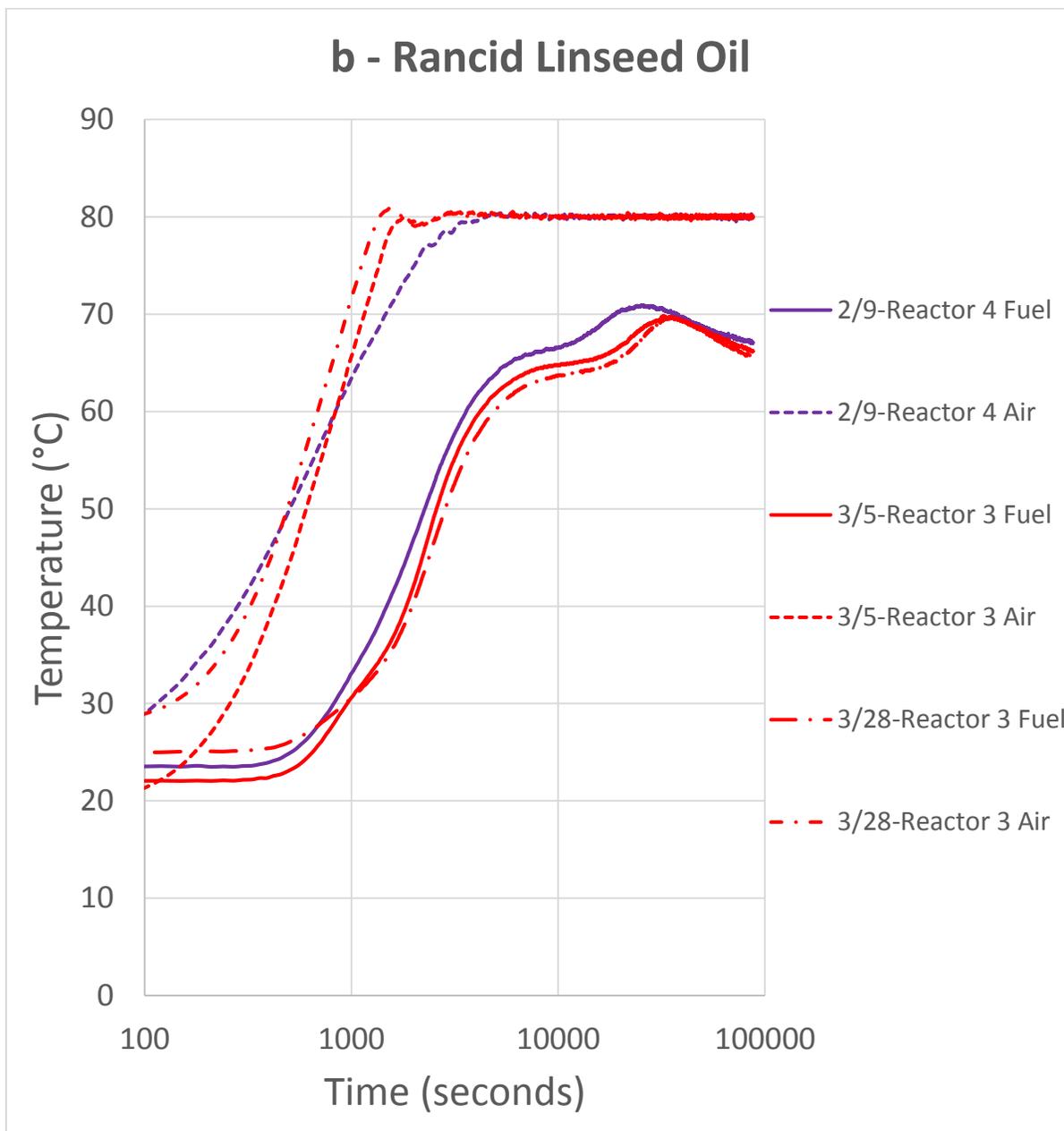


Figure A.3: b - Rancid Linseed Oil

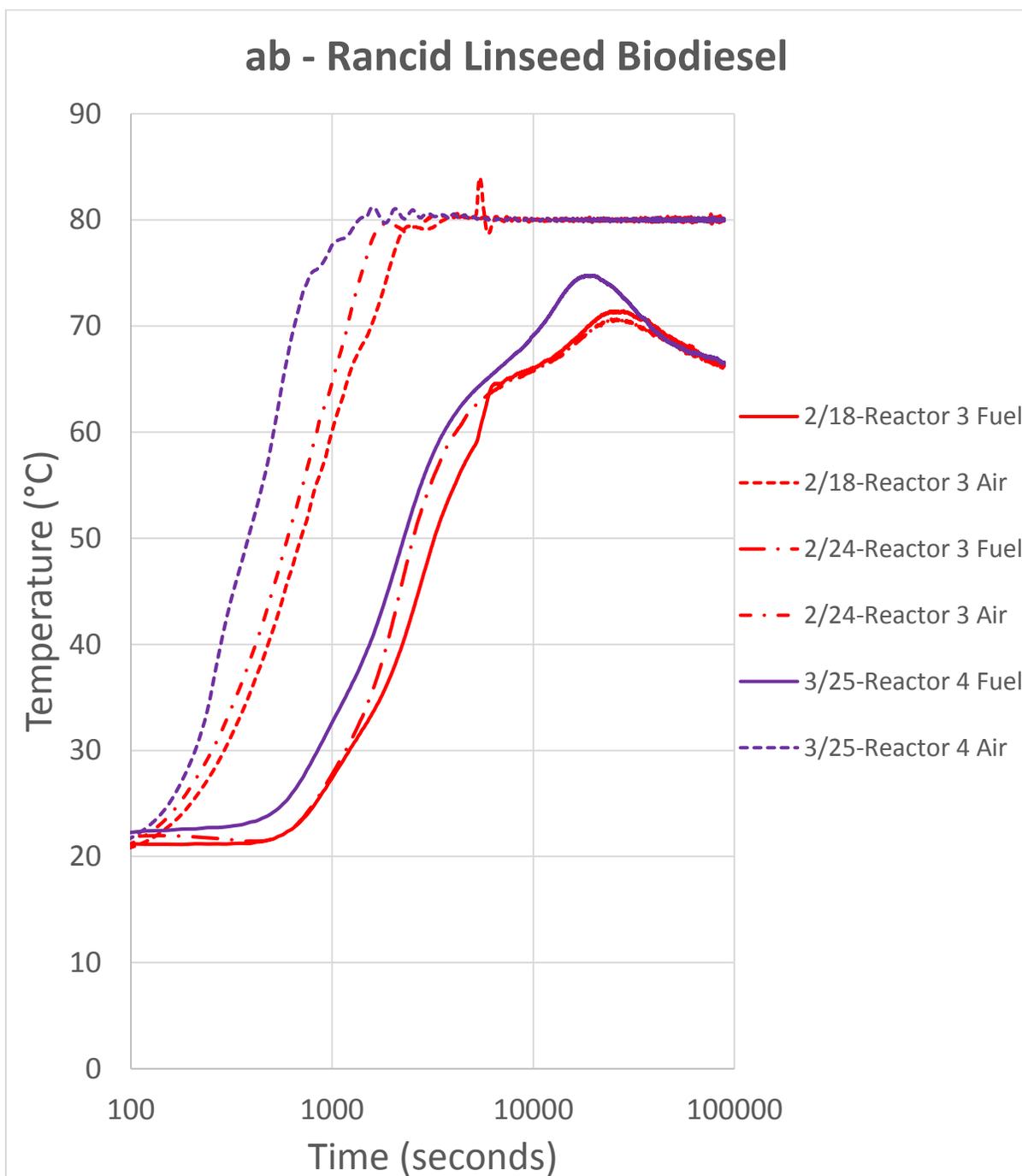


Figure A.4: ab - Rancid Linseed Biodiesel

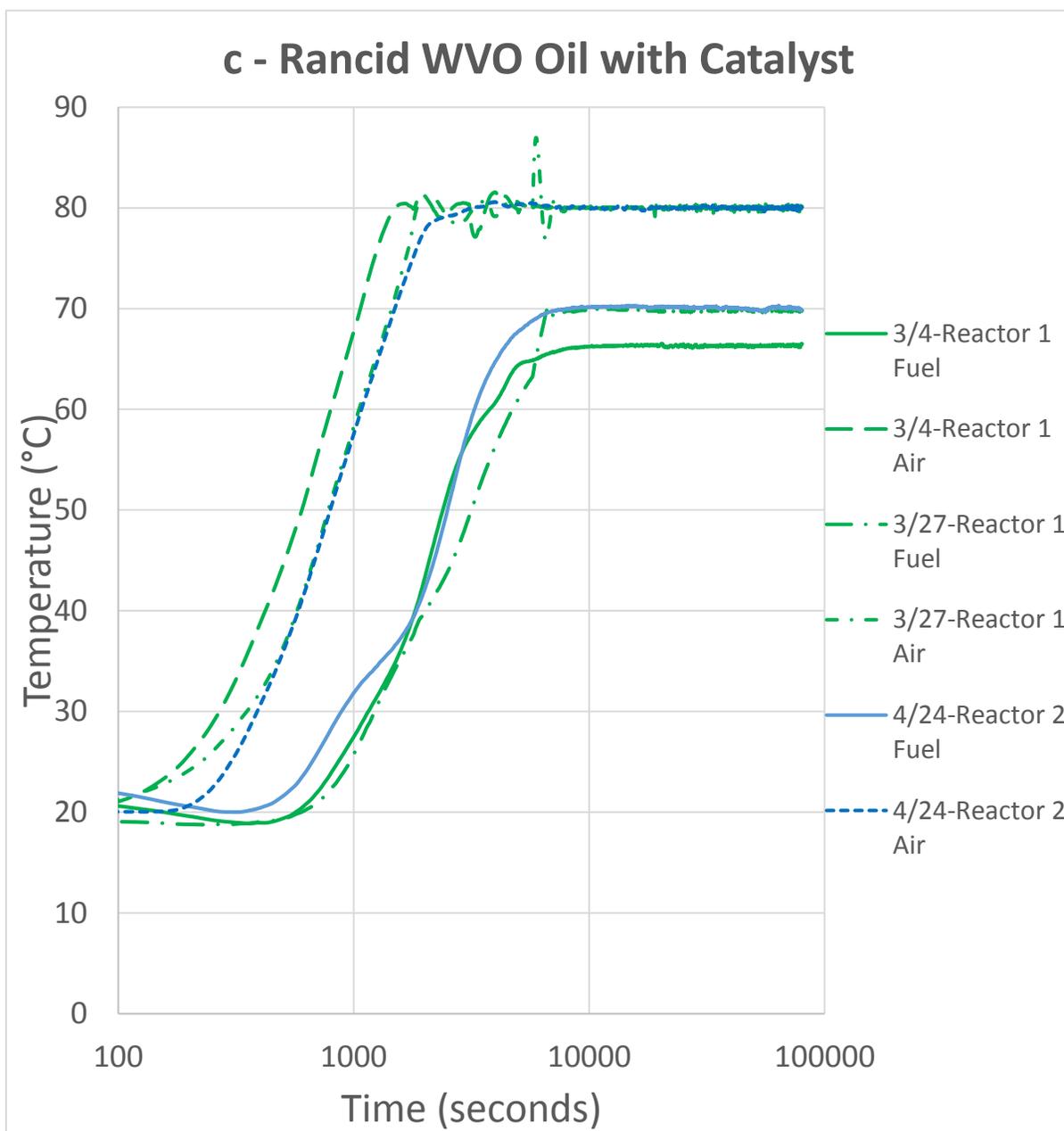


Figure A.5: c - Rancid WVO with Catalyst

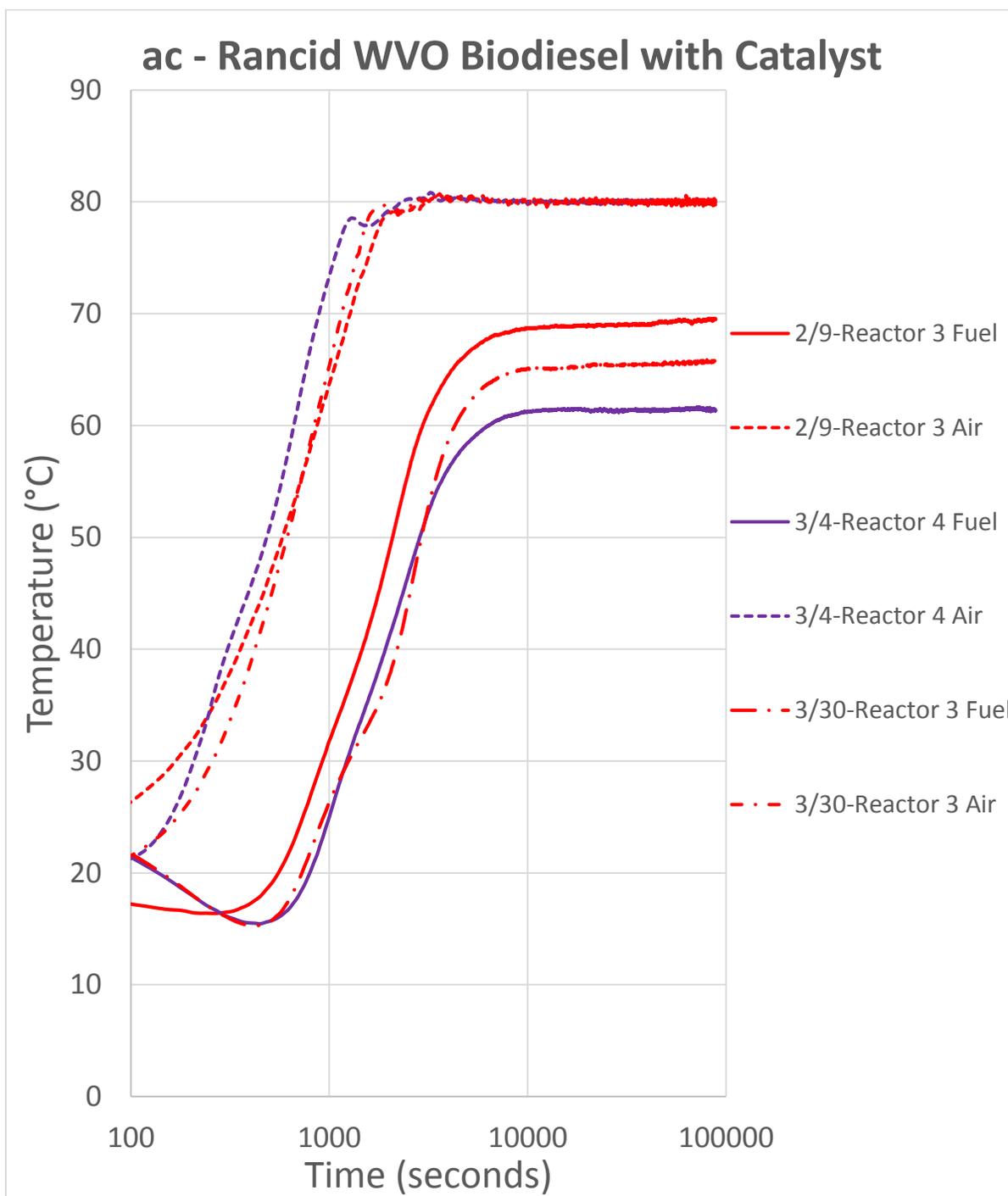


Figure A.6: ac - Rancid WVO Biodiesel with Catalyst

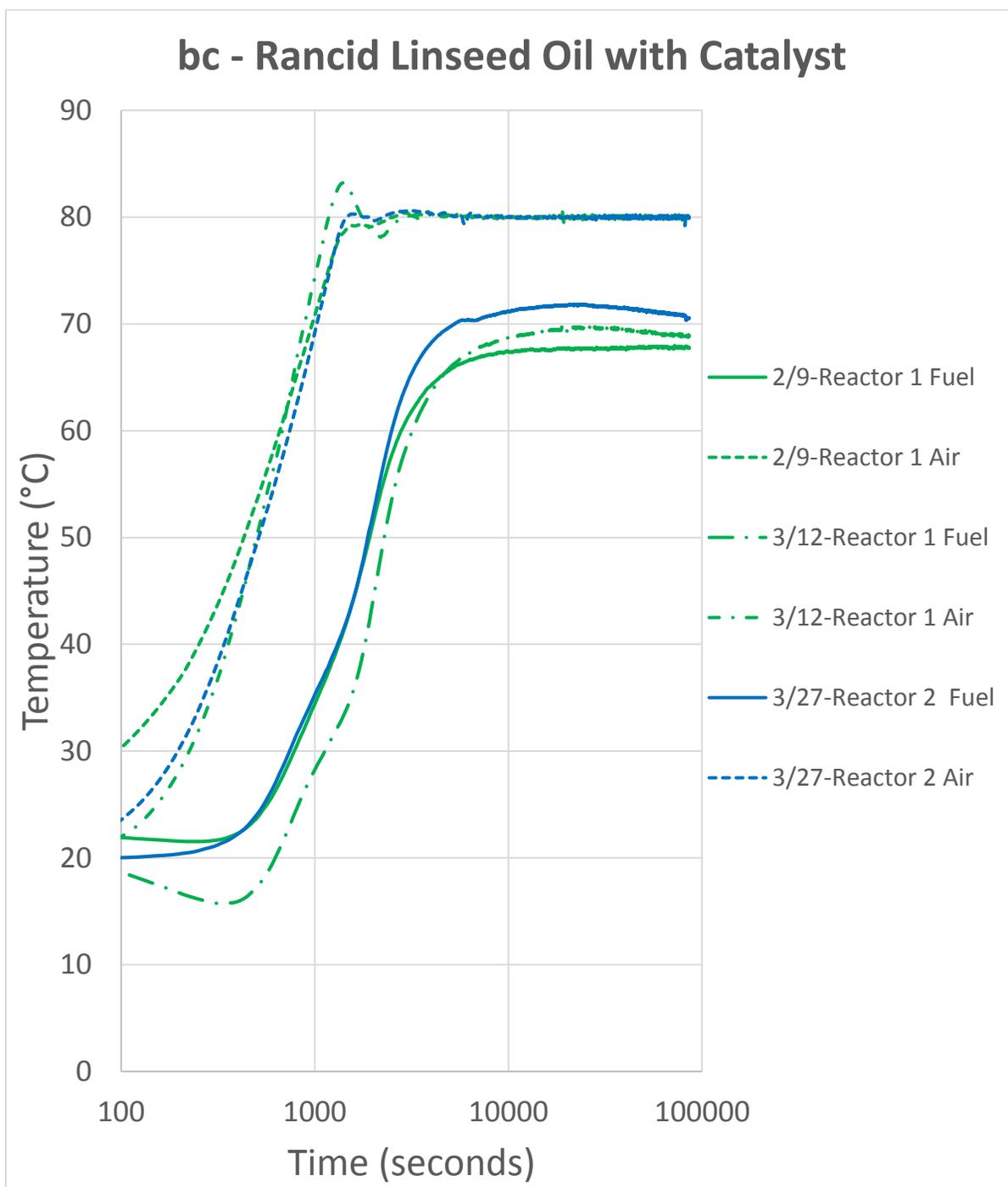


Figure A.7: bc - Rancid Linseed Oil with Catalyst

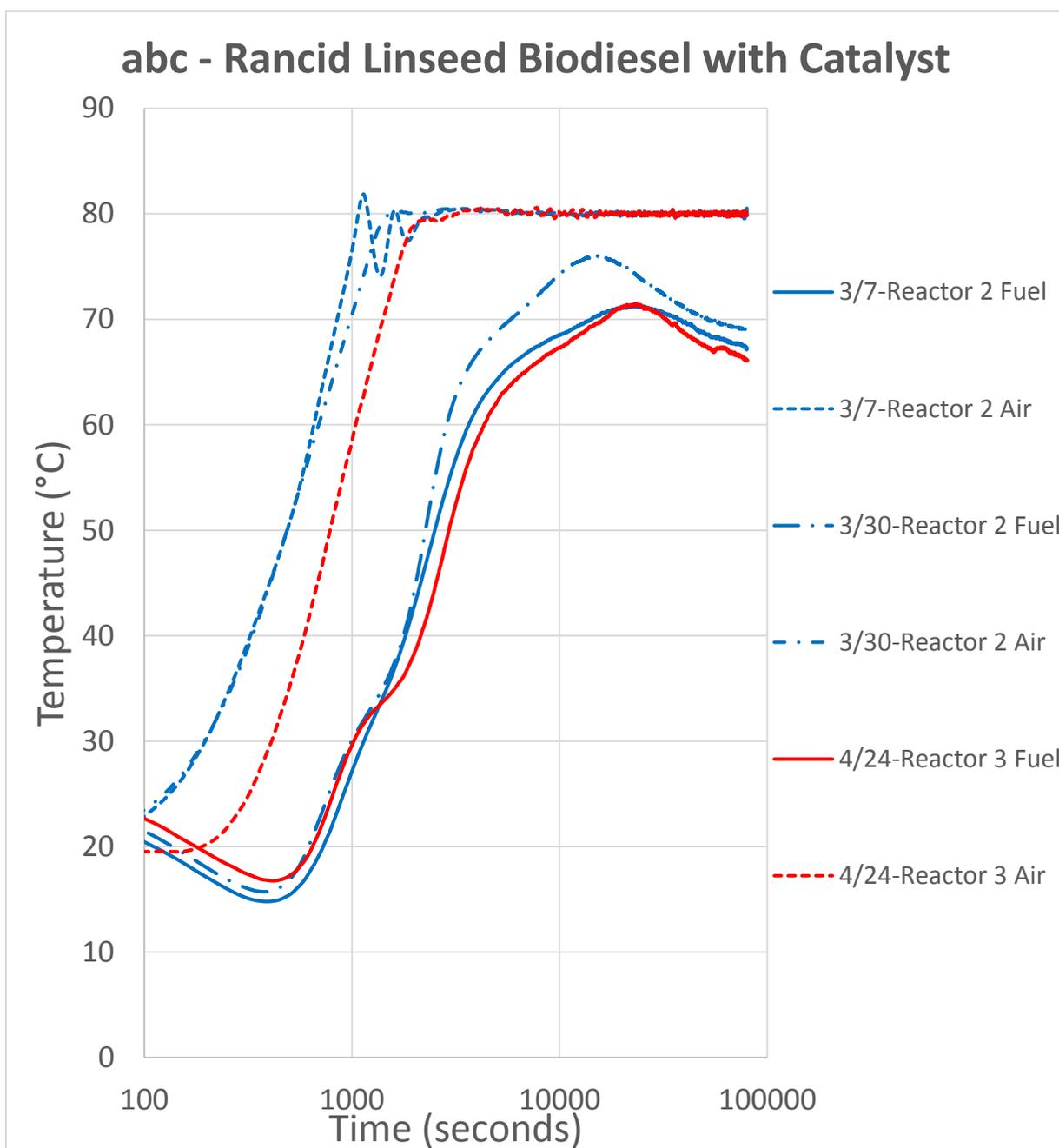


Figure A.8: abc - Rancid Linseed Biodiesel with Catalyst

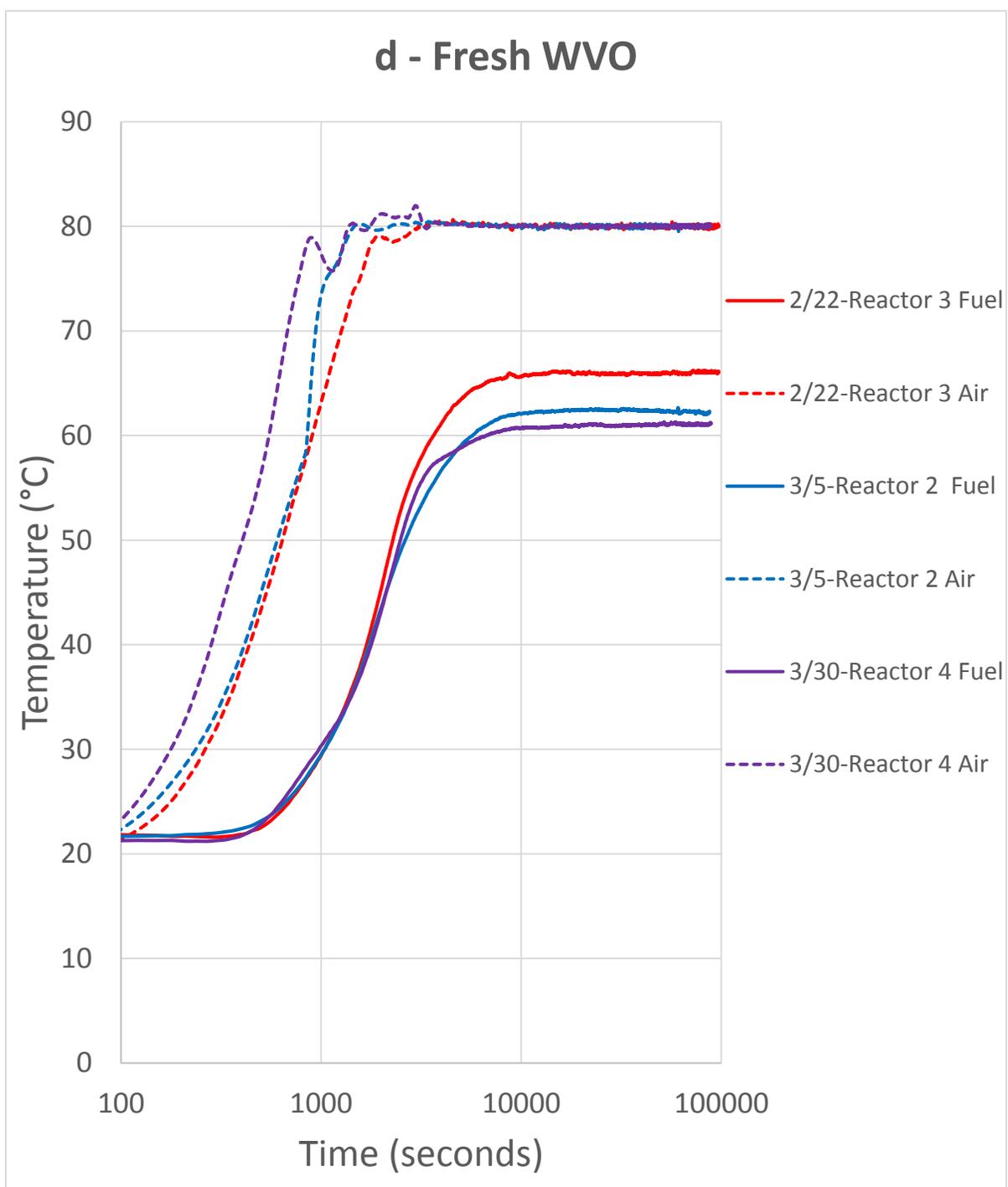


Figure A.9: d - Fresh WVO

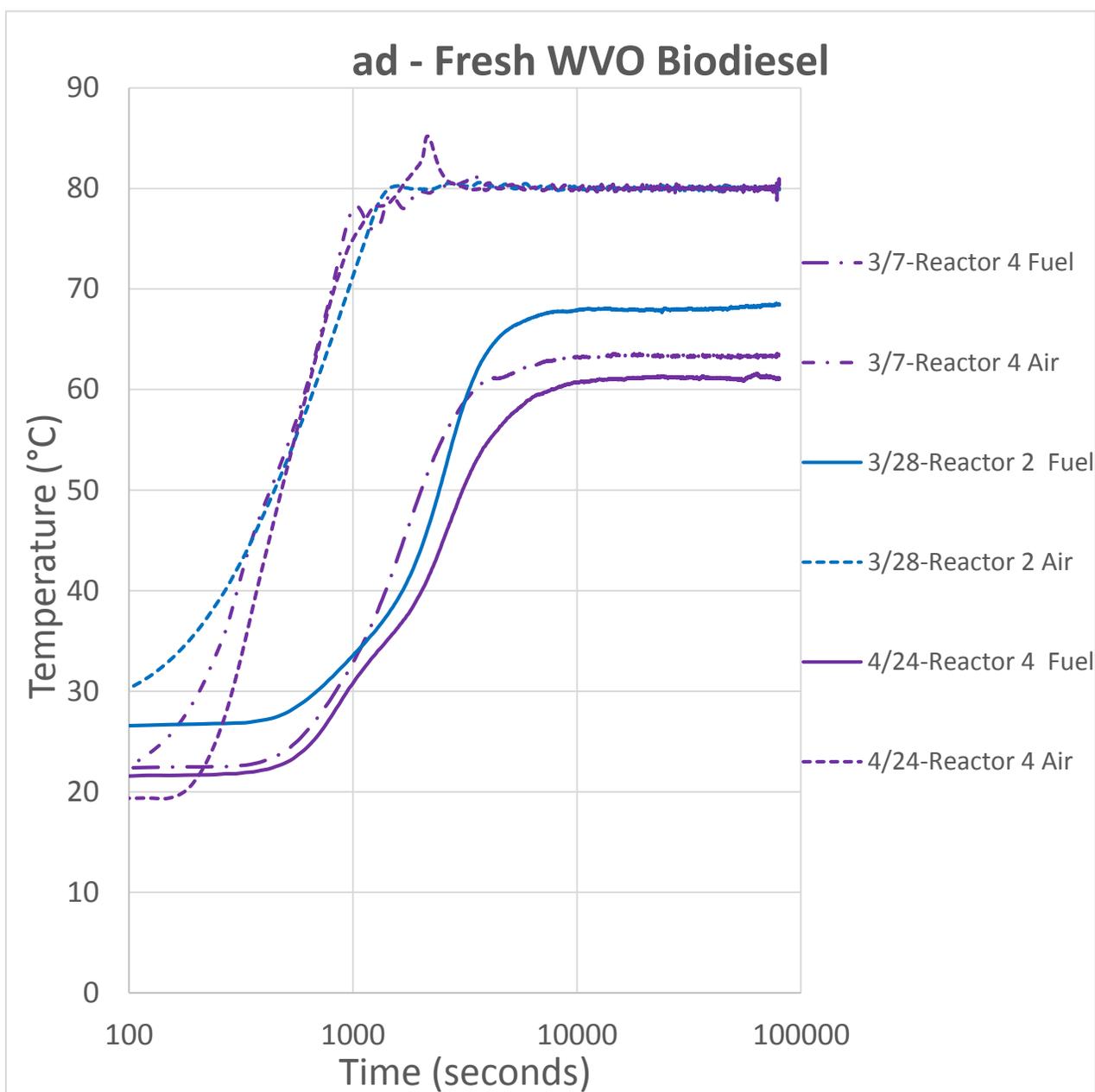


Figure A.10: ad - Fresh WVO Biodiesel

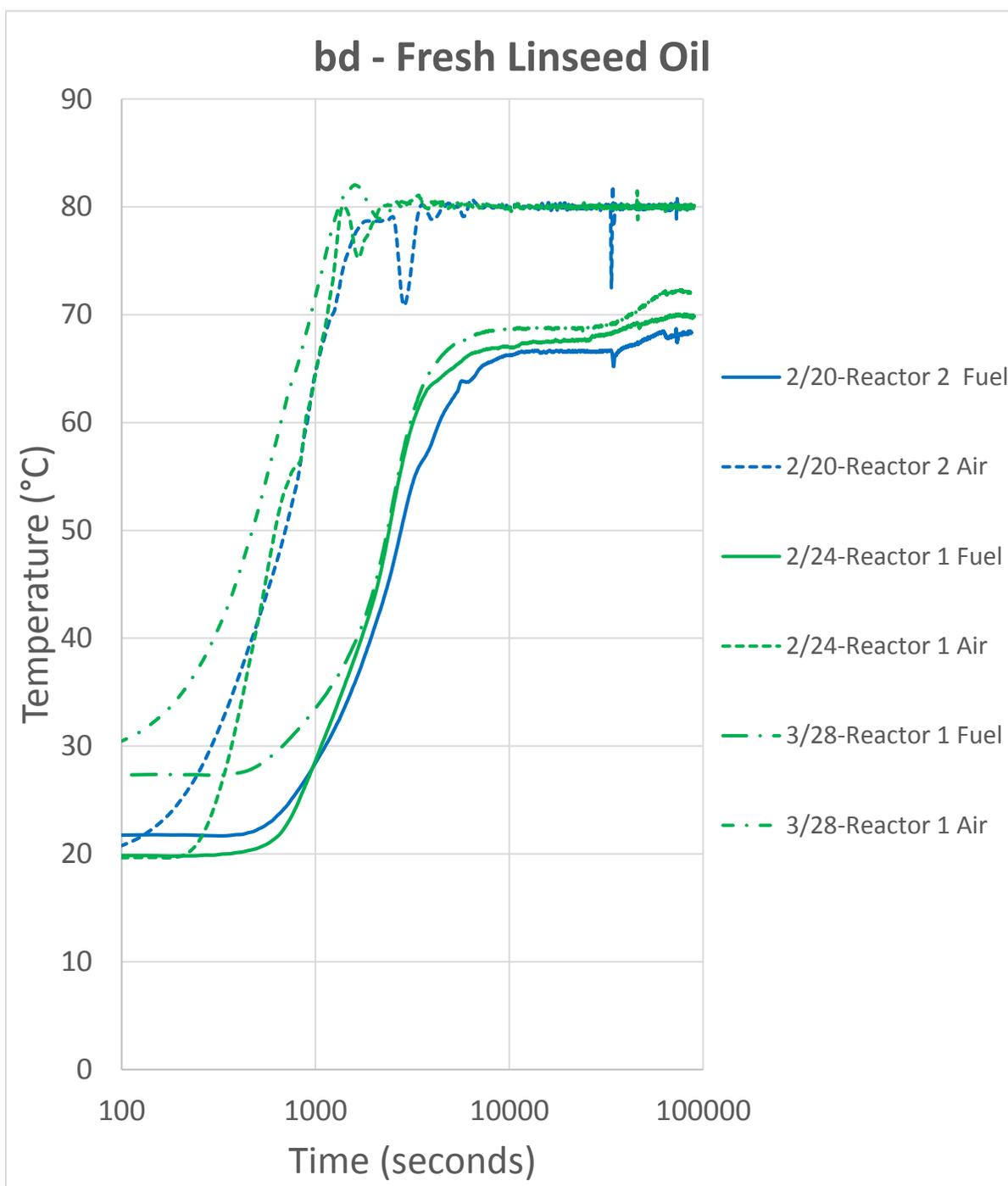


Figure A.11:bd - Fresh Linseed Oil

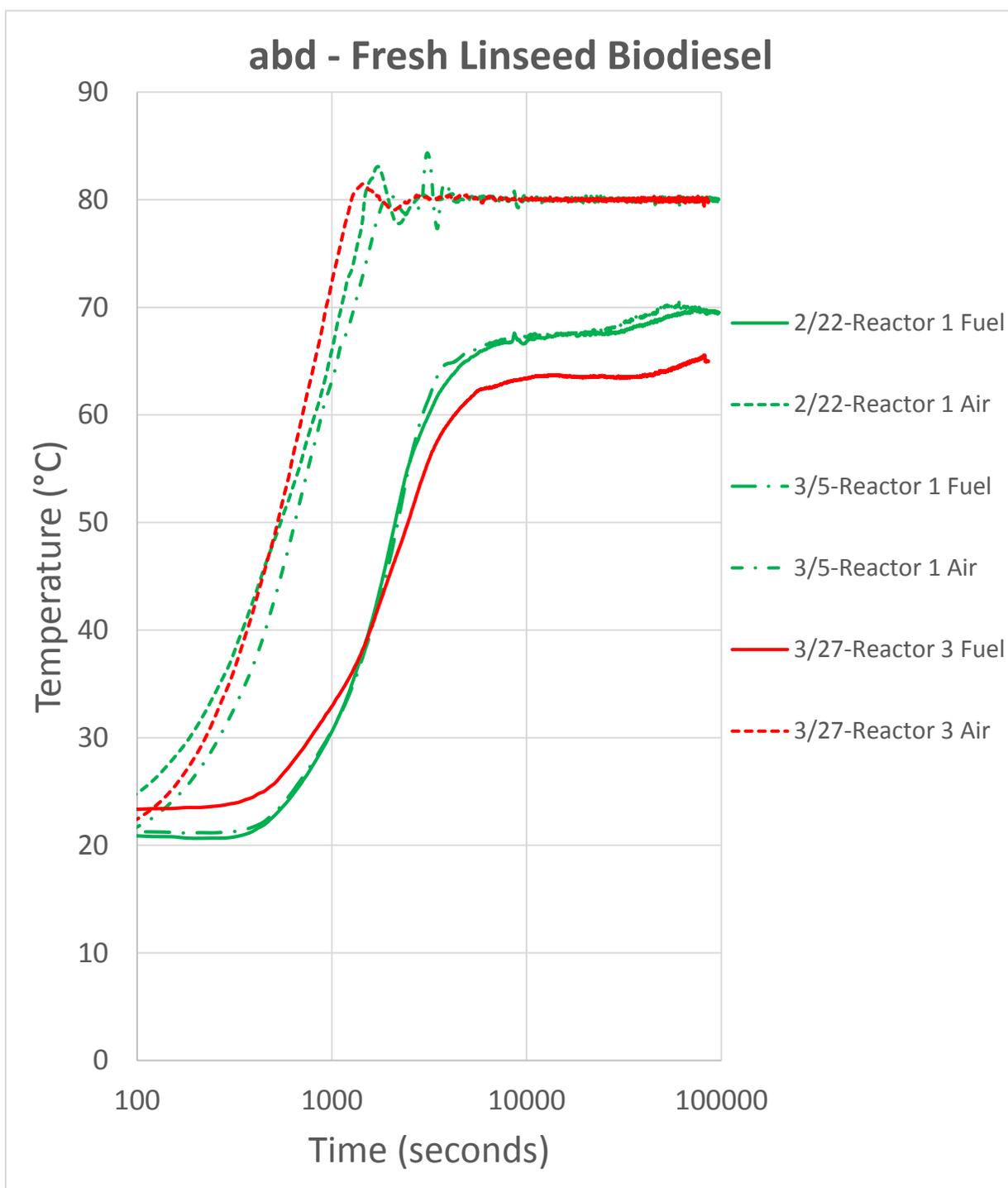


Figure A.12: abd - Fresh Linseed Biodiesel

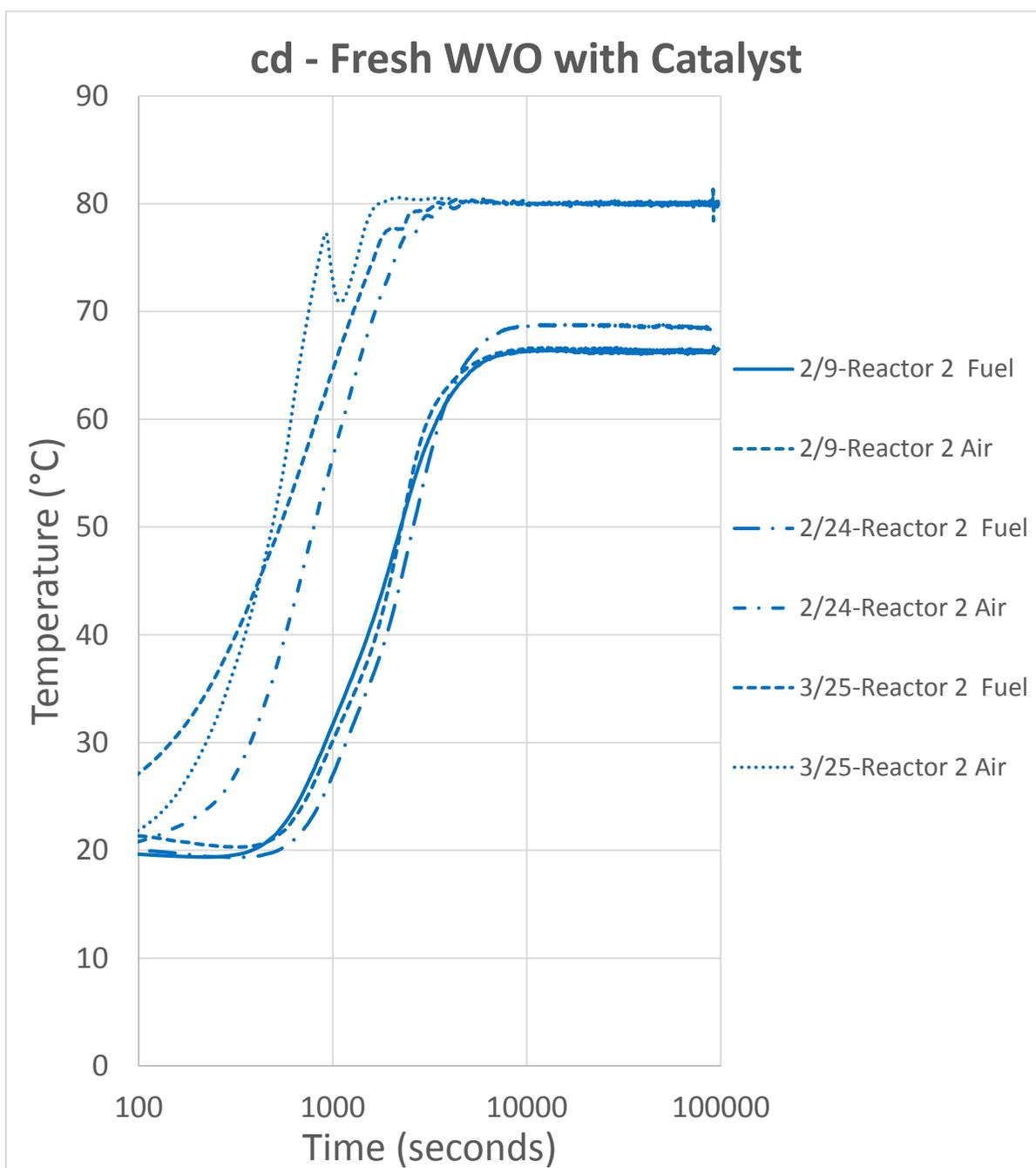


Figure A.13: cd - Fresh WVO with Catalyst

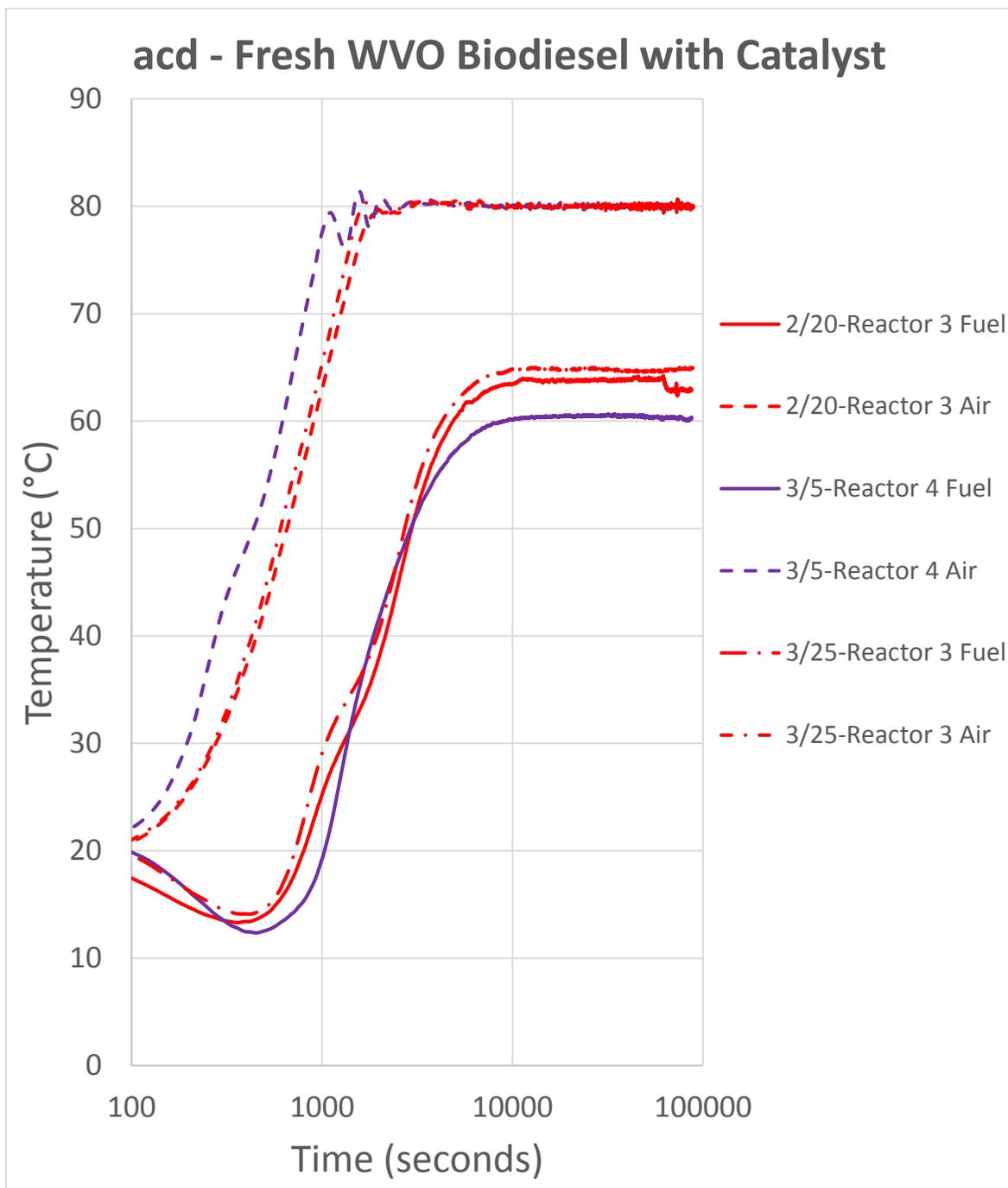


Figure A.14: acd - Fresh WVO Biodiesel with Catalyst

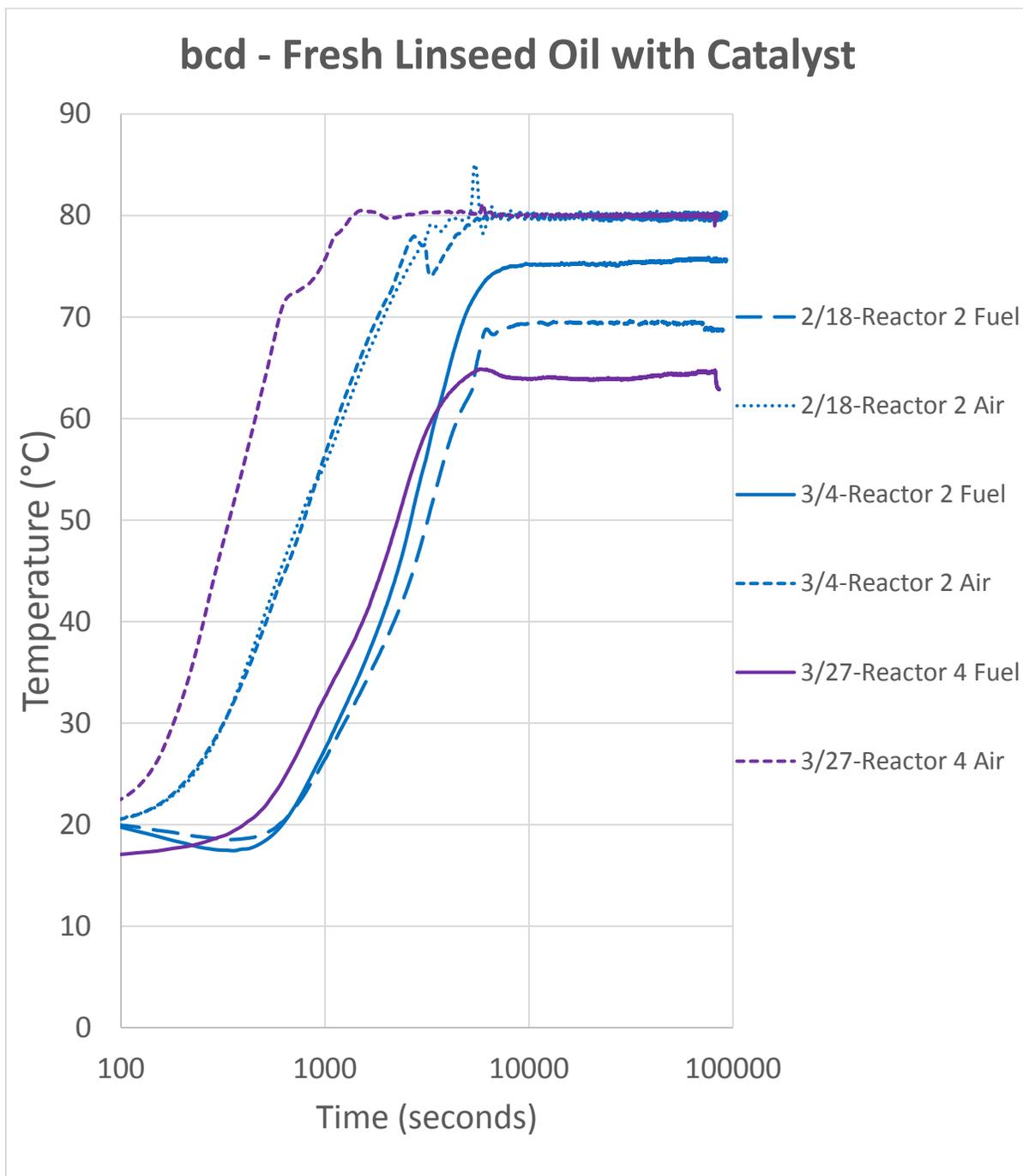


Figure A.15: bcd - Fresh Linseed Oil with Catalyst

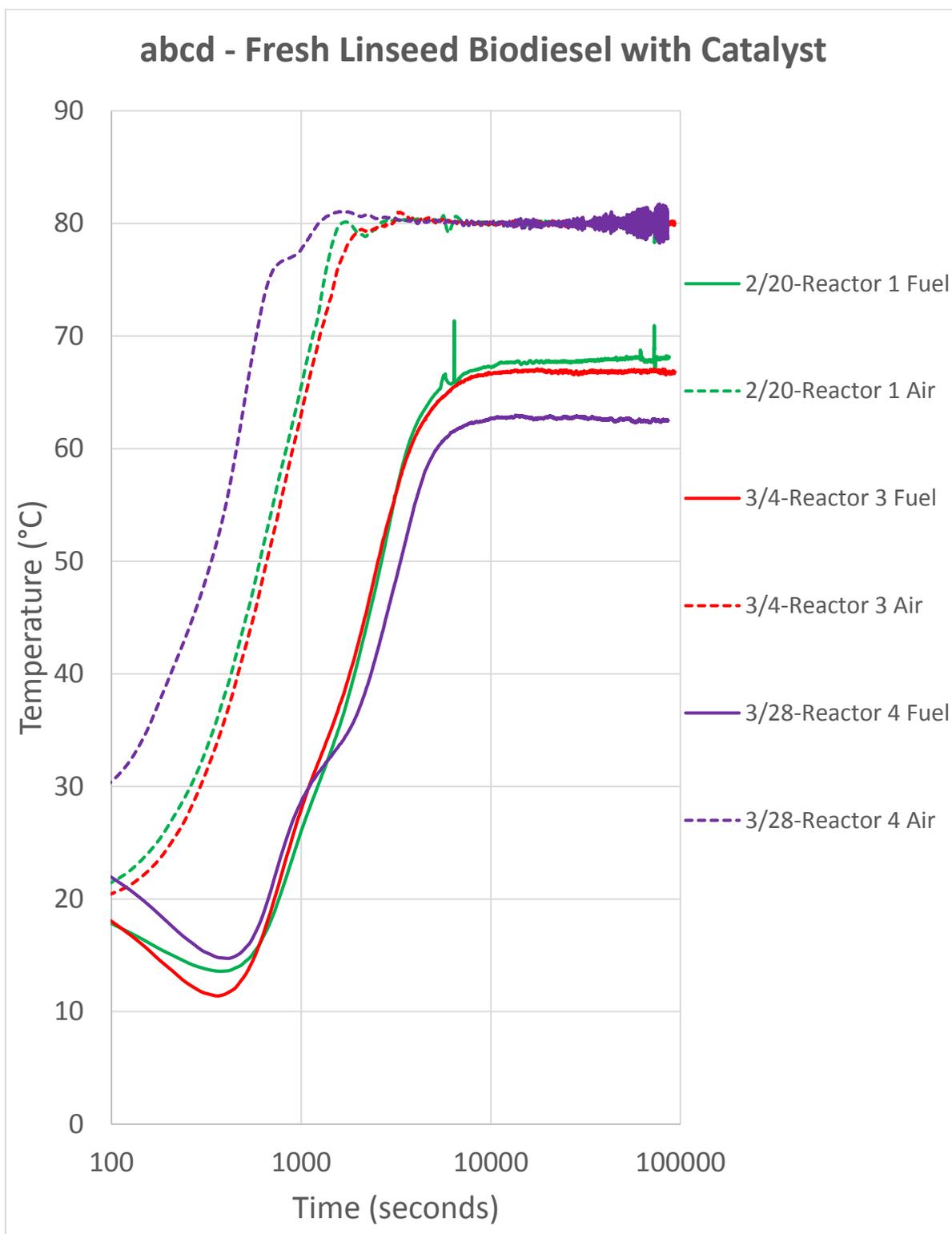


Figure A.16: abcd - Fresh Linseed Biodiesel with Catalyst

Table A.1: Experimental Data

Mixture	Run	3 hr. Temp	Max Temp	ΔT	Max Temp Time	SI80	SI80 * 1000
A	1	64.528099	66.119644	1.591545	33210	0.006469695	6.5
A	2	63.612492	65.263245	1.650753	79770	0.002793678	2.8
A	3	67.488495	69.128006	1.639511	38910	0.005688357	5.7
AB	1	66.310867	71.433571	5.122704	28080	0.024628385	24.6
AB	2	66.080368	70.662506	4.582138	24450	0.025300148	25.3
AB	3	69.791267	74.772362	4.981095	20100	0.033455116	33.5
ABC	1	68.757324	71.263901	2.506577	24480	0.013823035	13.8
ABC	2	74.783997	76.044823	1.260826	15420	0.01103836	11.0
ABC	3	67.635475	71.455856	3.820381	22950	0.022472829	22.5
ABCD	1	67.478752	68.758881	1.280129	61470	0.002811411	2.8
ABCD	2	66.731918	67.087639	0.355721	17610	0.002726992	2.7
ABCD	3	62.790268	62.96756	0.177292	13470	0.001776869	1.8
ABD	1	67.018181	69.837723	2.819542	72300	0.005264705	5.3
ABD	2	67.370369	70.584381	3.214012	60810	0.007135202	7.1
ABD	3	63.483543	65.391914	1.908371	79230	0.003251673	3.3
AC	1	68.730644	69.493439	0.762795	57930	0.001777617	1.8
AC	2	61.285522	61.628788	0.343266	71310	0.000649851	0.6
AC	3	65.132965	65.852028	0.719063	78900	0.001230336	1.2
ACD	1	63.768345	64.21405	0.445705	61920	0.000971741	1.0
ACD	2	60.204975	60.673397	0.468422	34260	0.001845796	1.8
ACD	3	64.803642	64.985947	0.182305	12540	0.001962614	2.0
AD	1	63.242252	63.629616	0.387364	79950	0.000654086	0.7
AD	2	67.990005	68.546196	0.556191	77700	0.000966355	1.0
AD	3	60.721172	61.606121	0.884949	63810	0.001872248	1.9
B	1	66.898422	70.913078	4.014656	25830	0.020982523	21.0
B	2	64.851021	69.81945	4.968429	32280	0.020778746	20.8
B	3	63.812614	69.650261	5.837647	35910	0.021946041	21.9
BC	1	67.465462	67.944397	0.478935	72240	0.00089502	0.9
BC	2	68.836464	69.993256	1.156792	19020	0.008210669	8.2
BC	3	71.260109	71.846008	0.585899	24000	0.003295682	3.3
BCD	1	69.356865	69.615295	0.25843	31350	0.001112856	1.1
BCD	2	75.148117	75.868881	0.720764	76020	0.001279968	1.3
BCD	3	63.898075	64.695625	0.79755	73650	0.001461904	1.5

BD	1	66.375389	68.700645	2.325256	72510	0.00432919	4.3
BD	2	67.028694	70.060379	3.031685	74310	0.005507704	5.5
BD	3	68.715012	72.30835	3.593338	73470	0.006602704	6.6
C	1	66.240509	66.532532	0.292023	20340	0.001938206	1.9
C	2	69.943024	70.009964	0.06694	11010	0.00082079	0.8
C	3	70.169861	70.269478	0.099617	14640	0.000918599	0.9
CD	1	66.359543	66.439415	0.079872	12930	0.00083393	0.8
CD	2	68.6651	68.777679	0.112579	17370	0.000874966	0.9
CD	3	66.526268	66.648003	0.121735	12780	0.001285933	1.3
D	1	65.702469	66.236267	0.533798	76530	0.000941627	0.9
D	2	62.075653	62.663311	0.587658	60810	0.001304618	1.3
D	3	60.732178	61.302635	0.570457	51840	0.001485565	1.5
I	1	65.736656	66.540955	0.804299	72510	0.001497454	1.5
I	2	69.558456	70.585167	1.026711	80010	0.001732358	1.7
I	3	65.990746	66.644966	0.65422	79740	0.001107596	1.1