PYROLYSIS AND SOLID DEPOSIT FORMATION OF LUBRICATION OILS

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Pyrolysis and Solid Deposit Formation of Lubrication Oils

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Many problems are caused by coking within engines with extreme operating conditions. Coking is a type of deposit formation and can interfere with reliable fluid flow and a machine’s mechanical movements, increase wear rates, decrease oil flow rates, damage mechanical seals, reduce heat transfer, and result in other issues as well. Temperature, hot-surface-contact, and oxidation with lubrication oils are crucial factors in deposit formation. To observe and examine the factors that lead to certain amounts of coke, an experimental coking rig was constructed. The rig consists of tubing, a pump, two oil reservoirs, a test-section tube, thermocouples, pressure transducers, medium pressure valves, high-temperature valves, adapters, a cooling element, and a flowmeter. After running SAE 5W-30 conventional and synthetic blend motor oils with a maximum test section surface temperature of 595 °C, there are clear differences in the degradation of these oils. The conventional motor oil underwent more extreme degradation resulting in coke compared to the synthetic blend oil that produced mostly sludge for the same operating conditions. The induction time for conventional oil was found to be 37.4 minutes, while the synthetic blend oil was found to have a 34.5-minute induction time. The difference

between the induction times could be explained by sludge forming quicker, however, more testing is required. Further investigation will help with efficient engine development and improvements in various industries with regards to oil flow and use.

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1. INTRODUCTION

1.1 Background Knowledge

1.1.1 Lubricants

Extreme engine temperatures can produce a solid residue called coke due to the lubricating oil being subjected to oxidative and thermal breakdown [1]. Coking is a type of deposit formation and can interfere with reliable fluid flow and a machine's mechanical movements, increase wear rates, decrease oil flow rates, damage mechanical seals, reduce heat transfer, and result in other issues as well. it is assumed that the oil degradation processes that lead to coke formation occur through thermal decomposition and oxidation reactions – namely when the oil's antioxidant package is depleted [8]. A lubricating oil is composed of two main parts – the basestock and an additive package.

The basestock, also known as base oil, comprises 72-96% of the majority of engine oils, and about 4-28% of the oil is comprised of an additive package that can contain antioxidants [5]. The basestock is the base fluid of the lubricant and is usually produced synthetically or by refining crude oil. Breaking down this component further, there are 5 categories of base oils grouped corresponding by the method of production according to the American Institute. Group 1 includes those that are solvent refined, which are the cheapest of the base oil types and are typically used in less extreme operating conditions. Group 2 includes oils that are made by hydrocracking (a more sophisticated process than solvent refining) and possess better oxidation properties and are slightly more expensive than Group 1 oils. Group 3 oils are also produced via hydrocracking (although with greater temperatures and pressures) and turn out purer as well.

Group 4 oils are made from a chemically engineered synthesized oil and provide amazing performance via great chemical stability and molecular uniformity. The base oils in Group 4 can be used in more demanding operating conditions with extremely low or high temperatures. Finally, Group 5 base oils are also chemically engineered but offer greater performance than other groups especially when mixed with other basestocks.

Additives are combined with the base oil to bring out desired properties and also muffle undesirable properties. Antioxidants, viscosity index improvers, detergents, and dispersants are some examples of additives. Antioxidants extend the operating life of the oil by delaying the oxidation process; however, the additive is depleted as it is used, which is why it is called a sacrificial additive. Viscosity index improvers maintain the viscosity of the fluid as temperature increases and can offer improved flow at lower temperatures. Detergents maintain the cleanliness of hot metal parts by guarding against deposits and prevent acids from forming within the oil. Finally, dispersants prevent contaminants from collecting within the oil.

1.1.2 Types of Deposit Formation

There are three types of deposit formation – sludge, varnish, and coke – each of which has distinct physical characteristics [2-7]. Sludge is a muddy substance that can flow about a system. It is a messy deposit, similar to grease, that can be wiped from surfaces with ease and can cause problems in valves and oil pathways by obstructing them, restricting the lubrication flow. Varnish is not as messy as sludge as it clings to surfaces better with its sticky nature. Nonetheless, it still causes problems by restricting the ability of the oil to transfer heat and congesting flow lines. Two known critical factors contribute to coke formation, which are time and temperature, and reducing these two factors can decrease coke formation [9]. The higher the temperature of the system, the resulting coking formation becomes darker and more brittle.

1.1.3 Oxidation and Pyrolysis

Another known crucial factor that contributes to oil degradation is oxidation. Within the researched literature, some papers list oxidation as mainly culpable for oil degradation and results in deposit formation [8]. Temperature plays a key role in the oxidation process as the rate of oxidation of the oil depends on the temperature. Arrhenius plots and the Arrhenius Rate Rule can be used to rank different lubricants on these processes.

The oxidation rate doubles for every 10°C increase in operating temperature according to a rule of thumb based on this the Arrhenius Rate Rule [5, 6]. Even just a 10°C change drastically impacts oil degradation. Arrhenius plots provide a convenient way to show the time when an antioxidant package is depleted for when the percentage of deposit formation versus time is graphed as shown in Figure 1.1. The time it takes for coke to start forming is called the induction time [9]. A log scale can be utilized for the induction time versus the inverse of absolute temperature as shown in Figure 1.2. This type of presentation allows for the lubricants to be ranked according to induction time and response to temperature. There are straight lines with very similar slopes, and the higher temperatures with lower induction time lines indicate that coking will initiate quicker while the lower temperature and higher induction time lines indicate that coking takes longer to initiate. Induction time can also be extrapolated to other temperatures of interest from the known slope and induction time.

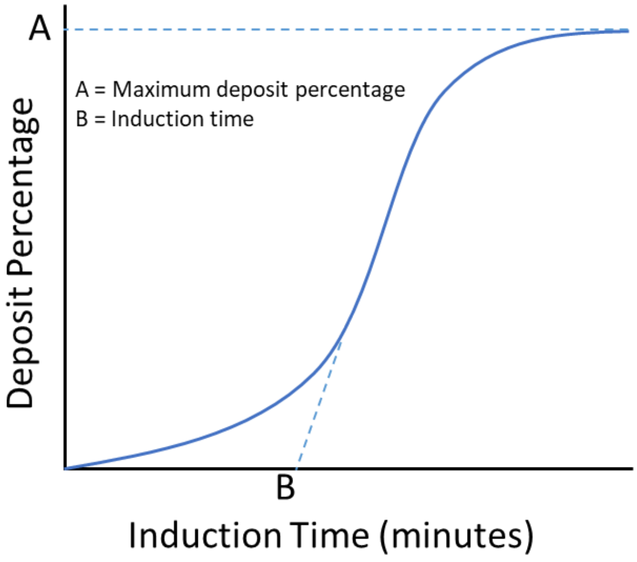

Figure 1.1: Arrhenius plot demonstrating that deposit percentage increases with time.

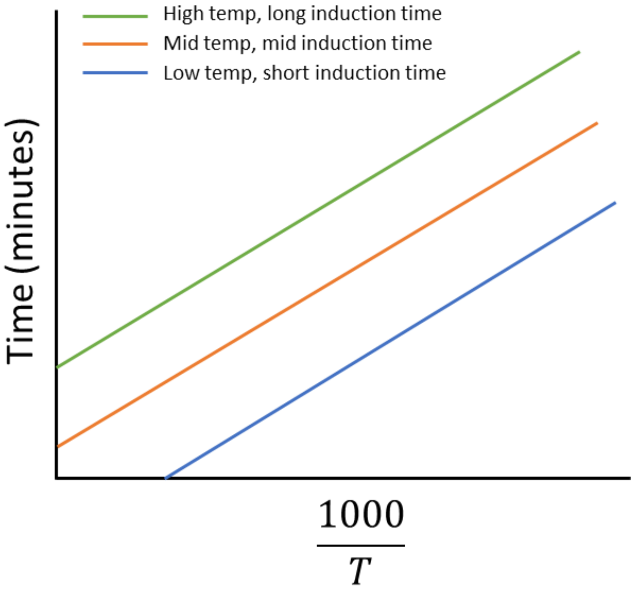

Figure 1.2: Arrhenius log scale plot displaying the rankings of different lubricants for certain temperatures and induction times.

It would make sense to think that the greater percentage of the oil that is antioxidant, an additive to the oil that resists oxidation, the better it would be to reduce the rate of deposit formation and increase the induction time. This reasoning is correct; however, there are some disadvantages that need to be considered as well. Larger deposits will potentially be produced from a larger antioxidant level. There is a balance that must be achieved in the ratio of additives so as to reduce the amount of deposit formation which also needs to be further investigated.

Other oil degradation factors include bulk oil oxidation and hot-contact-surface [6]. As an oil flows and cycles throughout a system, bulk oil oxidation occurs where water, metals, and air act as catalysts. This event can happen even with mild operating conditions. Lastly, when an oil is in contact with the metal surface of the system, thermal degradation or oxidation can occur due to high temperatures.

In addition to investigating oxidation, pyrolysis is another area of interest when it comes to oil degradation. Unlike oxidation, pyrolysis occurs in the absence of oxygen and causes thermal degradation solely due to temperature.

1.1.4 Previous Experiments

Some of the configurations for testing deposit formations that were found in the literature can be organized into three groups where the oil in a test rig is static, rests on a heated plate, or flows through a system. Static oil tests involve an oil sample under a high temperature, and samples of the oil are taken out and observed at an end of a test. For heated plate tests, an oil is heated via a plate where the plate is then examined for the resulting deposit weight and physical appearance. Some popular examples of other researchers’ test rigs include the Penn State Micro-Oxidation Test, the Panel Coker Test, and the Hot Liquid Process Simulator which are each examples of a static oil test, heated plate test, and a flowing oil test, respectively.

For the Penn State micro-Oxidation test, a low-carbon-steel cup is positioned within a glass tube that is enveloped by a constant temperature bath [10]. Then, once system equilibrium is reached, the lubricant oil is put into the cup. If the effects of thermal degradation are desired to be observed, then nitrogen is also input within the cup. If the effects of oxidation are desired to be observed, then air is put into the cup. After the test is concluded, the gained weight of the cup is measured to determine the amount of coking. For the Panel Coker Test, the oil is placed on a panel that is heated and at an incline [12]. A glass chamber contains the panel, providing the ability to control the atmosphere inside. Oil degradation is then analyzed after the conclusion of the test and the number of deposits are examined. Finally, with the Hot Liquid Process Simulator, it simulates oil flow passing through pressurized lines [13]. Three parameters are able to be controlled – the flow, pressure, and target surface temperature. A key feature of the configuration involves a tube that can be removed and the deposits can be analyzed.

1.2 Experimental Setup

For the rig constructed at Texas A&M University, a sample of oil runs through a heated test section used to measure coke formation. To simulate the most extreme operating conditions of oil, such as within a gas turbine, the system may be pressurized to up to 68 bar or 1,000 psia.

Depending on the subject of study, either oxidation or thermal degradation, air or an inert gas may be used as the pressurizing gas. Oil flows through the system at less than 10mL/min by a pump. A target temperature of up to 650 °C can be reached by electric heaters for the test section. Different test section geometries can be interchanged on the coking rig if desired. Heat transfer efficiency decreases as the oil flows through the test section and coke deposits are formed on the surface. By tracking the change in bulk oil temperature from the test section inlet to outlet over time, the rate at which the deposits form is determined. The oil then returns to the original reservoir for recirculation or is re-directed to a second reservoir if the effect of a single, high-temperature exposure is being studied. The effects of pressure, surface temperature, oil flow rate, level of exposure to oxygen, and oil composition may be observed by inspecting the coke deposit weight and appearance and by the comparison of the rate of coke formation. The coking rig and labeled components can be seen in Figure 1.3.

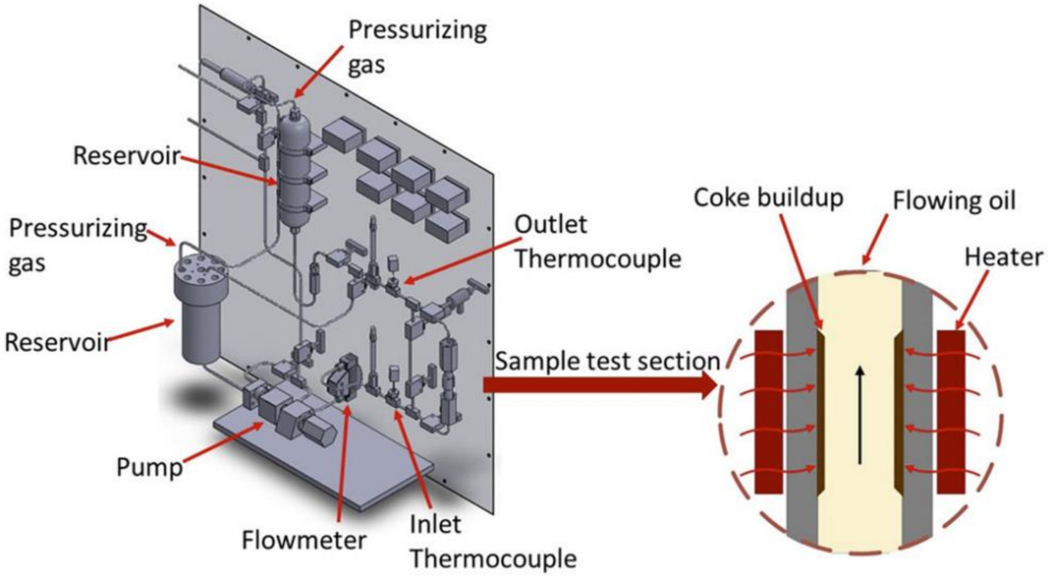

Figure 1.3: Coking rig and labeled components.

2. METHODS

The Test Rig consists of several components through which the oil flows and are listed in Figure 2.1. Before an experiment, a lubricating oil to be studied is injected into the system via a valve opening using a syringe. A gas manifold is used to pressurize the system with a gas through a gas cylinder connected to the gas manifold. Air is used if the experiment were to focus on coke produced through oxidation and nitrogen is used if the effects of pyrolysis are desired to be observed. To begin the experiment, the test oil flows out of the bottom reservoir caused by the pump, through a metal rotameter (flowmeter) to measure volumetric flow rate. A temperature controller is then set to a desired temperature of the two band heaters on the test section. One heater is placed towards the inlet of the test section and another is placed towards the outlet of the test section, each with a thermocouple attached. The oil then flows into the test section as shown in Figure 2.2 and is directed back into the bottom reservoir or to the top reservoir, depending on the focus of the experiment. The oil's pressure and temperature before and after flowing through the test section are measured by pressure transducers and thermocouples and are referred to as inlet and outlet pressures and temperatures. The majority of tubing used throughout the rig has an outer and inner diameter of 0.25" and 0.109", respectively. The test section tubing has an outer and inner diameter of 1.00" and 0.562", respectively.

As the test lubricating oil flows through the system, solid deposits form due to oil degradation and form on the inner wall of the test section. The rate of deposit formation is tracked by measuring the temperature of the oil flowing at the inlet and outlet thermocouples. Inlet, outlet, and reservoir temperature readings are recorded using a data acquisition system

(DAQ) for analysis. After the experiment has run for a desired period of time, the temperature controller and pump are shut down, the system is de-pressurized using the gas manifold and vent line, and the test lubricating oil is drained from the system.

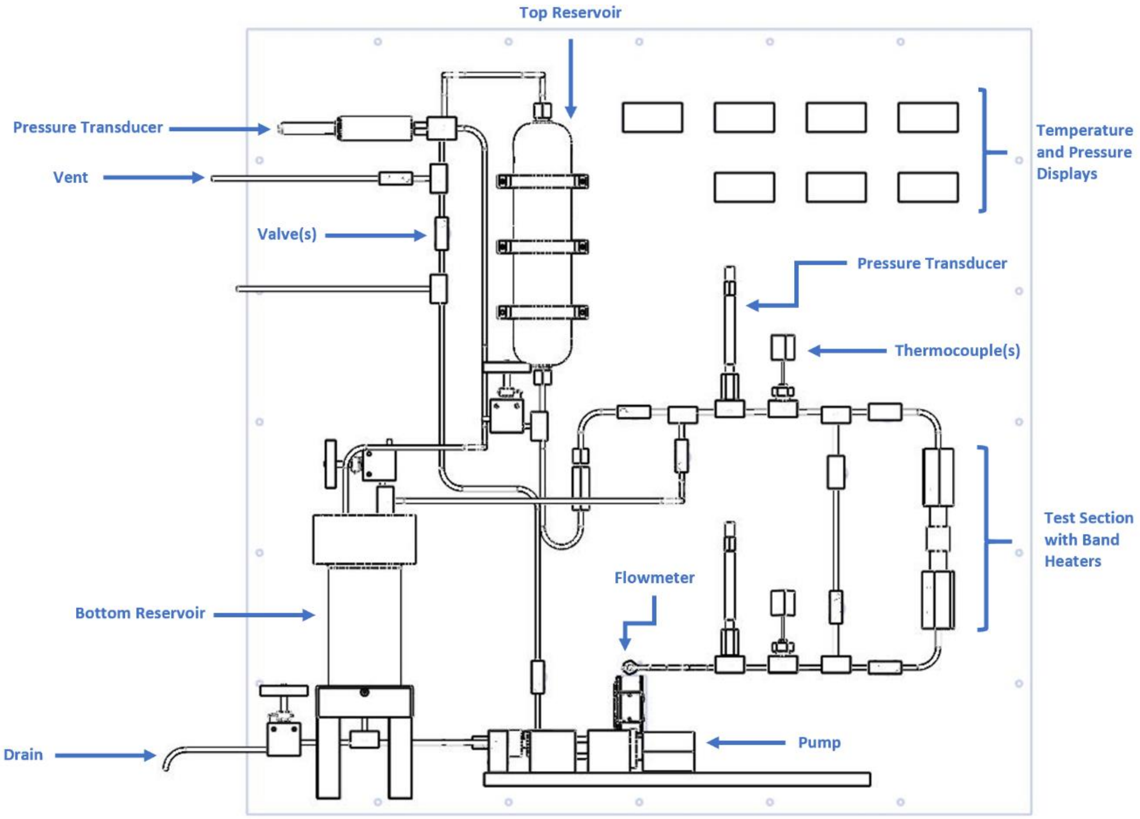

Figure 2.1: Test rig components.

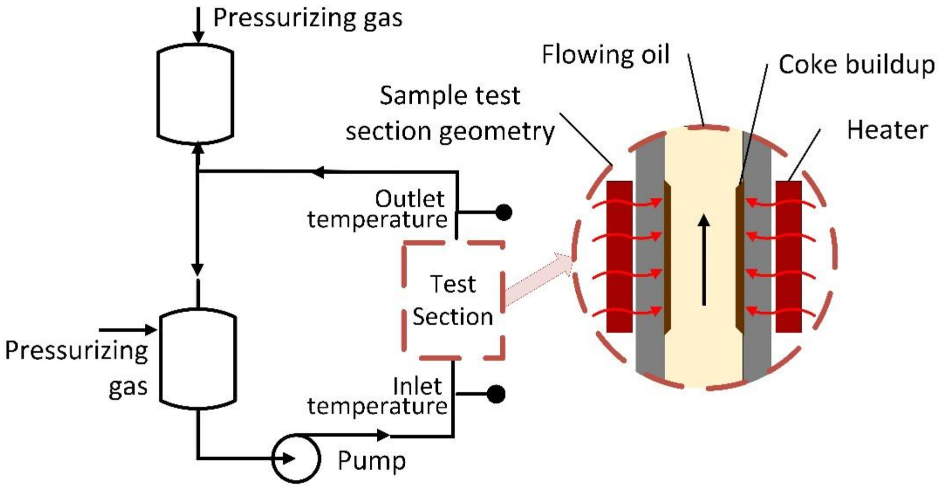

Figure 2.2: Oil flow chart for test section.

3. RESULTS

3.1 Deposit Formation

For the first set of data, approximately 900 mL of a conventional SAE 5W-30 motor oil was introduced into the bottom reservoir for testing. After pressurizing the system with nitrogen gas at 25 psi, the heaters were set to a target temperature of 595 °C. Then, once the heaters reached the target temperature, the pump was turned on and the system was left to run for approximately 350 minutes and shut off once the outlet temperature reached a clearly visible steady state. For the second set of data, the same process was repeated for approximately 800 mL of a synthetic blend SAE 5W-30 to observe any differences from the conventional oil in induction time and level of coke formation. The test section was taken out after the runs were completed to observe the levels of deposit formation that were developed. The deposits inside the test section can be seen in Figure 3.1 for the conventional motor oil (left) and for the synthetic blend motor oil (right).

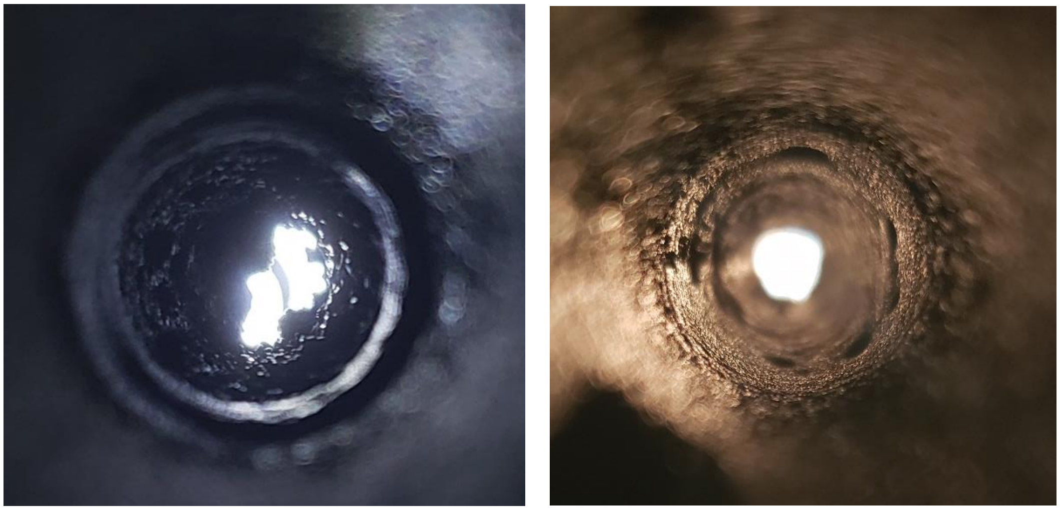

Figure 3.1: Deposits produced inside of test section for SAE 5W-30 conventional motor oil (left) and synthetic blend (right).

Comparing the two photos in Figure 3.1, it seems that the conventional motor oil generated a thicker layer of coke along the inner walls of the test section relative to the synthetic blend motor oil. Next, using a dental scaler scraping tool, the deposit formations were removed from the test sections and placed into viles as seen in Figure 3.2.

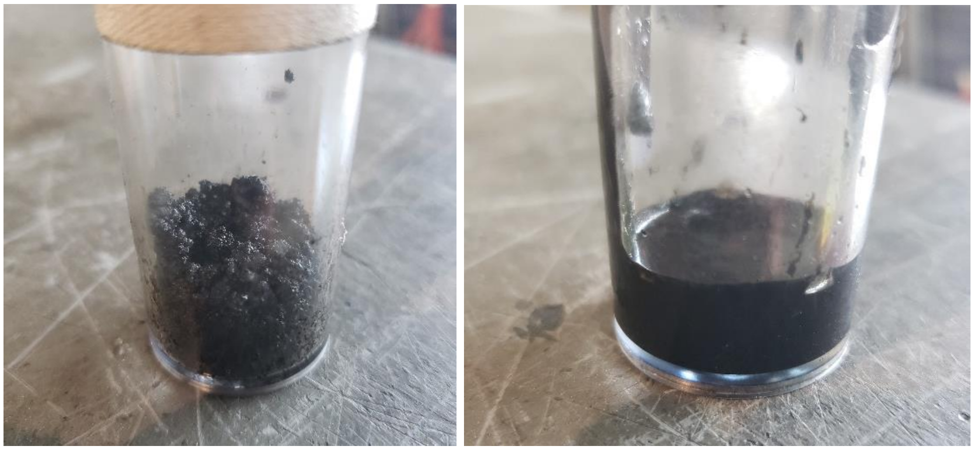

Figure 3.2: Collected deposits taken from test section for SAE 5W-30 conventional motor oil (left) and synthetic blend (right).

Comparing once more, the conventional motor oil seems to have produced substantially more solid deposits than the synthetic blend motor oil. The synthetic blend seemed to have mostly sludge as the resulting deposit formation, but did have some coke as well.

3.2 Induction Time

The channel temperatures for the test section, inlet, outlet, and reservoir were graphed with respect to time to view the effects of conventional motor oil deposit formation in Figure 3.3.

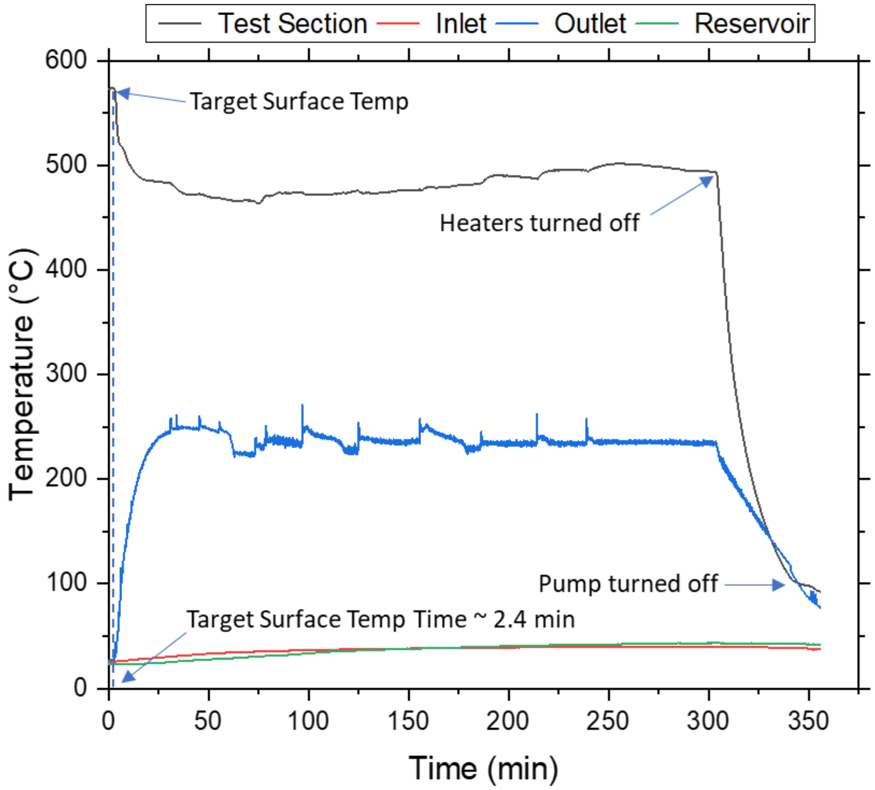

Figure 3.3: Channel temperatures for SAE 5W-30 conventional motor oil with a maximum surface temperature of 595°C.

The target surface temperature was 595 °C, however, the thermocouple used for recording the data did not match the programmed temperature on the heaters due to a temperature gradient in the test section. The gradient can be explained by the bottom thermocouple, which is wired to the DAQ and positioned on the lower heater, experiencing lower temperatures where the oil is flowing through only one heater. The top thermocouple, which is wired to the temperature controller and attached to the upper heater, experiences higher temperatures due to the oil having more time to absorb heat as it flows through the second heater. The difference in the temperature readings depends on the positioning of the thermocouples on the test section. The thermocouple connected to the temperature controller measured the temperature at a constant 595 °C throughout the run. In the future, there will be dual thermocouples to eliminate this discrepancy of temperatures.

There are several spikes on the graph for the outlet temperature due to venting. The pressure throughout the system increases due to increasing temperature. The nitrogen pressurizing gas was vented several times throughout the run in an effort to stabilize the gauge pressure at 25 psi. It was realized this could interfere with the results for induction time as it raises the temperature reading each time. The temperature rise with decreasing pressure was found to be peculiar. It could be that there is nitrogen that runs through the test section and becomes heated. Then, when vented, the heated nitrogen rushes past the outlet, briefly increasing the outlet temperature. The venting process was discontinued after about 250 minutes. In later tests, leaving the vent open will be considered to control the system pressure without spikes in temperature readings.

The time it took to reach the target surface temperature is about 2.4 minutes from reading the exported Excel data. It is easier to view the induction time from the difference in temperature between the outlet and inlet channels. The temperature difference is graphed in Figure 3.4.

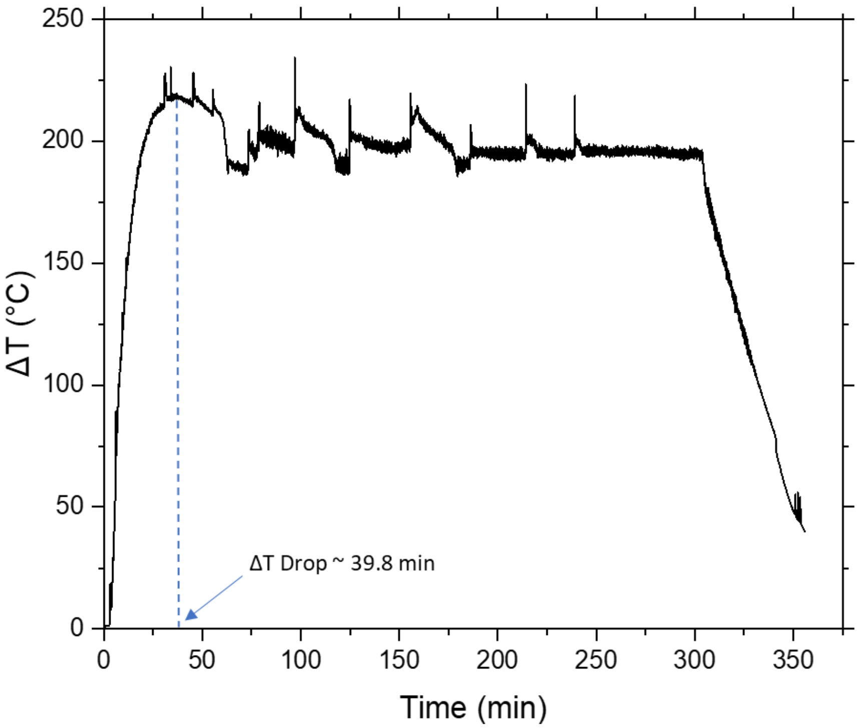

Figure 3.4: Difference in outlet and inlet temperatures for SAE 5W-30 conventional motor oil with maximum surface temperature of 595°C.

The beginning of the decline in ΔT was found to be approximately 39.8 minutes from the Excel data. This time indicates the beginning of deposit formation as it insulates the tube, decreasing the temperature change as coke reduces the rate of heat transfer from the surface of the test section to the lubricating oil. The difference between the target surface temperature time and the onset of the decline in ΔT provides an induction time of about 37.4 minutes for the synthetic blend motor oil.

The channel temperatures were again graphed for the test section, inlet, outlet, and reservoir with respect to time for the synthetic blend motor oil in Figure 3.5. The difference between outlet and inlet temperatures was plotted in Figure 3.6 to more clearly view the induction time.

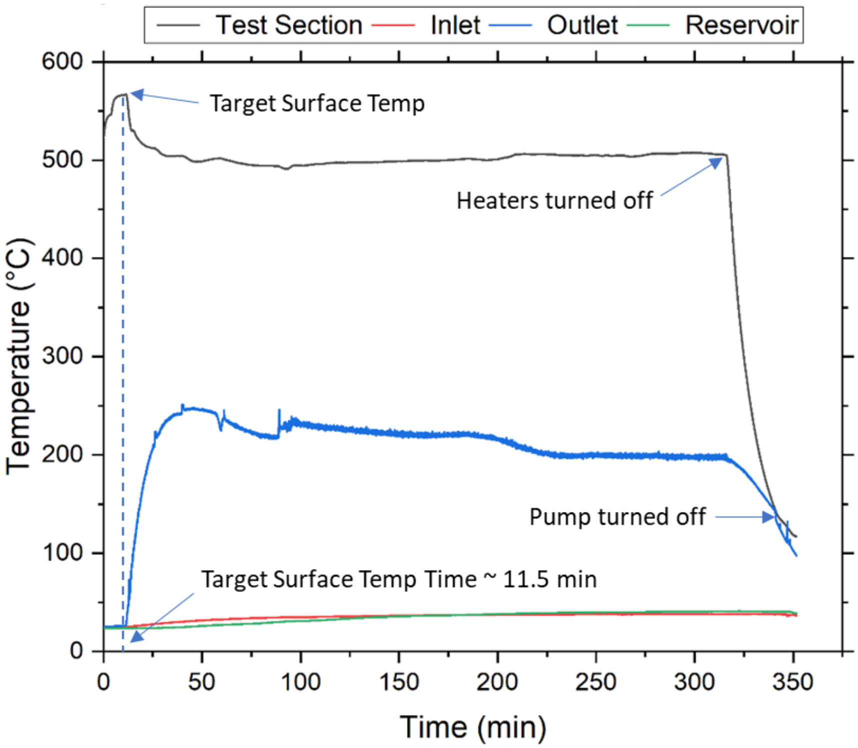

Figure 3.5: Channel temperatures for SAE 5W-30 synthetic blend motor oil with maximum surface temperature of 595°C.

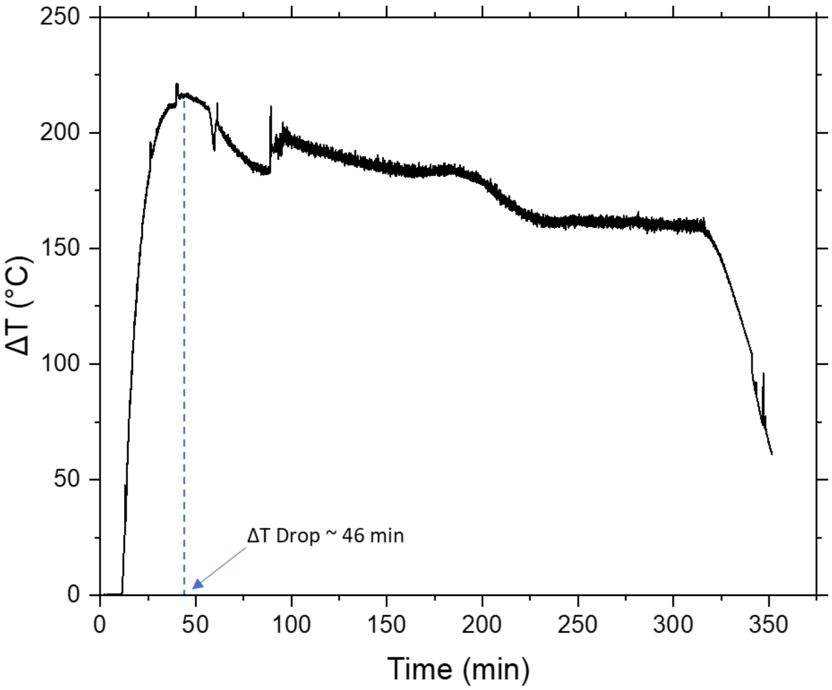

Figure 3.6: Difference in outlet and inlet temperature for SAE 5W-30 synthetic blend motor oil with maximum surface temperature of 595°C.

The time it took to reach the target surface temperature for this run was about 11.5 minutes. The difference between the time for target surface temperature and the start of the decline in ΔT yields an induction time of about 34.5 minutes for the synthetic blend motor oil.

4. CONCLUSION

After running the system with a maximum surface temperature of 595 °C, the differences in deposit formation caused by the heaters in the test section could clearly be seen between the SAE 5W-30 conventional and the synthetic blend motor oils. The conventional motor oil was observed to produce more solid deposits compared to the synthetic blend indicating that it was more susceptible to degradation under the same operating conditions. The synthetic blend motor oil produced mostly sludge, stemming from a lesser form of oil degradation, signifying that it has better properties than conventional motor oil. To further investigate the differences in deposit formation, the induction time for each oil was calculated. The induction time for conventional oils was found to be about 3 minutes longer than the synthetic blend. A possible explanation for the shorter induction time with the synthetic blend is that the sludge formed more quickly when insulating the test section. However, since there is such a small difference in induction time, this could be within the measurement error, and further testing is required to be more conclusive.

REFERENCES

[1] ExxonMobil Corporation, Tech Topic: Coking. 2016.

[2] Santos, J., Santos, I., and Souza, A., "Thermal Degradation Process of Synthetic Lubricating Oils: Part I—Spectroscopic Study", Petroleum Science and Technology, vol. 33, no. 11, pp. 1238-1245, 2015. Available: 10.1080/10916466.2015.1047031.

[3] Martynov, V., and Morozova, M., "Thermal Stability of Lubricants", Khimiya i Tekhnologiya i Masel, vol. 1, no. 11, pp. 46-50, 1965. Available: 10.1007/bf00719195.

[4] Livingstone, G., Thompson, B., and Okazaki, M., "Physical, Performance, and Chemical Changes in Turbine Oils from Oxidation", Journal of ASTM International, vol. 4, no. 1, p. 100465, 2007. Available: 10.1520/jai100465.

[5] Pawlak, Z., *Tribochemistry of Lubricating Oils*. Amsterdam: Elsevier, 2003.

[6] Fitch, J., and Gebarin, S., "Review of Degradation Mechanisms Leading to Sludge and Varnish in Modern Turbine Oil Formulations," *Journal of ASTM International*, vol. 3, no. 8, 2006. Available: 10.1520/jai13504.

[7] Diaby, M., Sablier, M., Le Negrate, A., El Fassi, M., and Bocquet, J., “Understanding Carbonaceous Deposit Formation Resulting from Engine Oil Degradation”, Carbon, vol. 47, no. 2, pp. 355-366, 2009. Available: 10.1016/j.carbon.2008.10.014.

[8] Kauffman, R., Feng, A., and Karasek, K., "Coke Formation from Aircraft Turbine Engine Oils: Part I — Deposit Analysis and Development of Laboratory Oil Coking Test," *Tribology Transactions*, vol. 43, no. 4, pp. 823-829, 2000. Available: 10.1080/10402000008982414.

[9] Kauffman, R., Feng, A., and Karasek, K., "Coke Formation from Aircraft Engine Oils: Part II—Effects of Oil Formulation and Surface Composition," *Tribology Transactions*, vol. 43, no. 4, pp. 677-680, 2000. Available: 10.1080/10402000008982395.

[10] Naidu, S., Klaus, E., and Duda, J., "Kinetic Model for High-Temperature Oxidation of Lubricants", Industrial & Engineering Chemistry Product Research and Development, vol. 25, no. 4, pp. 596-603, 1986. Available: 10.1021/i300024a601.

[12] Kagaya, M., and Ishikawa, S., "An Evaluation and Optimization of Lubricants for Turbocharged Gasoline Engines", SAE Technical Paper Series, vol. 840261, 1984.

[13] Watkinson, A., "Comparison of Crude Oil Fouling Using Two Different Probes", in Conference Proceedings of Heat Exchanger Fouling and Cleaning: Fundamentals and Applications, 2003.