Executive Summary

Lubricating greases play a vital role in the performance and functionality of nearly all tribocomponents such as bearings, gears, and the like. While some machine elements are grease-lubricated for life, many others require periodic replenishment to ensure that the mechanical component performs efficiently and to avoid premature failure. A grease’s performance tends to degrade with use due to prolonged shearing, evaporation, oxidation, etc.—akin to the well-known phenomenon of fatigue in mechanical systems. Thus, the determination of grease life is an important endeavor for both manufacturer—to gain a better understanding of the nature of degradation that leads to new and improved developments—and the users to ensure that tribocomponents are adequately lubricated.

This report provides the results of a potentially transformative approach in treating grease degradation modeling. The premise of this research is that degradation of grease is an irreversible dissipative process that ages the grease and affects the bearing performance. During normal operating conditions, as grease is sheared at contacts between rolling elements and raceways it experiences a breakdown of its thickener’s structure due to the cumulative energy dissipation. This is an irreversible mechanism related to the production of thermodynamic entropy associated with the dissipative processes involved. This realization provides a powerful enabling tool for assessing degradation, aging, and evaluation of remaining useful life.

A team of researchers at LSU Center for Rotating Machinery developed the framework and methodology of applying the thermodynamic entropy to evaluate grease degradation. This report contains the results of significant accomplishments made far beyond the original proposed expectations. Attached to this report are details of finding summarized in several papers. Specifically, two papers were presented at 1999 NLGI Conference in Las Vegas. Of the corresponding papers appeared in NLGI Spokesman in January 2020, and the other is due for publication in March 2020. Both papers underwent peer review. Other articles were published in Peer-reviewed tribology journals such as Lubricants, Tribology Letters, and Tribology International. We believe that this research has been extremely productive and worthwhile and gratefully acknowledge NLGI’s support with was augmented with additional resources from LSU Center for Rotating Machinery to make such enormous accomplishments to fruition.

Enclosure:
Predicting Grease Life with Entropy--A Practical Overview (pp. 2-16)
The Use of Entropy in Modeling the Mechanical Degradation of Grease (pp. 17-36)
Procedure for evaluating the mechanical degradation of a grease (pp. 37-50)
On the assessment of mechanical degradation of grease using entropy generation rate (pp. 51-73)
Experimental Investigation of the Chemical Degradation of Lubricating Grease from an Energy Point of View (pp. 74-103)
Predicting Grease Life with Entropy¹
A Practical Overview

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Abstract:
Though there exist estimates for the life of grease in specific applications which have been thoroughly examined, a widely accepted methodology to predict the life of grease is still lacking. A promising approach to estimating the life of a grease subjected to mechanical degradation by shearing well below the oxidation temperature has been put forward by applying the principles of irreversible thermodynamics. This paper reviews recent progress on this subject and provides suggestions for future research.

1. Introduction:
The unique properties of grease make it an ideal lubricant in many situations, such as rolling element bearings, slider bearings, gears, and flexible couplings [1]. Lubricating grease is composed of a base lubricating oil suspended in a thickener structure, with additives often added to improve performance in particular situations. The complex interactions of the two main components allow grease to flow like a liquid at high shear rates while resisting flow at low shear rates. As a grease is stressed, the thickener structure is broken down, releasing oil and allowing it to flow to the components that need it. When the grease is allowed to relax, its thickener structure mostly recovers, but not completely [2]. This means that there has been some irreversible damage done to the grease, and it has undergone degradation.

Though the structural damage induced by stress is an important mechanism of grease degradation, there are numerous other ways by which grease degrades. These mechanisms are categorized into physical and chemical degradation [3-7]. Chemical degradation refers to permanent changes to the grease’s properties due to oxidation of the base oil, thickener, and additives, or any other chemical reaction which occurs. Physical degradation encompasses shear degradation of the thickener structure, oil evaporation, and overall contamination. Shear degradation, also called mechanical degradation, is often the main determinant of a grease’s life, especially in situations where a grease is sheared at relatively high speed without reaching high temperatures [4]. Mechanical degradation can lead to excessive oil bleed, further

¹ Published in NLGI January 2020
leading to churning or leakage. The extent of mechanical degradation’s impact on a grease’s performance depends on the grease’s formulation [8]: fibrous-like thickeners often show significant changes due to mechanical degradation, while particle-like thickeners may not show any changes at all [9]. This paper focuses on greases with a fibrous thickener, for which mechanical degradation causes significant changes.

Degradation is an irreversible process that tends to accumulate with time and concomitantly reduces the system’s free energy and lowers the performance quality. Thus, a measure of irreversibility can be used to quantify deterioration. For this purpose, the concept of entropy as defined by the second law of thermodynamics provides a path forward. Every real process is irreversible at a fundamental level, meaning that entropy is always generated. Recent theoretical developments [10] have implemented the use of entropy in modeling degradation, allowing degradation models that are based on thermodynamics, rather than empirical formulations. This idea has been used with success in modeling processes such as wear [11-13], fatigue [14-17], battery degradation [18-20], and grease degradation [21-26]. Basic entropic models of mechanical grease degradation and latest development relative to degradation analyses [27] have been established and validated by researchers, and their use in predicting grease life is discussed in Section 4 after an introduction to the relevant measurements and experimentation techniques.

2. Measuring Degradation

In order to observe the changes to a system caused by degradation, one must first identify a particular measure of degradation. The ideal choice is clear for processes such as wear, where the amount of material worn indicates the amount of degradation which occurs. For grease, however, the changes to the microstructure can be described using a variety of degradation measures. The most common is shear stress, apparent viscosity, and consistency [18].

2.1 Shear Stress

The shear thinning, thixotropic nature of grease means that the shear stress is both a function of shear rate and time [28], as indicated by Figure 1 [21, 25]. The dependence of shear stress on time means that shear stress can be a description of a grease’s degradation state at a given time. Its weakness, however, is in the shear-thinning nature: the shear rate profile over the entire time spent shearing the grease must be known in order to compare shear stress values to form accurate conclusions on degradation. For devices operating at a constant shear rate, this concern is mostly alleviated. The only additional major source of uncertainty is the grease’s tendency to relax after being stressed, during which the broken structure partially rebuilds itself [2]. This adds another time scale that will affect measurement results.
2.2 Viscosity

The viscosity of a fluid is simply a measure of resistance to motion that can be quantified by dividing the shear stress by the shear rate. In other words, it is the slope of the shear stress-shear rate plot (Figure 1). It is a constant value for a linearly viscous (Newtonian) fluid. Because of the nonlinear behavior of shear stress on the shear rate for lubricating grease, the viscosity is not constant. Additionally, as shear stress (at a fixed shear rate) declines over time as a grease is sheared, the viscosity declines as well. Similar to shear stress, the viscosity is dependent on shear rate and time spent shearing, meaning that it has similar advantages and disadvantages to shear stress as a measure of degradation.

2.3 Consistency

Consistency is often considered to be the most important property about a grease, and it changes as a grease degrades. Consistency depends heavily on thickener type and concentration, but also on the base oil viscosity and operating temperature [1]. As a fibrous grease degrades, its thickener structure is fragmented, thinning its consistency. Therefore, measuring a grease’s consistency can be a viable approach for assessing its mechanical degradation.

The most widely accepted standard of grease consistency is a grade given by the National Lubricating Grease Institute (NLGI). The NLGI defines nine consistency grades ranging from 000 to 6. The grade 000 has nearly the consistency of oil and grade 6 has a consistency similar to cheddar cheese. These grades are quantified by performing a penetration test, in accordance with ASTM D217 standards [29]. This penetration test involves working (shearing) the grease in a specified grease worker and then immediately afterward, placing the worked grease sample in a specified cup and allowing a cone-shaped tool to fall (penetrate) into the grease sample. The amount of penetration is measured, and this value is compared to the penetration depth ranges for each NLGI grade to assign the grease its corresponding grade.
Another way of quantifying the consistency of a grease involves monitoring the changes to the crossover point or the yield stress. These are similar properties, describing how much stress it takes for the structure to break down so the grease begins to flow. Both are measured using oscillatory strain sweep testing, and their slightly different definitions will be discussed in Section 3.2.

### 2.4 Fourier Transform Infrared Spectroscopy

An important tool in observing the degradation of grease is Fourier Transform Infrared Spectroscopy (FTIR). The results of FTIR (shown in Figure 2) show the absorbance of light across a spectrum of wavenumbers (wavelengths per unit distance), revealing information about the chemical composition of the sample used. The difficulty in quantifying a change in absorbance renders FTIR a qualitative method of observing mechanical degradation. For chemical degradation analysis, however, FTIR is an excellent tool, since an absorbance peak at a particular wavenumber indicates a high concentration of a particular chemical species. Therefore, the changes to the peaks indicate chemical reactions. Overall, FTIR has little utility in quantifying mechanical degradation, but has great utility in establishing that chemical degradation is insignificant.

![Figure 2: FTIR for a grease at different stages of mechanical degradation](image)

### 3. Modeling Experiments with Entropy

In an effort to test changes to a grease’s structure due exclusively to mechanical degradation, experiments were carefully designed to minimize the influence of additional degradation mechanisms.

#### 3.1 Inducing Mechanical Degradation
Since mechanical degradation is induced by shearing, researchers developed equipment that sheared samples of grease for prescribed periods of time to “age” them. Some researchers chose to age grease samples between the plates of a rheometer while others [23, 24] manufactured custom rigs, such as the ones shown in Figure 3 [30] and Figure 4 [8, 23], to use for extended aging periods. In addition to shearing by pure rotation, many investigators [21-24] employed additional tools such as a grease worker. All aging procedures were conducted in the temperature range appropriate for isolating mechanical degradation. Temperatures too high lead to oxidation causing chemical degradation, while temperatures too low lead to condensation formation from the ambient air, so the desired range is near room temperature.

During rheometer and custom-rig aging tests, grease samples were aged by the rotation of a wall or plate. For rheometer aging, a grease sample is spread on a base plate and the top plate is lowered onto the sample at a prescribed gap distance above the base plate. Excess grease is removed from around the plates, and the top plate is set to rotate for the desired time. For the custom test rigs, the gap distance is fixed based on the chosen geometry, but the procedure is similar to rheometer tests. Throughout all tests, the shear stress and shear rate are monitored in order to calculate the amount of entropy generated.

![Rotating-bob aging machine used by Lijesh and Khonsari](image)

*Figure 3: Rotating-bob aging machine used by Lijesh and Khonsari [30]*
3.2 Degradation Measurement Procedures

Among the common methods of measuring degradation are shear stress, viscosity, and consistency. The behavior of - and measurement process for - shear stress and viscosity are similar, so these will be covered together. Consistency measurements, however, have procedures that can vary significantly.

Shear stress and viscosity are measured by a rheometer. The rheometer applies a varying rotational speed (shear rate) and measures the resistance to rotation at each shear rate, giving “flow curves” as an output. These flow curves show viscosity as a function of shear rate and shear stress as a function of shear rate. In order to assess degradation over time, one value should be taken from the flow curve to compare as a grease degrades. A common choice of comparative value is the zero-shear viscosity. Figure 5 [23] shows the change in zero shear viscosity as a function of entropy generated.
Figure 5: Zero-shear viscosity decrease as entropy is generated [23]

Since ASTM standard D 217 for measuring consistency requires a large quantity of grease, it is a poor method for assessing degradation both in experiments and in practice. Even with a ¼ scale standard penetration test given by ASTM D1403 [31], around 4 mL of grease is required at each time interval, which is an unreasonably large sample size for most machines. To reduce the quantity of grease needed, a rheometer is often used to measure grease consistency through the use of fixed-load compression testing or oscillatory strain sweep testing. These tests can be easily performed with less than 0.5 mL of grease and can still yield sufficiently repeatable results.

The fixed-load compression testing done by some researchers [21-24] uses a rheometer to obtain results in a modified penetration test. Rezasoltani & Khonsari [21] and Lijesh & Khonsari [24] use a plate-plate rheometer setting to provide a constant compressive force to a grease sample. Such a procedure involves placing a grease sample on the base plate of a rheometer and lowering the top plate until the desired gap is present. The rheometer is then set to provide a constant force for a prescribed period of time, and the resulting distance traveled by the top plate is recorded and used as an indicator of consistency.

Other researchers such as Kuhn [22] and Zhou et al. [23] used a rheometer to find yield stress or crossover stress, and these values were used as consistency measurements. These tests are done through oscillatory strain sweep in a rheometer, where a grease sample is placed between rheometer plates and the top plate oscillates at a fixed frequency but an increasing amplitude. The crossover point is the first point at which the storage modulus ($G'$) and loss modulus ($G''$) reach the same value; a typical strain sweep plot with the crossover point marked is shown by Figure 6 [32]. The yield stress has numerous definitions, but Cyriac et al. [33] define it as the first point at which the stress-strain plot deviates from a line by a prescribed amount, shown by Figure 7 [33]. The stress needed to reach the crossover stress or the yield
stress is indicative of a grease’s consistency and the two can be related by empirical curve fits such as those proposed by Speigel et al. [34].

Yet another method of monitoring degradation is through the use of a torque meter or ammeter. This method has the ability to be used with any machinery while it is running, and can provide instantaneous information about the shear stress and/or viscosity of the grease. This method, used by Lijesh & Khonsari [24, 30], requires a careful calibration of the unloaded conditions in order to monitor the changes to these conditions over time. Assuming proper lubrication is maintained, the torque over time and power drawn over time are proportional to the grease’s shear stress, which decreases over time.

3.3 Experimental Results
The first time the so-called Degradation Entropy Generation (DEG) theorem [10] was applied to grease degradation was in the work of Rezasoltani & Khonsari [21], where a linear trend between net penetration and entropy generated per unit volume, $S_{g,\text{vol}}$, was established, shown by Figure 8. Similar results were obtained by aging grease in a rheometer, in a journal bearing, and in a grease worker. Since this line was approximately the same across all tests performed, it indicated that this line represents the so-called “characteristic line” for the particular grease being tested. Assuming that other degradation mechanisms were not present during aging, the slope of this line represents the coefficient of proportionality between entropy generated and degradation which is specific to that grease. Therefore, if the grease is used in a device where mechanical degradation is its dominant degradation mechanism, the line obtained from these tests could be extrapolated and used to estimate grease life.

![Figure 8: Linear trend between penetration decrease and entropy generated [21]](image)

Kuhn [22] and Zhou et al. [23] sought to repeat these results to verify their utility. They used different ranges of $S_{g,\text{vol}}$ values, including relatively low values. This means that Kuhn and Zhou plotted degradation as a function of lower $S_{g,\text{vol}}$ values and they observed additional behavior. Similar to problems involving wear of tribo-component surfaces, there exist a transient region and a steady state region for grease degradation. The transient region is categorized by rapid structural degradation, while the steady state region serves as a grease’s working life, where degradation happens at a slower rate. Zhou et al. [23] and Lijesh & Khonsari [24] show the existence of the transient and steady-state region in Figure 9.
These results were also observed by Lijesh & Khonsari [24] who additionally found that this transient region is dependent on shear rate, and the degradation takes a longer time and $S_{g,vol}$ to reach a steady state when a grease is sheared at a higher shear rate. Since the shear rates used during the initial experiments of Rezasoltani and Khonsari can be considered relatively low, this is an additional justification for it making up a negligible portion of the obtained results. Because the most rapid degradation happens within this transient region, it is, of course, important to understand how a grease changes throughout this time to ensure that it still properly lubricates throughout this time and after it. However, on the scale of a grease’s total life, this transient region is typically brief.

4. Application of Results
These experimental results used in conjunction with the principles of modern degradation theory [10] are the foundation for recent grease life model development. Since degradation takes place as a function of entropy generation, the cumulative entropy which has been generated is an ideal description of the state of degradation of a grease at a certain point in time. Upon relating the entropy information to time, one can predict the life of a grease for any application. In addition, this model has the ability to be updated if information is available about a grease’s current state. Further, the model has the ability to account for changes to operational conditions, such as increasing the rotational speed of a shaft.

4.1 Predicting Grease Life
In order to define the life of a grease, one must identify a failure condition at which a grease is no longer suitable for a particular application. Two possible options are to use a drop in the consistency [25] or in entropy generation rate [24]. Rezasoltani & Khonsari [25] used consistency measurements from rheometer compression tests to determine a failure criterion. The aging was to be performed on an NLGI grade 2 grease, and the failure criterion was established as a consistency drop to NLGI grade 1. Lijesh &
Khonsari [24] used the same idea of a drop in NLGI grade but used the entropy generation rate as the measurement tool. Assuming that the grease is sheared at constant shear rate and temperature, the entropy generation rate is proportional to the instantaneous shear stress.

By the first method presented where consistency drop is used as a failure criterion, this criterion is quantified by establishing the consistency of the failed grease. Since Rezasoltani & Khonsari used a grade 2 grease and sheared it until it degraded to grade 1, the consistency of a grade 1 grease had to be established in the same manner as consistency measurements were to be taken so the values could be compared. Rezasoltani and Khonsari used fixed-load compression testing in a rheometer, and this method was used to test the consistency of a grade 1 grease. The amount of penetration for this grease was measured and used as the failure criterion for the grade 2 grease. Therefore, when the grade 2 grease is tested in the rheometer and has the same penetration as the grade 1 grease, it is considered fully degraded. This is shown in Figure 10 [25].

Figure 10: XHP 222 penetration vs $S_g$, $\nu\nu\nu\nu

Figure 10 shows the characteristic line given by a linear curve fit to Figure 8. This life estimation method determined that, in order to reach the penetration given by a grade 1 grease, the grade 2 grease must have an entropy input of $0.224 \frac{J}{mm^3 K}$. Therefore, if an equation relating the entropy generation to time is developed for a particular application, it can be used to estimate the grease life. Assuming that the shear rate and temperature are constant throughout shearing, the only parameter left to examine is the shear stress. Using the Maxwell model for estimating shear stress over time, the shear stress becomes a first-
order differential equation [25]. All necessary parameters can be found experimentally depending on machine operating conditions, and the grease life can be found.

An alternative technique for estimating grease life uses the change in entropy generation rate over time instead of the change in penetration depth over time. If the same failure criterion - a consistency drop by one NLGI grade - is used, then the initial entropy generation rate of the lower grade must be measured in order to establish when the higher grade grease has degraded to that point. Figure 11 [24] shows how the entropy generation rate of a grade 2.5 grease (solid black line) and a grade 1 grease (dashed blue line) change as they are sheared over a long period of time. The entropy generation rate from shearing the grade 2.5 grease eventually reaches the starting entropy generation rate of the grade 1 grease (shown by the dashed black line). At this point, the grease is considered failed, and the time it takes to reach this state is considered the grease’s life. This method used a torque meter, providing constant, online information about the state of degradation. If this method is used in practice, a machine could be relubricated when the entropy generation rate reaches a particular value.

4.2 Monitoring the Condition of In-Service Machinery

Taking online machinery out of service often has undesirable repercussions. Since a machine must be stopped for a grease sample to be removed for quality analysis, this should be performed as infrequently as possible. In addition, some quality monitoring techniques such as microscopy give data which cannot be easily quantified and applied in predicting the remaining life of grease.

The online monitoring of grease performed by Lijesh & Khonsari [24] proved to be an effective method for monitoring the status of a grease sample. This method has application for industrial machinery for which it is practical to dedicate a torque sensor. Using such a monitoring technique has the potential to drastically reduce machine failure since the grease’s condition can be monitored without significantly
affecting the machine’s operation. These preliminary results should be viewed as proof of concept and much more research is needed to take full advantage of how the method can be generalized and applied in the field.

5. Conclusions

Entropy has proven to be an effective tool in developing relatively simple and useful models for predicting grease life in situations where mechanical degradation is the dominant degradation mechanism. Thus far, this principle has been applied to assess mechanical-type degradation of a grease subjected exclusively to long-term shearing. There are other methods for physical degradation that must be considered, including evaporation, oil-thickener separation, and contamination. In addition, chemical degradation, especially oxidation, can prove to quickly degrade the grease in many situations. Since the nature of grease is quite complex, and each grease used has its own unique properties due to the base oil type, thickener type, and concentration of thickener, these other degradation mechanisms require significant analysis in order to be included in a more complete model of a grease’s life.

The life prediction models covered in this paper are sufficient for a general approximation of the grease life in a device, but the actual flow of grease throughout the bearing or other device is a complicated topic. In reality, grease does not degrade uniformly, and a superior model would describe grease degradation with a dependence on location. In addition, the model should include all possible degradation mechanisms. Future research is needed on the significance of these other degradation mechanisms and on the subject of using them all at the same time to model degradation. The limitations of the mechanical degradation model should be investigated such as the applicable thickener types, the temperature range within which it provides acceptable results, the amount of contamination allowed, and the amount of oil leakage allowed in order to have the best model possible for grease life in any device.

Acknowledgments

This research was made possible in part by NLGI for which the authors are grateful.

References

The Use of Entropy in Modeling the Mechanical Degradation of Grease

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Received: 21 August 2019; Accepted: 10 September 2019; Published: 20 September 2019

Abstract: Recent theoretical developments linking degradation to the thermodynamic concept of entropy have allowed a new approach to modeling all types of degradation. The theory has been successfully applied to wear, fatigue, and numerous other forms of degradation and experimentation has confirmed its applicability to modeling the mechanical degradation of lubricating grease. This paper overviews the mechanical degradation of grease, discusses past and present modeling techniques, shows how new techniques can be used to predict grease life, and provides suggestions for future research.

Keywords: Mechanical degradation; grease life; entropy; irreversible thermodynamics

1. Introduction

Grease is a common lubricant composed of base oil and a thickener and is used extensively in machinery due to its unique properties. It is often the first choice of lubricant for rolling bearings, journal bearings, slider bearings, gears, pivots, couplings, guides, pin-bushings, and sliding contacts, especially if these are to be placed in an inaccessible location [1, 2]. Because of its thickener structure, grease has a relatively thick consistency (firmness), which differentiates it from oil. In contrast to oil, this consistency allows grease to stay in place without the need for a complicated distribution system, supply arrangement, or reservoir. Grease has good sealing capacity, resists leakage, provides corrosion prevention properties, and needs little maintenance. Nevertheless, microstructural complexity and its degradation during long-term operation render the development of predictive models of grease behavior a difficult task. Grease is thixotropic, meaning its properties change with time upon agitation (shearing) [3]. When the shearing stops, the properties partially return to their initial state, but not completely [4]. The change in bulk properties due to shearing is mechanical degradation and is one of the main ways through which grease degrades.

Grease degradation can be broken down into two regimes: physical degradation and chemical degradation [5-8]. Physical degradation includes mechanical degradation of the thickener structure due to shearing, separation of the base oil and thickener, evaporation of the base oil, and contamination of the grease by foreign particles. Chemical degradation [9-11] involves all chemical reactions that take place, including oxidation of both the base oil and thickener and the depletion of additives. Chemical degradation is dominant at higher temperatures and during long-term storage of grease, while mechanical degradation is typically dominant when a greased interface is subjected to shearing or working the lubricant at high
Degradation is a central issue with the use of grease since it means a grease sample has a limited life. As grease is put to use, its thickener structure degrades, its base oil leaks and/or evaporates, both the thickener and base oil oxidize, and it tends to become contaminated with foreign particles. All of these elements cause the grease’s overall properties to permanently change. Eventually, the properties deteriorate so substantially from those of the pristine grease specified for its application that the degraded grease becomes unusable for its intended purpose and must be replaced. A key property that changes as a grease degrades is consistency: a measure of a grease’s overall “firmness”. Consistency generally determines a grease’s suitability for a particular application and has a major influence on a device’s performance. Pure mechanical degradation causes the consistency to become more fluid since the thickener structure is fragmented into smaller pieces [8, 13]. The destruction of the thickener can be visualized through microscopy such as AFM or SEM, and Figure 2 shows SEM comparing pristine grease to mechanically degraded grease [8].

Figure 1. Dominant degradation mechanism across shear rate and temperature including long-term storage (no shear); remade from Ito et al. [7]
Estimating grease life is important since a bearing using grease with degraded properties has the potential for premature failure. Ideally, grease is swept away from moving components once a freshly-greased device begins operation, leaving only a thin film [6]. The excess grease should then remain clear of these components, serving only as a lubricant reservoir. If degradation causes the grease’s consistency to thin sufficiently, the grease may begin to leak out of the bearing, causing lubricant starvation [14]. The degraded grease could also flow into space between moving parts, where it will be churned. Churning can also be catastrophic since it causes significant oil bleed and excessive heat to be generated. Since grease does not have an effective convective mechanism to adequately dissipate this heat, churning can lead to significant chemical degradation. Additionally, the bled oil may leak significantly and the grease will have overall dramatically different properties from what is desired, meaning the lubrication will be ineffective. Poor lubrication will lead to a decrease in mechanical efficiency, wear of solid surfaces, overheating, and eventually failure, causing significant damage to any machine [1].

Life models currently exist to ensure either a bearing or the grease within is changed before these issues can cause problems. Current widely-used estimates of grease life are mostly used in rolling element bearings and are developed by their manufacturers [2]. The models used are empirical and developed from testing bearings until failure in specially-designed test rigs. These bearing-dependent results are then analyzed with statistical techniques, resulting in the current grease life models used today. The $L_{10}$ parameter, which represents the amount of time needed for 10% of a set of bearings to fail, is commonly used as a bearing’s life [15, 16]. This is dictated by bearing type, geometry, and all modes of grease degradation [6]. Nevertheless, the bearing should be relubricated or replaced well before failure, and common guidelines are to relubricate bearings at approximately half of the $L_{10}$ [15] or at the $L_{91}$ [6].

The current grease life estimation methods used by manufacturers for bearings and other greased devices are only valid for those devices, and testing results cannot be reliably applied to others. In addition, these methods are generally incompatible with grease quality monitoring methods. This means that although a grease’s condition can be analyzed throughout its service life, predicting the remaining life based on this analysis is still not well-defined. Because of these two major issues, developing a model that can predict grease life for a general case and allow the user to update the model through monitoring methods would be a significant step forward in preventing machine failure due to poor lubrication.
Promising new approaches for assessing grease degradation that allows both the prediction of grease life and several updates of this estimate have been recently introduced [13, 17-24]. This approach involves the application of irreversible thermodynamics to model the irreversible changes that happen to the grease’s microstructure during use.

Irreversible thermodynamics refers to the second law of thermodynamics, which defines entropy (S) and necessitates that the entropy of the universe always increases. The most basic way of thinking about entropy is that it gives details about the direction and method by which processes occur since the entropy of the universe always increases with no exception. When a process involves no dissipative effects and is reversible, there is no change in entropy. A realistic case, however, is a process that has dissipative effects such as heat transfer or chemical reactions where entropy is generated. The generation of entropy means that this process is irreversible. For example, as a grease-lubricated bearing rotates, the grease sample between the moving parts is sheared, irreversibly breaking down its structure. This means that it will never again have exactly the same properties as it did initially. The use of entropy, therefore, offers excellent potential for describing degradation in general and is well-suited for lubricating grease.

Before applying the idea of irreversible thermodynamics to grease, a general framework for formulating degradation was developed and applied to problems involving wear and fatigue. Bryant et al. [25] established the framework for this by proposing the Degradation-Entropy Generation (DEG) theorem, which proposes a degradation measure to be directly proportional to the entropy produced for each dissipative process that occurs. The theorem also establishes that if there is a critical value of degradation at which a failure occurs, there is also a corresponding critical value of accumulated entropy generation. This idea was then successfully applied to problems involving wear [26-29] and fatigue [30-34], where the results consistently gave further support to the DEG theorem.

The use of irreversible thermodynamics to model grease degradation was validated as a promising idea by Rezasoltani and Khonsari [17], who established a linear trend between penetration values (a measure of mechanical grease degradation) and entropy density generation (entropy generated per unit volume). This work probed the tribology community to examine the results and to explore the use of entropy generation as an indicator of grease degradation. If a model for grease is fully developed, the DEG theorem could be used to identify the critical accumulated entropy generated by significant degradation processes that results in a sufficiently degraded grease. This then leads to a life estimate for any greased device operating under any conditions. This paper reviews recent development toward this goal, with a summary table of relevant literature given by Table 1.

The outline of this paper is as follows. In Section 2, the evolution of grease degradation theory is presented. Section 3 then gives details of recent experiments and results, indicating the usefulness of entropy in modeling grease degradation. Section 4 presents a practical application of experimental results and presents a need for future research. Concluding remarks and future suggestions are given in Section 5.
Table 1. Summary of literature relating entropy and the mechanical degradation of grease

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<tr>
<th>Paper</th>
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<tbody>
<tr>
<td>Friction and Wear of a Grease Lubricated Contact [35] Kuhn, E.</td>
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<tr>
<td>Correlation between Mechanical Degradation and Entropy [17] Rezasoltani &amp; Khonsari</td>
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<td>Correlation between Entropy and Structural Changes [18] Kuhn, E.</td>
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<tr>
<td>Tribological Stress of Lubricating Greases [19] Kuhn, E.</td>
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<tr>
<td>Engineering Model to Estimate Consistency Reduction of Grease [20] Rezasoltani &amp; Khonsari</td>
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<tr>
<td>Mechanical Degradation of Lubricating Grease in an EHL Line Contact [24] Rezasoltani &amp; Khonsari</td>
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<td>Assessment of Mechanical Degradation Using Entropy Generation [21] Lijesh &amp; Khonsari</td>
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<td>Proposes a model describing entropy flow in a grease system</td>
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<td>First to model consistency reduction of grease using DEG theorem; establishes linear trend</td>
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<td>Provides new structural degradation model; proposes crossover stress as an indication of degradation</td>
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<td>Compares mechanical structural degradation for different grease chemistries</td>
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<td>Proposes a method for predicting grease life that allows variable operating conditions; proposes failure as drop by one NLGI grade</td>
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<td>Identifies three distinct regions of grease lubrication</td>
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<td>Shows two phases of grease mechanical degradation; proposes an aging equation</td>
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<td>Included the effect of temperature to previous results</td>
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<tr>
<td>Explains two regions of mechanical grease degradation; proposes online degradation monitoring method</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measures energy dissipated, resulting in temperature increase</td>
</tr>
<tr>
<td>Measures comparative penetration using rheometer; validated using grease worker and bearing tests</td>
</tr>
<tr>
<td>Uses dissipated frictional energy and temperature increase to calculate entropy generated</td>
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<tr>
<td>Uses a model of shear stress over time with characteristic line to estimate grease life</td>
</tr>
<tr>
<td>Rollers pressed together, exposing grease to high shear rates</td>
</tr>
<tr>
<td>Grease aged through Couette aging device at various shear rates; properties measured with a rheometer</td>
</tr>
<tr>
<td>Used Couette aging device with added temperature-controlled bath</td>
</tr>
<tr>
<td>Included the effect of temperature to previous results</td>
</tr>
<tr>
<td>Uses torque meter to estimate entropy generated; estimates the time until grease drops by one NLGI grade</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Provides detailed model of entropy flow within a model grease system</td>
</tr>
<tr>
<td>DEG theorem can be applied to grease using “net penetration” as the degradation measure</td>
</tr>
<tr>
<td>Structural degradation vs entropy supply shows different slopes at low entropy values</td>
</tr>
<tr>
<td>Differences in grease chemistry lead to vastly different degradation behavior</td>
</tr>
<tr>
<td>Life prediction model shows agreement with experimental data</td>
</tr>
<tr>
<td>Grease within EHL contact degrades very quickly but is held in place by grease walls</td>
</tr>
<tr>
<td>Rapid degradation occurs initially followed by slower degradation; entropy concept validated</td>
</tr>
<tr>
<td>Higher temperatures increase mechanical degradation; temperature component added to the previous model</td>
</tr>
<tr>
<td>Mechanical degradation is akin to running-in followed by steady-state; steady-state is reached faster at low shear rates</td>
</tr>
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</table>
2. Grease Degradation Theory

Degradation is a process by which a system goes from some initial state to one of lesser quality or desirability. Since degradation, by nature, can only decrease the quality or desirability of the studied system, it is inherently linked to the production of entropy. Though the basic idea is a rather simple one, quantifying this information so that it could be used is often difficult. Initial grease degradation models compared the amount of energy used in shearing a grease to the damage on the microstructure. This model [37-39] showed promise, but uses many specific parameters unique to one particular shearing situation. It was only after the Degradation-Entropy Generation theorem [25] was established in 2008 that a new modeling technique was developed using entropy. The initial application of the DEG theorem to mechanical degradation of grease [17] showed promising results, making this approach the most recent modeling tool available in describing grease degradation.

2.1. Quantifying Mechanical Degradation

A variety of techniques exist for monitoring the mechanical degradation of grease [8]; each of which tracks a particular property as the grease is sheared. To make the best use of results, the information gathered should be easily quantifiable. Therefore, properties such as shear stress, viscosity, and consistency [22] are used in modeling degradation over time.

2.1.1. Shear Stress

A fundamental property of grease is that it is a shear-thinning fluid, meaning that its viscosity drops with increasing shear rate. This means that the shear stress within a grease is not linearly dependent on shear rate as is true for a Newtonian fluid, shown by Figure 3a [17]. Therefore, the viscosity is a function of shear rate and it has an “apparent” value at a given shear rate. This adds complexity to calculations since the shear rate profile must be known over the entire shearing time in order to accurately calculate the energy dissipated. More importantly in the context of mechanical degradation, grease is thixotropic, meaning that shear stress is a function of time even at a fixed shear rate, shown by Figure 3b [20]. Shear stress can be directly associated with mechanical degradation of grease since the accumulation of stress from shearing causes the structure to break down.
2.1.2 Viscosity

Viscosity can also be used to assess a grease’s degradation. Once again, the shear thinning, thixotropic nature of grease provides somewhat of a challenge, as the viscosity depends on shear rate and time, similar to shear stress. The viscosity of grease over time declines similarly to the shear stress, so viscosity has similar advantages and disadvantages to shear stress as a tool for assessing the mechanical degradation of grease. Overall, the viscosity and shear stress can be measured by a variety of tools such as a rheometer, viscometer, or torque meter by measuring the grease’s resistance to shear at a given shear rate.

2.1.3 Consistency

Consistency is a complex property of grease, which represents the overall “firmness”. Consistency depends heavily on the base oil type, thickener type, thickener concentration, thickener structure, and temperature [1]. Since mechanical degradation causes the thickener structure to permanently change, it results in an overall change to the consistency of a grease sample. Therefore, at a given temperature, the degradation of grease can be assessed by measuring its consistency. The actual methodology for determining consistency has only one formal standard: the cone penetration test given by ASTM standard D217 [40] in which a particular cone-shaped weighted tool is allowed to fall into a standardized cup of grease. The depth of penetration after 5 seconds is measured and used as a measure of consistency. Many researchers find this test requires too large a grease sample and inadequate for monitoring grease degradation, so they opt to establish consistency through methods discussed in Section 3.1.2.

2.1.4 Infrared Spectroscopy

Grease can also be analyzed through infrared spectral analysis, where the absorbance at a range of wave numbers is established. This method is extremely useful for examining the extent of changes to the chemistry of the grease structure since any chemical reactions will cause a shift in the absorbance. Changes in base oil content (due to evaporation) and additive content (due to oxidation) can be established by

\[ \text{Figure 3. (a) Grease’s shear-thinning nature [17] and (b) grease’s thixotropic nature [20]} \]
infrared spectroscopy [8, 41], but its use is limited in monitoring mechanical degradation. Rather, it can be used as a justification that mechanical degradation is dominant by finding that chemical reactions do not take place [13, 36].

2.2 An Energy Approach

Before the DEG was established, Kuhn developed a promising approach for characterizing a grease’s degradation behavior subjected to shear [37-39]. This approach involved relating the changes in a grease’s microstructure to the work done by shearing it, and he developed a grease degradation model with similarities to solid body wear models. By relating wear rate with viscosity degradation rate and establishing a limiting viscosity, Kuhn then found the amount of frictional energy required per unit volume to be dissipated in the grease to reach the limiting viscosity [37]. This was established as the limiting energy density. The accumulated energy dissipated per unit volume, $e_{rh}$, can then be compared to the limiting energy density for that particular grease to assess microstructure damage. The calculation of $e_{rh}$ is given by Equation (1). Here, the accumulated frictional energy, $e_{rh}$, is a function of shear rate, $\dot{\gamma}(t)$, and shear stress, $\tau(t)$, integrated over the shearing time interval.

$$e_{rh} = \int_{t_i}^{t_f} \dot{\gamma}(t) \cdot \tau(t) \, dt$$  

Once a grease reaches the limiting energy density, the grease has reached the state of maximum structural degradation. By using an empirical relation for $\tau(t)$ given by Equation (2), $e_{rh}$ can be given as a function of time and structural degradation intensity, $n$. $\tau_{lim}$ and $t_{lim}$ are the shear stress and time corresponding to the state of limiting viscosity.

$$\tau(t) = \tau_{lim} \cdot \left(\frac{t}{t_{lim}}\right)^{-n}$$  

Equation (2) is then used with Equation (1), yielding Equation (3). This equation describes the structural degradation as a function of time, but the exponent $n$ depends both on the grease used and the shearing conditions.

$$e_{rh}(t) = \tau_{lim} \cdot \left(\frac{1}{1-n}\right) \left(\frac{t}{t_{lim}}\right)^{1-n}$$  

While this method is grease- and process-specific, it is a promising approach since if the details are known about a specific shearing process, then the critical accumulated energy density could be used as a criterion for failure, and this is simply a material property. The problem that arises is that this analysis is limited to one specific process with one specific grease and changes to either one means that $n$ must be reevaluated. Therefore, a more robust method that can be more easily applied to any shearing process with any grease is highly desirable.

This energy approach, related to mechanical wear quantification techniques, was used due to the existing degradation theory. However, as the use of entropy to model degradation was studied further, researchers found encouraging results. Experimental results which strongly link entropy to degradation date back to 2000, when many researchers [42-44] found a strong correlation between wear and the
production of entropy. As this linear trend between degradation and entropy was observed in an increasing variety of experiments, a theory was developed to link them.

2.3 The Entropy Approach

2.3.1 Degradation-Entropy Generation Theorem (2008)

The DEG theorem [25] was established in 2008 upon consideration of the gap between existing testing machinery capabilities and a scientific theory that had the ability to model degradation dynamics. The main idea of the DEG theorem is to use entropy generation as a fundamental measure of degradation, leading to the creation of appropriate degradation models that are consistent with the laws of thermodynamics. The power of the DEG theorem is in its description of some measure of degradation, \( w \), as a function of some quantity, \( i \), of dissipative processes. This degradation measure is a linear combination of the entropy generated, \( S'_i \), by each process multiplied by a corresponding degradation coefficient, \( B \). The simplified main equation can be given in rate form as (4).

\[
\frac{dw}{dt} = \sum_i B_i \frac{dS'_i}{dt} \tag{4}
\]

For example, if two independent dissipative processes cause a system to degrade, (4) can be rewritten as (5), with a dot signifying a derivative.

\[
\dot{w} = B_1 \dot{S}'_1 + B_2 \dot{S}'_2 \tag{5}
\]

After identifying each dissipative process, their corresponding \( B \) values can be determined through isolation, and thus the degradation rate can be defined as a function of entropy generation rate. An important consequence of this relation is that if there is a critical degradation measure at which the studied system is considered sufficiently degraded, there is a corresponding sum of accumulated entropy generation from each dissipative process which consistently yields that state.

Immediately after the DEG was proposed, it was found to yield remarkably accurate results compared with existing degradation equations, such as Archard wear [45] and fretting wear [46]. In fact, it was shown that the use of the DEG theorem results in a relationship that subsumed Archard’s adhesive wear model. Further, by using the DEG theorem, these equations could be examined in greater depth [27, 47]. More importantly, the DEG theorem was then used to describe degradation mechanisms that did not have previously existing equations, such as fatigue fracture [31, 47, 48] in metals and composites, battery degradation [22, 49, 50], and grease degradation [13, 17-24]. In fact, its use in modeling fatigue fracture led to the discovery of a so-called Fatigue Fracture Entropy. The DEG theorem is currently being used with success in an increasing number of fields, and it has proven to be a useful tool in modeling many types of degradation.

2.3.2 Entropy Generation by Shearing Grease

Entropy is produced through dissipative processes. These processes could include heat transfer, adhesion, abrasion, plastic deformation, fracture, phase change, chemical reactions, diffusion, mixing, or some combination of these [22]. For quantifying the rate of change of the specific entropy of a tribological system in the context of wear, (6) is used. The derivation of which is given by Lijesh et al. [29].
\[
\dot{s}_g = \frac{\sigma \cdot \dot{\gamma}}{\rho T} - \frac{\dot{e}_{mt}}{T} + k \frac{(\text{grad } T)^2}{T^2} - \dot{s}_{g, mt} - \sum_k \eta_k dN_k
\]  

(6)

This equation breaks down the total rate of entropy change of a system into five terms. The first (and most dominant in describing mechanical grease degradation) consists of stress induced by shearing, \(\sigma\), strain rate, \(\dot{\gamma}\), density, \(\rho\), and temperature, \(T\). This first term describes the entropy generated from friction between two rubbing bodies which plastically deforms the asperities in contact. The second term describes entropy generated from mass transfer, and consists of the rate of heat removed through mass transfer, \(\dot{e}_{mt}\), and temperature. The third term gives the entropy produced by heat transfer through conduction and uses the thermal conductivity, \(k\), the temperature gradient, and the temperature. The fourth term, \(\dot{S}_{g, mt}\), represents the entropy flow due to mass leaving the control volume. Finally, the fifth term uses the chemical potential, \(\eta_k\), and the number of moles, \(N_k\), to describe entropy change due to chemical reactions.

Through reasonable assumptions for investigating mechanical degradation of grease, this equation can be heavily simplified. The second and fourth terms are eliminated by considering a grease sample as a closed system. The third term can be eliminated by assuming that a negligible temperature increase occurs due to shearing the grease, which is acceptable for the aging devices used to induce mechanical degradation. The fifth and final term can be eliminated by neglecting all negligible chemical reactions that may take place during mechanical aging. This leaves only the first term, which describes an accumulation of stresses induced by shearing. This term can be rewritten in its most useful form for grease shearing as (7) [17].

\[
S_{g, vol} = \int_0^t \frac{\tau(t) \cdot \dot{\gamma}(t)}{T} dt
\]  

(7)

This equation gives the accumulated entropy density generation, \(S_{g, vol}\), as a function of the shear stress, \(\tau\), and shear rate, \(\dot{\gamma}\). According to the DEG theorem and assuming the grease only degrades through shear, this \(S_{g, vol}\) value is directly proportional to the degradation of the grease with a coefficient, \(B\), to be found experimentally.

3. Application of DEG Theorem to Grease - Testing and Results

The first use of the DEG theorem for describing grease degradation was performed by Rezasoltani and Khonsari [17], whose experimental results showed a clear linear trend between comparative penetration values and \(S_{g, vol}\) in 2014. This is shown in Figure 4. The trend remained true independent of shear rate and temperature, although a limited temperature window exists in which the temperature is not too high to induce significant oxidation and not too low to induce excessive condensation from the air in the room. The trend was even validated through the use of completely different testing devices. This initial work connecting the DEG theorem to grease proved a major step forward in gaining the ability to accurately predict grease life.
3.1 Experimental Procedures

To test the application of the DEG theorem to mechanical degradation, experiments were carefully designed to ensure that mechanical degradation was the dominant degradation mechanism.

3.1.1 Aging Methods

To induce mechanical degradation, grease is stressed in some way. For a short period of aging time, this can even be done with a rheometer [17, 18] which allows continuous measurements of rheological properties during the degradation. To age grease for extended periods of time, researchers [13, 21] developed custom Couette-type rigs such as the one shown in Figure 5 [13]; others used a journal bearing [17] or a paint stirrer [23]. Additionally, researchers used a grease worker to age grease similarly to the prolonged working section of ASTM standard D217 [13, 17, 21].

![Figure 4. Rheometer aging test results [17]](image)
3.1.2 Degradation Measurement

Common choices for measuring mechanical degradation are changes in shear stress, viscosity, and consistency. As previously discussed, shear stress and viscosity are intimately related properties that change similar to degradation. Consistency, however, is a bulk property with numerous proposed methods for its quantification, and each can give slightly different results.

Shear stress and viscosity can be found by measurements with numerous rotating measurement devices, such as a rheometer, a viscometer, and a torque meter. Use of a rheometer and viscometer provides a direct way of measuring viscosity or shear stress, as a range of shear rates are imposed on the sample and the resulting resistance to rotation is measured by the device. These machines output “flow curves”, which can show viscosity or shear stress as a function of shear rate. Results can be compared over time to observe the decrease in shear stress or viscosity at a given shear rate. The use of a torque meter is not quite as straightforward, as it must be linked to a motor or other rotational power supply. The initial conditions for the torque meter must be carefully determined so that future measurements are accurate. Lijesh and Khonsari [21] give a methodology for the use of a torque meter in monitoring mechanical degradation, and its implementation proves useful in allowing online degradation monitoring.

Consistency measurement has one accepted standard – the cone penetration test - but its use in mechanical degradation experiments is impractical. ASTM standard D217 [40] requires a large cup of grease in order to perform tests. Even a ¼ scale penetration test [51] requires a quantity of grease that is excessive for many mechanical aging devices. Therefore, researchers use alternative methods, such as a fixed-load compression test or an oscillatory strain sweep test in a rheometer to evaluate consistency. The fixed-load compression test is similar to the cone penetration test. In this test used by references [17] and [21], a grease sample is placed at the base of a rheometer and the top plate is lowered until a gap of 1.5 mm exists between it and the base. A compressive force of 2 N is applied, and the resulting displacement of the top plate is used as an indication of consistency in a similar manner as the cone penetration test.

Alternatively, the yield stress or crossover stress of a grease sample can be used as an indication of consistency. There exist numerous methods of calculating yield stress, with each method potentially...
yielding vastly different results. Cyriac et al. [52] propose a yield stress evaluation method that gives repeatable results. This procedure uses an amplitude sweep oscillatory test in a rheometer; typical results of which are given by Figure 6a [13]. This test involves placing the grease sample between rheometer plates, where the top plate oscillates at a fixed frequency but an increasing amplitude. As stress begins to build within the grease, it will eventually reach the yield stress, where grease structure begins to break down. Cyriac et al. [52] define the yield stress as the first point on a stress-strain plot at which there is 0.5% deviance from a line (shown in Figure 6b [53]). This is calculated based on a piecewise third-order polynomial curve fit among adjoining measurement points. The crossover stress, \( \tau_c \), can also be found in the amplitude sweep oscillatory test, and is marked in Figure 6a. Both the yield stress and crossover stress can be used as an indication of consistency, but depend on the oscillatory frequency chosen.

![Figure 6. (a) Typical results of amplitude sweep oscillatory test with crossover point marked [13] and (b) test results used to determine yield stress [53]; note that these figures are from different studies](image)

3.2 Experimental Results

Rezasoltani and Khonsari [17] established a linear trend between net penetration and entropy generated per unit volume, \( S_{g,vol} \), for mechanically degraded grease, shown by Figure 4. Similar results were obtained through aging in a rheometer, grease worker, and journal bearing, indicating that this line was indicative of the degradation behavior of that particular grease. Using the linear nature of the DEG theorem, the slope of this “characteristic line” relating consistency (a measure of degradation) and entropy represents the B coefficient for mechanical degradation from (2).

Additional experiments were performed by various researchers [13, 18, 21] seeking to repeat and more completely describe this behavior. Zhou et al. [13] performed mechanical aging across a wider range of \( S_{g,vol} \) values and calculated representative penetration values for direct comparison to the results of Rezasoltani and Khonsari, shown in Figure 7. These results indicated two separate regions of grease degradation with two different slopes: an initial, relatively brief, region with rapid degradation followed by a long region with slower degradation.
Lijesh and Khonsari [21] compared this behavior to the transient/run-in and steady-state regions of mechanical wear and reported that the length of the transient region is dependent on shearing conditions. They showed that degradation takes a longer time to reach steady-state when sheared at a higher shear rate. This information was then used as an explanation for why two slopes were not observed during the initial experiments of Rezasoltani and Khonsari: the shear rates used for this experimentation could be considered relatively low, meaning the transient region makes up a negligible portion of the total aging period. Despite its typically brief nature, it is important to understand how a grease changes throughout the transient region to ensure that proper lubrication is maintained throughout and after it. Nevertheless, since grease degradation is associated with prolonged shearing, the effect of the first slope is typically negligible.

4. Practical Application

These experimental results are an encouragement for the use of the DEG theorem in grease life modeling, showing that the cumulative amount of entropy generated in shearing a grease serves as an ideal description of the grease’s state of mechanical degradation. Such a model only requires the user to establish the amount of entropy generated in order to determine how much mechanical degradation has occurred. Once the amount of entropy generated can be described in terms of time, a life prediction model can be developed.

4.1 Predicting Grease Life

The first step in developing a grease life model is establishing a point at which grease is considered failed. Since grease is often selected for its consistency for a given application, some researchers [20, 21] have defined grease failure as the point at which grease is no longer within the same NLGI grade as intended. This means that once the consistency of grease has degraded to that of the grade below it, it can be considered failed. Using this information, one can simply determine the amount of entropy that must be generated in order to reach this failure state.

The steady-state characteristic line (from Figure 5) of a grease provides the ability to estimate the life of grease based on a change in the consistency. By defining failure as a drop in consistency by one NLGI grade
grade, one must first find the consistency of the lower NLGI grade by the same method that will be used to describe degradation. Rezasoltani and Khonsari used fixed-load compressive tests in a rheometer and found the penetration corresponding to a grade 1 grease. The characteristic line of a grade 2 grease was then used to find the amount of entropy generated corresponding to this amount of penetration, shown in Figure 8 [20]. Generating this amount of entropy through purely mechanical degradation should then consistently yield this failure state, so details about a particular shearing situation are required to find the time needed to generate this much entropy.

**Figure 8.** NLGI grade 2 grease penetration vs $S_g$ with failure criterion [20]

Equation (4) gives the entropy generated as a function of time for pure mechanical degradation and can be used in estimating grease life. Assuming the shear rate and temperature are constant throughout shearing, the only parameter that must be determined is the shear stress. Using the Maxwell model for estimating shear stress over time, the shear stress becomes a first-order differential equation [20]. All required information then becomes available for predicting the life of a grease. Though it will complicate the evaluation of (7), this model allows for changes in operating conditions, such as a change in rotational speed of a shaft. This concept is demonstrated by Rezasoltani and Khonsari [20], who apply this model to a grease sheared for 22 hours at one shear rate, then at another until its consistency drops by one NLGI grade. Calculations show good agreement with experimental data.

Alternatively, a method has been proposed [21] which monitors the entropy generation rate as a grease degrades. This method proposes that grease has failed once its entropy generation rate reaches the starting entropy generation rate of a grease one NLGI grade below it. If grease is sheared at a constant shear rate and temperature, the entropy generation rate is proportional to the shear stress. The relationship is demonstrated in Figure 9 [20, 21].
Figure 9. (a) Shear stress vs time [20] compared with (b) entropy generation rate vs time [21] at a fixed shear rate.

Figure 10 shows the decrease in entropy generation rate over time for an NLGI grade 1 grease. The dashed blue line represents the starting entropy generation rate of an NLGI grade 00 grease, and the grade 1 grease is considered failed once its entropy generation rate declines to this point. The calculation of the entropy generation rate was performed through the use of a torque meter, which recorded the instantaneous torque acting on the shaft. By comparing torque readings across time, one can monitor the changes to a grease’s rheological properties. This allows online monitoring of the grease’s state of degradation.

Figure 10. Entropy generation rate over an extended period of time [21]
Such an online monitoring method has the potential to drastically reduce machine failure since it can give details on the lubrication performance in real-time. This method can be applied to any industrial machinery for which it is practical to dedicate a torque sensor. Though only minimal testing has been performed and this should be viewed as a proof of concept, this method could provide another significant step forward in improving machine reliability. Further improvements in this technique should include additional information such as oil bleed, film thickness, and temperature. Though monitoring only the temperature of a bearing can be an effective way of determining that it is about to fail [54], this method does not give sufficient warning, meaning significant damage may occur before it can be taken out of service.

4.2 Future Directions

The application of irreversible thermodynamics has provided a path forward for the evolution of grease life models, but there remains research to be performed before the models can be confidently used in practice. The overall intent of these models is to describe grease performance so that machinery operates as efficiently as possible or for as long as possible. To this end, quantifying the failure conditions for each particular device should be further explored. For example, the proposal that grease is failed upon a consistency or viscosity reduction to a lower NLGI grade should be adjusted to more completely describe conditions leading to failure.

So far, the entropic model has been applied to pure mechanical degradation with success, but the testing environments used do not resemble field applications of grease. All research discussed has treated grease as homogeneous, without considering the intricate and chaotic nature [54] of grease flow within a field environment. Therefore, a complete model would likely have to be developed for each particular grease application, since the conditions can vary significantly. Such a model would account for the transient phases of grease flow, oil separation and leakage, and the corresponding changes to the effectiveness of lubrication.

In addition, there are clearly other mechanisms of degradation that lead to machinery failure and are not included in mechanical degradation. For some grease microstructures, mechanical degradation does not even have a significant effect on the overall changes to the structure [12]. For these greases especially, a model that includes other forms of degradation - particularly oxidation – is essential. A promising start to incorporating thermal effects (without oxidation) into mechanical degradation models has been introduced by Zhou et al. [36]. Additionally, Osara and Bryant [23] provide a DEG-based approach that incorporates thermal effects with high accuracy, and this proves a step forward in the development of a complete model. Further research can expand on this approach, adding further degradation mechanisms such as contamination and evaporation. Overall, any model developed must be validated with field testing in order to be used with confidence.

5. Conclusions

Entropy has proven to be an effective tool in developing models of degradation, and its application to grease shows promise for useful life prediction. This approach is the first to be based on thermodynamic degradation theory instead of empirical studies, meaning it is not restricted to a particular set of degradation conditions. Experimentation conducted so far shows that a basic model of pure mechanical degradation of any grease can be easily developed. For greases that show dramatic changes through mechanical degradation and are used in situations where mechanical degradation is dominant, such a basic model could be reasonable for estimating grease life. For many situations, however, mechanical
degradation is relatively insignificant and a model must include additional degradation mechanisms. In addition, the details of grease lubrication are complicated, and many simple models are inadequate to properly describe the changes to grease properties and grease flow that lead to failure.

Further research should be performed linking changing grease properties to machinery failure for a range of operating conditions, which will help establish more suitable failure criteria for grease degradation. This information can then be used with advancing thermodynamic grease models to give more meaningful life estimations. Additionally, all mechanisms of grease degradation must be considered, particularly oxidation, contamination, and oil leakage. Most importantly, any model developed must be thoroughly field-tested to ensure it can be reasonably applied to real situations. Overall, the concept of entropy has proven to be a promising tool in modeling grease degradation, and these thermodynamic models have enormous potential to allow grease-lubricated machinery to last significantly longer.

Acknowledgments

This review paper is a part of a research initiative conducted at LSU Center for Rotating Machinery and funded in part by NLGI (LSU #46895). The authors gratefully acknowledge this support.

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Procedure for evaluating the mechanical degradation of a grease

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Abstract

A thermodynamically-based approach is proposed for evaluating the degradation of the grease, which requires a meager amount of grease for testing. To test the validity of the approach, a prototype device is developed, tested, and the results of a series of experiments are reported for an NLGI grade 1 grease. The capability of the device in characterizing the real-time degradation of grease is explored. Based on the results, a procedure for determining the degradation rate of grease is proposed.

Keywords: Power; grease degradation; first law of thermodynamics; mechanical degradation

1. Introduction

In contrast to lubricating oils, grease is expected to possess good sealing property [1], minimum maintenance, tolerate contamination [2], and function without requiring recirculating arrangements [3]. Due to these beneficial properties, grease is employed in bearings [4-5], gears [6-7], slideways [8], and the like. However, given that the rheological properties of the grease tend to degrade with time, determining the rate of degradation has prodigious importance to the industry for scheduling re-lubricating intervals in order to avoid loss of efficiency and even component failure.

The cause of grease degradation can be chemical, physical, or both [9, 10]. The present work focuses on proposing a methodology for determining the degradation due to mechanical shearing, which is classified as a physical degradation. One measure of mechanical degradation is by means of a penetrometer, where a cone assembly is released and allowed to drop freely into the prolonged worked/degraded grease for 5 ± 0.1 s. Based on the penetration depth value, the grease is designated with an NLGI grade between 000 to 6, representing grease from the lowest to highest viscosity. However, this method generally requires a fairly large mass of grease samples (e.g., 1
lb) to be collected periodically from a component for testing. This is a time-consuming process and not easily applicable for real-time monitoring since the operation of the machine has to be halted during the sample extractions. Further, the applied shearing rate conditions are typically fixed, making it difficult to induce different degradation rates for empirical studies [11 - 12].

Recently, a number of researchers [13-20] have employed the thermodynamic approach for assessing the real-time degradation of tribo-pairs in terms of wear. Relevant to grease, Rezasoltani and Khonsari [12, 21, 22] came up with a method for monitoring the evolution of degradation by employing a parallel plate rheometer, which requires a small amount of grease with the flexibility of being able to modify the working conditions. From the obtained results, they established a correlation between the mechanical degradation of the grease and the entropy generation density through the application of irreversible thermodynamic laws. Recently, Lijesh and Khonsari [23] extended this methodology for evaluating grease performance by continuously measuring the degradation of the grease in a ball bearing setup, through frictional torque and angular velocity values. From the obtained results, they established a criterion for assessing the mechanical degradation of a grease by monitoring the time of entropy generation rate of a higher grade grease (e.g., Grade 1) to reach entropy generation rate of a lower grade grease (e.g., Grade 00).

Nevertheless, implementing this method requires a precision torques sensor, an appropriate data acquisition system and a voltage measuring analog system with the necessary software. These requirements limit its full-fledged implementation in the industry. In this paper, we report the design of a prototype of a device called Grease Degradation Monitoring Unit (GDMU) capable of assessing the mechanical degradation of grease through the laws of thermodynamics and offers good potential in industrial application.

The outline of this paper is as follows. In Section 2, we present the description of the experimental set up followed by the background of the theoretical modeling approach. Results and detailed discussion on the obtained results are provided in Section 3. The application of the proposed methodology is demonstrated in Section 4. Conclusions are presented in Section 5.

2. Methodology
It is hypothesized that reduction in the rheological properties of the grease, during its shearing with time, can be correlated to the power extracted by the motor. To validate the hypothesis, a test setup to shear the grease at the desired shear rate is developed and a series of experiments for different rotational speeds are performed for NLGI grade 1 grease. During the shearing of grease, the power consumed by the motor is continuously monitored using the GDMU. Description of the experimental setup followed by the procedure used to acquire the current from the setup using GDMU is presented in the following section. The appropriate equations used for the calculation of power from the recorded current are also provided.

2.1 Experimental Setup

In the present work, an NLGI grade 1, a lithium-complex based greases is utilized to demonstrate the efficacy of GDMU. The property of the considered grease is provided in Table 1. A custom-built setup is developed to shear the grease at the desired rotational speeds by employing a small amount of grease.

Table 1 Properties of different grades

<table>
<thead>
<tr>
<th>Grease</th>
<th>NLGI Grade</th>
<th>Appearance, color</th>
<th>Thickener</th>
<th>Viscosity @ 40°C (m²/s) × 10⁻⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>XHP 221</td>
<td>1</td>
<td>Soft, Blue</td>
<td>Li-Complex</td>
<td>220</td>
</tr>
</tbody>
</table>

The schematic representation and the developed setup are shown in Fig. 1. In this setup, the grease sample is sheared between the rotating and stationary parts. The rotating part has a top and bottom half with the top half connected to the motor while the bottom half facilitates the shearing of grease with respect to the stationary surface. The gap between the bottom surface of the stationary and the rotating part is 1.5 mm. The diameter of the stationary surface is 50 mm. Therefore, the volume of the grease employed in the present work is 2.944 × 10⁻⁶ m³. The desired motor speed is set and maintained by using a controller. The setup is connected to a computer using the RS-232 connection and the speed of the motor is controlled by inputting the data in the computer. The schematic representation of the connection of the grease shearing setup to GDMU is provided in Fig. 2. The power supply of the setup is connected to the current sensor and the sensor is in turn connected to a data acquisition setup (DAQ). The acquired data is transferred to a laptop/smartphone using a wifi sensor. The 5 V supply to the sensors is provided using a battery.
2.2 Mathematical modeling
The schematic representation of the setup and the control volume is provided in Fig. 3. The grease is placed between the stationary and rotating surfaces and is sheared by rotating the cylinder at an angular speed of $\omega$ for shear rate $\dot{\gamma}$. It provides work $W$ on the grease due to the friction and the heat is conducted into the contact surfaces in a closed system environment as there is no transfer of matter across the boundary of the control volume. Now, for a closed local thermodynamic equilibrium (LTE) system, the entropy generation rate per unit volume $\dot{S}_{g,vol}$ can be determined by Eq. (1) assuming that the grease is experiencing only mechanical degradation without appreciable temperature rise. The detailed derivation is provided in reference [23].

$$\dot{S}_{g,vol} = \frac{\tau \cdot \dot{\gamma}}{T}$$

(1)

where $\tau$ is the shear stress, $\dot{\gamma}$ is the shear rate and $T$ is the operating temperature. For the considered setup and operating conditions, the temperature and volume can be considered constant. By representing the product of the volume of grease $vol$ and temperature as constant $\alpha$, Eq. (1) yields:

$$\dot{S}_{g,vol} = \alpha \cdot \tau \cdot \dot{\gamma} \cdot vol$$

(2)

Note that $\tau \cdot \dot{\gamma} \cdot vol$ has the units of Watt and represents power $P$. Based on this description, Eq. (2) can be written as:

$$\dot{S}_{g,vol} = \alpha \cdot P$$

(3)

From Eq. (3) it can be concluded that for a constant volume of grease and temperature, the entropy generation rate per unit volume can be suitably correlated to the power consumed.

Power can also be determined by measuring the current and voltage of the system. In the developed setup, the power extracted to shear the grease at the desired speed is the sum of the power required to rotate the motor and the shear resistance offered by the grease. Therefore, the power consumed by the setup for only shearing of the grease is determined by calculating the difference between
the power consumed by the setup with and without the grease. For this purpose, the system is run initially without grease at the desired rotating speed and the power consumed is monitored. Next, the system is operated with the grease sample at the same rotating speed and power consumed is recorded. From the recorded power values, the power required to shear the grease is determined by calculating the difference.

The developed setup employs an alternating current (AC) motor for shearing the grease and the power $P$ of the variable speed AC motor during the shearing operation is determined using Eq. (4)

$$P = V \cdot (I_t - I_0) \cdot \cos \phi$$

(4)

where $I_t$ is the instantaneous value of the acquired current, $V$ is the voltage which is considered as a constant value of $\sim 120$ V, and $\phi$ represents the phase angle between the voltage and current. $I_0$ is the current consumed by the setup without grease and is determined by operating the rig without grease. The phase angle $\phi$ can be determined by measuring the angle between the resistance $R$ and impedance $Z$ of the motor, as given in Eq. (5):

$$\phi = \cos^{-1} \left( \frac{R}{Z} \right)$$

(5)

The resistance of the motor is determined by measuring the resistance of the winding using digital multi-meter and impedance is calculated from the ratio of voltage and current consumed by the motor at their respective operating condition.

3. Results and discussion

Experiments were performed for the NLGI grade 1 grease at three rotational speeds: 100 rpm, 250 rpm, and 500 rpm. The current values of current obtained for all the three rotational speeds for 3000 s are plotted in Figs 4 and 5. The current drawn when running without grease is 0.165 A and its value increases linearly with the rotational speed. For this setup, the following curve-fit relationship can be used to determine the current requirement for this set up without grease at different speeds.

$$I = 0.165 + 0.00012 \cdot rpm$$

(6)
To determine the current consumed during shearing, experiments are repeated by applying the grease to the bottom of the stationary part (see Fig. 6a) and the rotating bottom part (see Fig. 1). Initially, the experiments are performed at 100 rpm and the current values are recorded. The grease on the bottom of the stationary part after shearing at 100 rpm for an hour is shown in Fig. 6b. It clearly reveals that grease is uniformly sheared during the experiment. The measured current values during the shearing at 100 rpm are plotted in Fig. 7. Close examination of this figure shows that there are four regions: (i) Region I - current obtained by operating the system without grease, (ii) Region II- a non-uniform variation of the current that lasts only a short period of time, (iii) Region III - running-in region, and (iv) Region IV - steady-state region of current variations. The inset of the Region III is provided in the figure shows a magnified picture of the transient region.
The variation in the current values in the Region II may be due to the variation caused by the non-uniform spreading of grease and it lasts for \( \sim 40 \) s. Once the grease is uniformly distributed, Regions III and IV are observed. The running-in and steady-state regions during the shearing of grease have been observed elsewhere [23], and it is postulated the process is akin to that of wear of a tribo-pair during its running-in period, which involves transient and steady-state regimes [24, 25]. The transient behavior in a tribo-pair is due to the wear of the surface asperities during the breaking-in period as the surfaces are polished. Apart from the surface effects, it is noted that the grease itself exhibits a brief transient behavior initially before the process becomes steady.

(a) Before shearing
(b) After shearing

Fig. 6 Before and after shearing of grease at 100 rpm

Fig. 7 Different regions for Grade 1 grease at 100 rpm

The continuous degradation of grease with time (Fig. 7) is due to the alignment of chains in the direction of shearing and breakage of the thickener chains in the carrier oil, as schematically shown.
in Fig. 8. With the breakage of the thickener’s chains, the grease becomes less viscous but the viscosity still remains higher than that of the carrier oil [26, 27]. The reduction in the viscosity of the grease with time results in imparting lower shear stress on the rotating surface, thereby reducing the current drawn by the motor.

![Fig. 8 Breakage of the thickener chains of grease with time](image)

Referring again to Fig. 7, it can be observed that the value of the current in the steady-state region ($I$) is greater than that obtained from the setup without grease ($I_0$) (see Fig. 4). The difference in the current values represents the current required to shear the grease.

![Fig. 9 Current recorded for Grade 1 grease at different speeds](image)

Insofar as degradation is concerned the short period associated with the running-in is less important if one is interested in the long-term operation of a component. Therefore, in the following studies, the steady-state current values will be considered for determining the degradation of grease. The change in the current when operating at 100 rpm, 250 rpm, and 500 rpm is provided in Fig. 9. Now, comparing this figure and Fig. 4, it can be observed that the current values acquired from
the setup with the presence of grease are more than the values of the current recorded without grease.

Using the recorded current values, the consumed power is calculated for different rotational speeds using Eq. (4) and plotted in Fig. 10.

4. Proposed procedure

From the results presented in Section 3, the values of current are continuously reducing with time. Therefore, it is difficult to predict the useful life of the grease in practice. Rezasoltani and Khonsari [15] have proposed a deterministic method to quantitatively characterize the degradation of grease in terms of entropy generation. They postulated that grease may need to be replaced if its NLGI’s grade drops to a lower value. The severity of the reduction in grade should be judged by the practitioner’s experience and the application. Following the same logic, in the present work, the values of the current drawn by the motor are employed to determine the degradation of the grease. For this purpose, the following steps are taken:

Step 1: Experiments are performed for a higher NLGI grade grease at a desired rotational speed and their real-time current values are recorded.

Step 2: The experiment is repeated for a lower NLGI grade grease and their starting current value is recorded and considered as the threshold value.

Step 3: Using the curve fit method, the variation in the current values is extrapolated to determine the time to reach the initial current value of lower grade grease.

To demonstrate the efficacy of the proposed methodology, NLGI grade 1 grease is considered to be the appropriate grade grease for the machine to run efficiently and it is assumed that if the
prolonged degradation by shearing causes it to drop to NLGI grade 00, then it has to be replaced. For Step 1, the current value with time for NLGI grade 1 at 100 rpm, plotted in Fig. 7 is considered. For Step 2, the experiment is repeated for a lower grade grease i.e. NLGI grade 00 at 100 rpm and the current values are recorded and plotted in Fig. 11. From this figure, it can be observed that the current values are almost constant and is determined to be 0.172 A.

Referring to Fig. 7, the variation of the current values with time follows the power curve fit equation provided in Eq. (7).

\[ I = At^B + C \]  

(7)

Using the regression method, the coefficients \( A \), \( B \), and \( C \), depicting the variation of current with time for NLGI grade 1 is determined to be 0.3, -0.014 and 0.0932, respectively. The current values obtained from the curve fit equation is plotted in Fig. 11. Now, Eq. (7) is extrapolated by incrementing the value of time \( t \) and the value of \( t \) for which the value of \( I = 0.172 \) A is determined to be \( t \approx 10^7 \) s (approximately 4 months of continuous operation).

5. Conclusions

This work endeavors to provide a deterministic procedure for determining the degradation of grease using a small sample of grease and employing analogy between thermodynamic principle and electrical system. Through mathematical derivation, it was established that for a constant temperature and volume of grease, the entropy generation rate is proportional to the power generated by the system. Further, it is hypothesized that the power generated in the system can be
determined by measuring the current and voltage drawn by the driving motor of the system. To validate the hypothesis, a prototype device is built and employed for characterizing the degradation of grease with time. Experiments were performed for NLGI grade 1 for different rotational speeds. From the obtained results it was observed that the power drawn by the motor can effectively characterize the degradation of grease at different rotational speeds. Finally, a simple procedure for determining the degradation rate of grease is proposed. Further research is needed to fully investigate the effectiveness of the developed prototype and proposed procedure in the field.

Acknowledgments
This research is in part supported by NLGI. The authors also acknowledge the support of LIFT Program at LSU for the development of a sensor for evaluation of material degradation.

References


On the assessment of mechanical degradation of grease using entropy generation rate

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Abstract:

A methodology for continuous monitoring of grease degradation subjected to mechanical shearing is proposed. It is hypothesized that the mechanical degradation of grease is akin to the running-in process in a tribo-pair with both transient and steady-state regimes. To validate the hypothesis, a series of mechanical shearing tests are performed on three grades of grease: NLGI 00, NLGI 1, and NLGI 2.5 by employing a rheometer. From the results, a more effective method using the entropy generation rate is proposed for continuous monitoring of grease degradation. The proposed method is extended to estimate the time for a grease subjected to mechanical shearing to degrade to a lower grade. The efficacy of this method is demonstrated via long duration testing in a custom-built ball bearing test apparatus.

Keywords: Entropy generation rate; transient regime; steady state regime; grease degradation

2.Introduction

Grease is a semi-solid material made of a thickening agent of (3 % to 30 %) suspended in a base oil (70 % to 90 %) with remaining percentage of suitable additives [1]. Other ingredients with special properties can also be included to improve performance [2]. Compared to lubricating oils, a grease possesses high viscosity and good sealing property [3], demands less frequent maintenance, does not require auxiliary supply arrangements and/or recirculation [4-6], and can even tolerate operating in a contaminated environment [7]. Usefulness of the greases has been realized in a wide range of industrial elements such as many types of rolling element bearings, pin bushings and journal bearings [7-17], gears [18-20], slideways [22-23], and the like. Nevertheless,
Grease has a finite working life that is directly influenced by the rate at which it physically and/or chemically degrades. Therefore, determining the life of the grease has prodigious importance to the users and operators in order to appropriately schedule the re-lubricating intervals and avoid catastrophic component failure.

Grease degradation induction mechanism(s) can be chemical, physical or both [24,25]. There are several analytical methods available to evaluate the chemical degradation including Fourier-transform infrared spectroscopy, worked penetration method, differential scanning calorimeter, acid number, IR spectra, linear sweep voltammetry, and by means of measuring extracted base oil viscosity at 40 °C from the grease [24].

The worked penetration method is widely accepted and practiced in the industry for evaluating the degradation of grease having National Lubricating Grease Institute (NLGI) number between 000 and 6 at 25 ± 0.5 °C [26, 27]. In this method, a cone assembly of the penetrometer is released and allowed to drop freely into the worked or the prolonged worked grease for 5 ± 0.1 s. The worked grease is either sheared by rolling in a roll-shear stability tester (ASTM standard D-1831) [24] or in double-stroke shearing in a grease worker (ASTM standard D 217 – 0) [27]. In the latter case, after performing a prolonged shearing test, the grease is sheared for 60 s at 25 ± 0.5 °C, before performing the penetration test. This method requires grease samples of at least 0.4 kg (1 lb). The requirement of a large quantity of grease for testing restricts its applicability for real-time monitoring, particularly when one is interested in tracking the evolution of degradation. Further, in these methods, the applied shearing rate conditions are fixed, making it difficult to induce different degradation rates for empirical studies [27-29].

Recently, Rezasoltani and Khonsari [28] came up with a method for monitoring the evolution of degradation by employing a parallel plate rheometer, which requires a minimal amount of grease with the flexibility of being able to modify the working conditions. In this method, the worked grease of 1.5 mm thickness is placed between the stationary and moving plate (circular cross-section of 25 mm diameter) and squeezed under a desired applied load for 60 s. After 60 s the displacement of the moving part is recorded. From the obtained results, they established a correlation between the mechanical degradation of the grease and the entropy generation density through the irreversible thermodynamic theory. They observed a linear relationship between mechanical degradation and entropy generation. Recently, Zhou et al. [29] extended their studies and concluded that there exist two phases of degradation (i) initial phase
higher degradation rate and (ii) second phase with slower degradation rate. Therefore, the first objective of the present work is to provide further insight to the mechanical degradation by performing experiments on different grades of grease and identify the reason for the existence of two slopes reported by Zhou et al. [29].

Here, we hypothesize that the degradation behavior of grease is akin to the material removal process observed during wear i.e. a transient wear rate followed by a steady state wear rate. We test the validity of this hypothesis by performing two types of experiments with three types of greases of grades NLGI 00, NLGI 1, and NLGI 2.5. Experiments are conducted using a rheometer to measure their dynamic rotational and penetration during the course of the tests. In dynamic rotational experiments, the vane of rheometer is rotated at a desired shear rate with no external load, and in the case penetration experiments the procedure proposed by Rezasoltani and Khonsari [28, 30] is followed. However, this method is dependent on the experimental conditions such as applied load during the test, the quantity of grease, the duration of the applied load, etc. Therefore, an alternative approach for evaluating the degradation of grease is desirable. Khun [31, 32] applied the laws of thermodynamics to correlate grease degradation in terms of the number of thickener chains and entropy generation. This is a promising approach but a quantitative analysis of the number of chains in a particular grease may be a difficult task. Further, all of these methods require periodically collecting grease samples for evaluation. In practical applications, this necessitates stopping the machine for extracting samples, resulting in downtime.

In the present research, an attempt is made to develop a methodology to evaluate the performance of the grease by continuously measuring the entropy generation rate from the values of friction torque and angular velocity. The application of the proposed method for continuously monitoring of degradation by defining the time for the entropy generation rate of a higher grade grease to reach the lower grade grease —as a criterion for assessing grease degradation— is presented. The efficacy of the proposed methodology is demonstrated by conducting a series of experiments in a custom-built ball bearing testing apparatus.

2. Experimental Setup

In the present work, three different NLGI grades of lithium-complex based greases shown in Table 1 are considered for the comparison and to test the proposed hypothesis. Further, to illustrate the proposed theory in the real-time application of the degradation criterion, experiments
are performed on a ball bearing setup. Details of the rheometer and ball bearing setup are elaborated in the following subsections.

### Table 1 Properties of different grades

<table>
<thead>
<tr>
<th>Grease</th>
<th>NLGI Grade</th>
<th>Appearance, color</th>
<th>Thickener</th>
<th>Viscosity @ 40°C (m²/s) ( \times 10^{-6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>XHP 222</td>
<td>2.5</td>
<td>Applesauce, Blue</td>
<td>Li-Complex</td>
<td>220</td>
</tr>
<tr>
<td>XHP 221</td>
<td>1</td>
<td>Soft, Blue</td>
<td>Li-Complex</td>
<td>220</td>
</tr>
<tr>
<td>XHP 005</td>
<td>00</td>
<td>Normal grease, Blue</td>
<td>Li-Complex</td>
<td>220</td>
</tr>
</tbody>
</table>

### 2.1 Rheometer

Shearing and penetration tests on different grades of grease are performed using the Anton Paar MCR 301 rheometer (see Fig. 1). This rheometer is equipped with a rotating vane ~25 mm in diameter connected to the driving motor using a coupling. Air is supplied to the bearing using an air compressor, and a controller adjusts the movement of the rotary motor in the vertical direction. The specifications of the rheometer are as follows: torque 0.1 mN•m –200 mN•m with resolution of 0.001 µN•m and accuracy of 0.2 µN•m; applied load of range 0.005 N to 50 N with resolution of 0.002 N, accuracy ± 0.03 N; rotational speed of \( 10^{-6} \) rpm –3000 rpm; and operating temperature can be controlled in the range of -40 °C up to 200 °C with an error of ± 0.1 °C. However, in this study, the temperature is maintained at ~ 25 °C.

Following the work of Rezasoltani and Khonsari [28], shear and penetration tests were performed. The shear test involves longer durations whereby the grease sample is placed in the gap between the rheometer vane and the stationary surface and the sample is sheared for a long period of time at the room temperature. The gap thickness is maintained constant throughout the experiment for 1.5 mm with zero penetration. During the experiments, the values of rheological parameters such as shear rate, shear stress, torque as a function of time are measured and recorded. The entropy generation density is then calculated from the shear stress values at the given rate; see Section 3. The selection of shear rate is based on the grades of the grease since a higher grade grease requires a higher shear rate while a lower shear rate for a lower grade grease. The applied shear rates for different grades of grease are provided in Table 2.
### Table 1: Sample Grades

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Grade 2.5</th>
<th>Grade 1</th>
<th>Grade 00</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>900</td>
<td>300</td>
<td>100</td>
</tr>
</tbody>
</table>

![Rheometer diagram](image1)

**Fig. 1 Rheometer**

![Penetration gap graph](image2)

**Fig. 2 Penetration gap with time**
Immediately after the completion of the shearing experiment, a penetration test is performed using the rheometer at the same temperature. In the penetration experiments, the grease sample is squeezed between the plates of the rheometer with a normal force of 2 N for 60 s. The displacement of the plate with time for one of the greases is plotted in Fig. 2. From this figure, it can be observed that during the first 20 s, the value of the penetration gap gradually drops in a linear fashion until it becomes saturated and levels off. Therefore, in the present work, the penetration value is determined for 20 s instead of 60 s. The net penetration of the grease is then determined by calculating the difference of the initial (1.5 mm) and final position of the plate. In all the penetration tests, the temperature is kept ~ 25 °C.

2.2 Ball bearing apparatus

A custom-built ball bearing apparatus designed in-house is utilized to analyze the degradation of the grease in a real-time application. The experiments are performed for 50 hrs and the performance of the grease is evaluated by measuring the torque as well as acceleration. The setup consists of a 5 hp AC motor, two couplings, a torque sensor, an accelerometer, two ball bearings, a shaft, data acquisition system and a disk. A disk is attached at the end of the shaft to provide eccentric loading on the bearing.

![Fig. 3 Setup to analyze the grease performance](image)

An ICP Accelerometer of measuring range ± 50 g, frequency range 0.5 Hz - 10 kHz and sensitivity 100 mV/g is used to evaluate the performance of the bearing by measuring its vibration. The accelerometer is placed on the casing of the ball bearing and the measured values are saved
onto the computer using NI 9234 and NI USB 9162 data acquisition system manufactured by National Instruments. A contactless torque sensor of 15 N•m capacity is attached between the rotating and motor shafts using the aluminum jaw couplings to measure the torque between the motor and bearings. It will be shown that the torque sensor is capable of providing the details of the deterioration in the grease viscosity; see Section 3.1. The torque sensor requires the input of 12 VDC to 28 VDC supply and provides output in the range of ± 5 VDC. The value of torque from the torque sensor is acquired using 16-Bit NI USB-6210 multifunction data acquisition system.

3. Results and Discussion

The first set of experiments involve testing Grade 2.5 grease for the shear rate and test duration provided in Table 2. The obtained penetration depth for different shear rate is plotted in Fig 4a. The penetration depth with respect to entropy generation density is plotted in Fig. 4b. The entropy generation density \( S_{g,vol} \) is calculated using Eq. (1); see Appendix A for details.

\[
S_{g,vol} = \int_0^t \frac{\tau \dot{\gamma} dt}{T} \quad (1)
\]

where \( \dot{\gamma} \) is the shear rate, \( \tau \) is the shear stress, \( T \) is the temperature, and \( t \) is time of operation. From Fig. 4b, two slopes of penetration depth with entropy generation density is observed, which agree with the observations of Zhou et al. [29].

A similar methodology is followed for Grades 1 and 00, and their obtained values of penetration depth with entropy generation density are plotted in Figs. 5a and b, respectively. From these figures the existence of two slopes can be observed.
Fig. 4 Penetration depth at different time and entropy generation density for Grade 2.5

(a) Grade 1

(b) Grade 00

Fig. 5 Penetration depth with entropy generation density for Grades 1 and 00

We now proceed to investigate the physical mechanism of different rates observed in the Figs. 4b and 5. For this purpose, the penetration data with time are analyzed by developing a curve-fit equation to the penetration data points for each shear rate and grades.

The variation of the penetration depth with time is akin to that of wear of a tribo-pair during its running-in period that involved a transient and steady-state regimes [33-35], as shown in Eq. (2).

\[ d_v = A_1 e^{\frac{-Bt}{C}} + C t \]  

\[ (2) \]

In this equation the first term on the RHS, \( A_1 e^{\frac{-Bt}{C}} \), represents the transient wear behavior and second term, \( C t \), represents the steady wear. Note that the steady state wear rate \( \dot{w}_v = C \) is a constant, independent of time. Here, \( A \) and \( C \) are constants to be determined from experimental results. They are depended on the shear rate and grade of the grease. Considering the curve fit equation of wear volume \( w_v \) Eq. (2), the proposed equation for penetration depth \( \delta \) is expressed in Eq. (3). Unlike wear volume of a tribo-pair, there exists a penetration depth value at \( t = 0 \), which represents the penetration depth of a fresh grease. To characterize the statement, a third factor \( D \) is introduced in Eq. (2) and represented as.

\[ \delta = A(1 - \exp(-Bt)) + C t + D \]  

\[ (3) \]

The obtained penetration depth values with time for different shear rate and for three grades of lithium greases are plotted in Fig. 6. These figures also show the curve fit values using Eq. (3).
From Fig. 6 it can be observed that equation Eq. (3) is capable of appropriately characterizing the variation of penetration depth with time. This figure also clearly indicates that the process involves two regions: transient followed by linear regions.

![Graphs showing penetration depth and curve fit values for different grade greases](image)

(a) Grade 2.5  
(b) Grade 1  
(c) Grade 00

Fig. 6 Penetration depth and curve fit values for different grade grease

The obtained penetration rates with time for all tested greases are plotted in Fig. 7. From these figures, it can be observed that the time to reach steady-state for a grease operating at a high shear rate is greater than that of a grease subjected to a lower shear rate. Thus, if an experiment is operating at a low shear rate, its transient regime would be short, and it reaches steady-state quickly. However, if the experiment is performed at a very low shear rate, the existence of the first slope will be diminutive. This finding provides an explanation for the results presented by the Rezasoltani and Khonsari [28] as well as those by Zhou et al. [29]. Zhou et al. [29] considered the
duration of an experiment by including both transient and steady state, while Rezasoltani and Khonsari [28] focused on the steady-state regime and, therefore, their operating time was longer than the running-in transient time. So, Rezasoltani and Khonsari [28] reported a single degradation rate that corresponds to the steady-state operation. Further, in Section 4 it will be demonstrated that the existence of two regimes is not restricted to the rheometer but also exists in real time applications like a ball bearing lubricated with grease. In addition, it will be shown that the steady state regime plays a more important role in evaluating grease degradation than the transient regime. In summary, it can be concluded that the first slope observed by Zhou et al. [29] is similar to the running-in phase of the grease, and the second slope pertains to the actual working life of grease with a long duration.

![Diagram](image_url)

Fig. 7 Penetration depth rate for different grade grease

(a) Grade 2.5  
(b) Grade 1  
(c) Grade 00
3.1 Entropy generation rate

Penetration measurement is an indirect method for measuring the degradation of grease. It depends on the applied load during the test, quantity of grease, time of application of load, etc. In practical applications stopping the machine and taking the samples for testing would result in a reduction of production time and cost. Further, the location at which the degraded grease samples are collected can impact the results. Therefore, an online measuring method to evaluate grease degradation is highly desirable. Here, instead of evaluating the grease performance using the penetration rate, an attempt is made to evaluate the grease degradation by measuring the entropy generation rate. The entropy generation can also be determined from the product of frictional torque and angular velocity as a function of time $t$; see Eq. (4) [28].

$$S_{g,t} = \frac{\int_0^t T_{or,t}(\omega)}{T} \, dt$$

(4)

Note that the angular velocity $\omega$ is constant but the frictional torque changes with time, and it is represented as $T_{or,t}$. The instantaneous value of torque is directly obtained from the rheometer. For a field application, a torque sensor would be needed for this purpose. The obtained entropy generation rate for Grades 00, 1 and 2.5 greases are plotted Fig. 8a-c, respectively.
4.2 Entropy generation is grease worker

Now, employing this procedure, an endeavor is made to provide an explanation for the procedure commonly adopted industry practice where a grease worker is used to work the grease for 60 s at the shear rate of 1 1/s, before usage. Experiments were performed using the rheometer at 1 1/s shear rate for 10 minutes. The value of entropy generation is calculated from the torque, shear rate and assuming $T = 300$ K. The obtained entropy generations with time for Grades 00, 1 and 2.5 are plotted in Fig. 9. From the obtained data, the entropy generation rate is determined for different grades of grease and plotted in Fig. 10. Examination of the results reveals that irrespective of the grease grades, the rate of entropy generation is reaching the steady state at $t \approx 60$ s.
Next, to further validate the results, experiments were performed on the grease worker with the Grade 1 grease at a shear rate of 1 l/s. The experiment was performed, and the torque values were measured in the rheometer for 30 s, 60 s, 120 s, and 240 s. The obtained values are plotted in Fig. 11. From this figure, it can be observed that the second slope reveals itself at ~ 60 s. This provides an explanation for the reason that a practitioner typically works the grease for 60 s in the grease worker machine before performing penetration tests.

4.3 Continuous assessment of grease aging

We now proceed to develop a method for continuous assessment the aging of grease by a similar criterion defined in ref. [30]. The objective is to predict when the performance of grease may be considered unacceptable for a given application. The methodology involves determining the length of time for the entropy generation rate of a higher-grade grease to drop to a lower grade grease level, at a given shear rate. For example, the time for entropy generation rate values of Grade 1 grease to reach the Grade 00 or entropy generation rate values of Grade 2 to reach the
Grade 1 (or Grade 00) can be considered as an effective end of useful life. For this purpose, curve fit Eq. (5) is employed.

\[ \dot{S}_g = At^B + C \quad (5) \]

The entropy generation rate of Grades 1 and 00 at the shear rate 100 1/s, is plotted in Fig. 12a. The value of coefficients \( A, B \) and \( C \) for Grade 1 is determined to be \( A = 2.87 \times 10^{-3}, B = -0.085 \) and \( C = -3.9 \times 10^{-4} \). Substituting these coefficients into Eq. (5), the time, \( t \), required for Grade 1 to reach the starting entropy generation rate of Grade 00 \( \sim 2.77 \times 10^{-4} \text{ J/K} \) is \( t \approx 3 \times 10^7 \text{ s} \).

The extended graph showing the merging of the entropy generation rate for Grades 00 and 1 greases are plotted in Fig. 12b. From this figure, it can be observed that the time to reach for the entropy generation of Grade 1 to reach Grade 00 is \( t \approx 4 \times 10^7 \text{ s} \).

Similarly, the time for Grade 2.5 to reach the starting entropy generation of Grade 1 can be determined from Fig. 13. Referring to Fig. 13, the starting entropy generation rate is \( \sim 6 \times 10^{-3} \text{ J/K/s} \) shown as a dotted line. It is observed that the rate of degradation of Grade 2.5 is so low that under the operating conditions tested, entropy generation rate does not induce enough mechanical degradation for the grease consistency to reach to that of Grade 1; however, although it was not tested, the grease may degrade to Grade 2.

![Fig. 12 Comparison of entropy generation rate for Grades 00 and 1](image)
4. Application

The usefulness of the proposed methodology for determining using the entropy generation rate is now demonstrated in a grease-lubricated ball bearing (a real-time application); see Fig. 3. For this purpose, the following sets of experiments were performed: Case 1- without grease and Case 2 with grease. In Case 1, the setup is operated initially without grease at 1500 rpm (25 Hz) and the readings from the torque and accelerometer sensors were recorded. In Case 2, the ball bearing 2 is filled with grease and experiment is repeated for 50 hrs. Initially, the experiments were performed on Grade 1 grease. The recorded values of torque for Cases 1 and 2 are plotted in Figs. 15a and b, respectively. In Case 1 (Fig. 14a), it can be observed that after a few seconds of running the value of torque became steady when the torque reached 0.43 N.m. For Case 2, the transient region was observed until 4.5 hours, considerably longer than the Case 1. As observed in the rheometer testing, the variation of the variation of entropy generation values (which is a function of torque, rotational speed and temperature) is the same as the variation in the torque values observed in the ball bearing setup. Therefore, it can now be concluded that torque value provides a good indication of the degradation of the grease in the real-time applications. However, it is also necessary to check that the performance of the ball bearing is not deteriorated with the time. For this purpose, the vibration of the ball bearing is determined using the accelerometer.

![Fig. 13 Entropy generation rate for Grades 2.5](image-url)
Fig. 14 Torque value acquired from torque sensor for Cases 1 and 2

Fig. 15 Acceleration value acquired from accelerometer for Cases 1 and 2

Fig. 16 Acceleration value acquired from accelerometer for Case 2 at different interval of time

The accelerometer recording for Case 1 is plotted in Fig. 15a. For Case 2, the first data was recorded after 1.5 hours followed by recording after 9 hr, 15 hr, and 50 hr for 300 s. The initial 1.5
hr data is plotted in Fig. 15b and the remaining cases are plotted in Fig. 16. Comparing Figs 15a and b, it can be observed that the magnitude of acceleration for Case 1 is more than Case 2. In other words, with the addition of grease the vibration is reduced. Further, the magnitude of acceleration is almost constant with time.

Now, to obtain meaningful conclusions from the acceleration data, fast Fourier transform (FFT) is performed on the acceleration data. The determined FFT values for Case 1 are plotted in Fig. 17a and from this figure it can be observed that the second peak (25 Hz) represents the operating frequency and other peaks represent the harmonics of the operating frequency. For evaluating the bearing performance, the magnitude of FFT of the first peak is considered and for Case 1 it is determined to be 0.0091. Similarly, the FFT obtained for initial data until 600 s for Case 2 (shown in Fig. 15b) is plotted in Fig. 17b. The magnitude of the first peak of FFT for the considered data is determined to be 0.0054 and it is worth observing that the value reduces compared to Case 1. In a similar fashion, the magnitudes of the FFT for the other cases are determined and they are plotted in Fig. 17 is determined and their values are consolidated and shown along with curve fit equation in Fig. 18. From this figure, it can be observed that the magnitude of the FFT is also providing the two regimes with transient regime followed by steady-state regime.

Fig. 17 Acceleration value acquired from accelerometer for Cases 1 and 2
To determine the time for the degradation of grease grade 1 to reach grade 00, the ball bearing was cleaned and filled with grade grease 00. The experiment was performed, and the starting torque value was determined to be ~0.23 N•m and magnitude of FFT was determined to 0.00585. Now, the time for the torque of the grease grade 1 to reach 0.274 N•m is determined by extending their curve fit equation and it is determined to be ~2 × 10^8 s. Similarly, time for the FFT value to reach 0.00585 is \( t = 2.1 \times 10^8 \) s. It is worth observing that both the torque and acceleration methods are providing almost the same time for the grease to degrade from Grade 1 to Grade 00.

5. Conclusions

In the present work, a methodology to determine the life of grease experiencing mechanical degradation is proposed. For this purpose, initially, a relationship between the entropy generation density and penetration depth for three types of grease NLGI grades: NLGI 00, NLGI 1, and NLGI 2.5 was studied on a rheometer. Two degradation regimes were observed in which the degradation. The first region had a faster rate than the second region and this observation was the same as the results in the published literatures. To gain further insight, the results were extended by studying the penetration rate with time, which comprised of the initial transient running-in region followed by steady state akin to the running-in process associated with wear rate. Further, it was concluded that for a lower shear rate experiment the steady state was attained faster when compared to higher shear rate. Since the penetration rate method is dependent on the operating conditions, the entropy generation rate was employed to measure of the degradation rate of grease. Using this entropy
generation rate, the time for the degradation rate of a higher grade grease to drop to a lower grade was established and an explanation for the practice of working the grease for 60 s in the double stroke grease worker is provided. This concept was extended for a ball bearing setup in which the efficacy of the proposed method is demonstrated by determining the time for entropy generation rate of grease of grade 1 to reach the entropy generation rate of grade 00. Finally, it is established that the time for the degradation of grease from grade 1 to 00 determined using the proposed method and using the magnitude of FFT obtained from acceleration data provided almost the same value.

Acknowledgements
This research was conducted at LSU Center for Rotating Machinery and funded in part by NLGI (LSU #46895). The authors gratefully acknowledge this support.

References
[34] Singh, T., Banerjee S. K., Ravi K. Grease composition for lubrication of journal bearings used in sugar mill, Greasetech India (2010): 23-26


Appendix A

Fig. A1 shows the schematic representation of the rheometer and the control volume considered for the present work. The grease is placed between the stationary surface and vane and is sheared by rotating the vane at an angular speed of \( \omega \) for shear rate \( \dot{\gamma} \). The rotating vane imparts work \( W \) on the grease due to the friction and the heat is conducted outside through the contact surfaces. The system considered is a closed system, where the transfer of matter is across the boundary of control volume does not prevail. Further, it is worth observing that during the initial stage of shearing of grease, the rheological properties are transient and after certain time reaches a steady state. It is erroneous to assume that the process is completely at steady state; however, thermodynamic state changes with time can be assumed to occur along a quasi-static isothermal process [33] or in other words they are at local thermodynamic equilibrium (LTE). A system is said to be in LTE if the thermodynamic state of a tribo-system at a given time is completely defined by properties of the system. The degradation of grease is one such process where the variation in the parameters is well defined. In this regard, Lijesh et al. [33] has established an equation Eq. (A1) for determining the entropy generation rate per unit volume \( \dot{s}_g \) for tribo-pair experiencing a transient as well as steady state wear and is given as:

\[
\dot{s}_g = \frac{\sigma \dot{\epsilon}_p - \dot{\epsilon}_{mt}}{\rho T} + k \frac{(grad T)^2}{T^2} - \dot{s}_{g_{mt}} - \sum_k \eta_k dN_k
\]  

(A1)

where \( \sigma \) is the stress developed by the shearing process, \( \dot{\epsilon}_p \) is the rate of strain responsible for plastic degradation, suffix \( p \) indicates the plastic deformation of the surface, \( \rho \) is the density, \( T \) is the temperature, \( k \) is the thermal conductivity of the material, \( J_q \) is heat flux, \( \dot{\epsilon}_{mt} \) is the rate of heat removed with wear particles, \( \dot{s}_{g_{mt}} \) is the rate of entropy flow of the matters from the control volume, \( \eta_k \) and \( N_k \) are chemical potential and number of moles of species \( k \). Eq. (A1) is adapted for the present work for determining the entropy generation during the degradation of grease under mechanical shearing.
Fig A1 Considered grease system with control volume

Since the present work focuses on the mechanical degradation of grease, the contribution of chemical reaction during the shearing process can be considered negligible. Also the system considered is a closed system, the transfer of the matter to the control volume does not prevail. Assuming that the permanent mechanical degradation of grease chain occurs at the shear of $\dot{\gamma}_p$ and shear stress of $\tau$, Eq. (A1) reads:

$$\dot{s}_g = \frac{\tau \dot{\gamma}_p}{\rho T} + \frac{k (\text{grad } T)^2}{T^2} \quad (A2)$$

Further, in the present work, the grease is sheared at room temperature the change in temperature can be neglected. Now, using Eq. (A2), the entropy generation rate density inside the grease during the shearing process after time $t$ can be represented as:

$$\dot{S}_{g,vol} = \frac{\tau \dot{\gamma}_p}{T} \quad (A3)$$

Now, given that permanent degradation of the grease can happen even at lower shear rate, it is logical to assume $\dot{\gamma}_p \approx \dot{\gamma}$. Therefore, the total entropy generation density can be determined by integrating the entropy generation rate till time ‘$t$’, and Eq. (A3) yields Eq. (A4)

$$S_{g,vol} = \int_{0}^{t} \frac{\tau \dot{\gamma} dt}{T} \quad (A4)$$
Experimental Investigation of the Chemical Degradation of Lubricating Grease from an Energy Point of View$^4$

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Abstract

The chemical degradation/oxidation of lubricating grease is investigated experimentally from an energy point of view. A Pressure Differential Scanning Calorimeter (PDSC) is used to measure the activation energies of two lithium-complex greases and to monitor their chemical degradation through induction time. For this purpose, an experimental setup consisting of a heating chamber, a temperature controller and an energy meter is designed, built, and calibrated to heat up grease samples and measure pure energy absorption during the chemical degradation at different test temperatures. A relationship between the energy absorption of the grease and its chemical degradation is established that is independent of the testing time and temperature. It is shown that the energy absorption of the grease approaches to an identical maximum value in a shorter time in high temperatures and a longer time in low temperatures. The maximum energy absorption depends on the grease type and experimental results reveal that it can be used to estimate the grease chemical life. A roller tester rig is used to measure and compare the lubrication ability of two chemically degraded grease samples and to validate the results of the research. To gain further insight, experimental results are presented to examine the flow characteristics of a chemically degraded grease in an elastohydrodynamic (EHL) line contact with a comparison to that of the fresh grease.

Keywords: Chemical degradation; grease energy absorption; grease activation energy; grease useful life

1. Introduction

An in-service lubricating grease is susceptible to physical and chemical changes that influence its lubricating effectiveness to the extent that machine failure can occur if it is not replenished. By definition, the gradual loss of the lubricating ability of grease as a result of the physical and chemical changes is called grease degradation. A comprehensive literature review on the physical and chemical degradation processes, method for monitoring their rates, and available empirical and analytical models are presented in [1]. More recent research can be followed in [2-9].

Mechanical degradation—a form of physical degradation—occurs as a result of shearing the lubricant and is the dominant mechanism of degradation in low- and medium temperatures below 60 °C. This mode has been investigated from an energy/entropy point of view in [10-16]. Chemical degradation is generally

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$^4$ Published in Tribology International 137 (2019) 289-302
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associated with oxidation and is the dominant mechanism of grease degradation when exposed to high
temperatures. Thermal oxidation mechanism of greases with lithium soap and diurea thickeners has been
experimentally studied in [17]. Despite numerous studies on the subject of grease chemical degradation, an
analytical model capable of predicting chemical life of grease is still lacking [1, 18, 19].

In this paper, the results of an investigation of the chemical degradation of two Li-complex grease from
an energy point of view are presented. For this purpose, a test rig is designed and built to study chemical
degradation. A relationship between chemical degradation and the thermal energy absorbed by grease is
proposed based on extensive tests on two greases. A theory is developed and verified for chemical
degradation of Li-complex grease based on the experimental results.

2. Experimental

2.1. Lubricants

Two different greases were used to conduct the tests. Their properties are listed in Table 1.

<table>
<thead>
<tr>
<th>Grease</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLGI Grade</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Thickener type</td>
<td>Li-Complex</td>
<td>Li-Complex</td>
</tr>
<tr>
<td>Penetration, Worked, 25º C, ASTM D 217</td>
<td>280</td>
<td>305</td>
</tr>
<tr>
<td>Dropping Point, ASTM D 2265</td>
<td>280</td>
<td>275</td>
</tr>
<tr>
<td>Base oil type</td>
<td>Mineral</td>
<td>Synthetic</td>
</tr>
<tr>
<td>Viscosity of Oil, ASTM D 445 cSt @ 40º C</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>

2.2. Pressure Differential Scanning Calorimeter (PDSC)

A PDSC machine (Fig. 1) was utilized to measure the activation energy of the greases and to monitor
their chemical degradation process. The machine was calibrated according to the ASTM D5483 standard
[20] and all the tests were performed according to the recommended procedure. Accordingly, 0.002 gram
of grease is weighed in a small standard aluminum pan, inserted inside the high-pressure cell of the
apparatus, and is oxidized under 3.5 MPa of oxygen pressure at a constant test temperature. An empty pan
is also inserted inside the cell as a reference (Fig. 2). The machine heats up both pans at the same rate to
the test temperature and maintains it at the desired specification. When the oxidation reaction initiates, the
heater under the sample pan needs to generate less heat to maintain the test temperature (since the oxidation
reaction is exothermic), compared to that of the heater under the reference pan. The difference in the heat
flow is recorded and plotted as a function of time to measure the induction time. The grease induction time
(oxidation time) is defined as the instant in time when heat flow curve rises due to initiation of exothermic
reactions after the depletion of antioxidants. It is measured on the time axis at the intersection of two tangent
lines to the heat flow curve drawn before and after the rise in the heat flow. The activation energy is
calculated using the measured induction times at two different temperatures. More details are provided in Section 3.1.

2.3. Heater setup

PDSC machine as described in the previous section is used to measure the activation energy of an oxidation reaction by comparing the difference in the heat flow required to maintain an equal temperature of the sample and reference pans in a high pressure of oxygen environment. The machine is not capable of measuring the total energy absorbed by a grease sample during the chemical degradation in atmospheric pressure of air at different temperatures. Thus, a customized heater setup was designed and operated. The grease sample was heated for several hours at high temperatures to examine the relationship between energy and chemical degradation. Fig. 3 shows a schematic of the test set up. It consists of a thermally insulated heating chamber (shown in Fig. 4) whose temperature is controlled by a temperature control unit (Fig. 5) and a Watt-meter (Fig. 6) that measures the electrical power consumed to heat up the chamber.
Fig 3. Schematic of the experimental setup

Fig 4. Thermally insulated heating chamber

Fig 5. Temperature control unit
The heating chamber is a small electric furnace with a capacity of 520 W and the maximum temperature of 1150 °C. It has an inside cylindrical empty space with heating elements with a small hole on the top wall for inserting the thermocouple (yellow wire in Fig. 4). The temperature control unit has a maximum load capacity of 10 A, and the Watt-meter is a plug-in type energy meter with an accuracy of ±1.5%.

Although the heating chamber is thermally insulated, some heat is likely to escape to the surroundings. The heat loss should be measured and deducted from the final results at each test temperature since it does not contribute to degradation. For this purpose, before performing the actual test with grease, the chamber with empty grease container is heated up to the test temperature and after the temperature is stabilized, the electrical energy per hour necessary to maintain the temperature of the empty chamber is measured by the Watt-meter and recorded as the heat loss rate. This is the steady rate of heat being lost from the chamber at each test temperature and —since it is measured after reaching to the test temperature— it does not include the electrical power used to raise the temperature of the chamber. This procedure is repeated for each test temperature.

After recording the heat loss rates for all the test temperatures, the actual test procedure begins as described next. The empty chamber is heated up to the desired test temperature and maintained long enough until the steady state is attained. Next, 25 grams of the grease sample is weighed in an aluminum container (Fig. 7) and the container is inserted into the heating chamber. The Watt-meter is reset at this point and the energy (Watt-hours) measurement begins.
The consumption of energy is recorded during the test time. Small samples (0.1 gram) of grease are extracted from the heating chamber frequently during the test time. The samples are used to monitor the changes in the induction time of the grease during the heating process. The samples’ induction times are measured by the PDSC machine described in Section 2.2. The sample extraction was done as quickly as possible without opening up the chamber to minimize the heat loss during the sampling process.

2.4. Roller tester rig

The roller tester rig, introduced and described in [15], was used in this study to validate the theory. The instrumentation, calibration, and alignment of the machine are the same as described in [15]. The test procedure is different and will be described in the validation Section 4.

3. Theoretical

3.1. Activation energy calculation

The activation energy of grease is measured using the PDSC induction time measurements at two different temperatures according to the procedure described in [22]. According to the Arrhenius model, the oxidation reaction rate is related to the oxidation temperature by the following relation [23]:

\[ k = k_0 e^{-\frac{E_a}{RT}} \]  

(1)

where \( k \) is the rate constant, \( E_a \) is the activation energy, \( R \) represents the universal gas constant (8.314 J/mol.K), \( k_0 \) is a frequency factor, and \( T \) is temperature in Kelvin. The grease oxidation is a first order kinetic reaction (depends linearly on only one reactant concentration) and can be expressed in terms of fractional conversion \( x \) and the rate constant \( k \) [23]:

\[ t = \frac{-\ln(1-x)}{k} \]  

(2)

where \( t \) is the induction time and \( x \) is the fractional conversion. The fractional conversion \( x = \frac{n(t=0)-n(t)}{n(t=0)} = 1 - \frac{n(t)}{n(t=0)} \) is defined as the changes in the number of moles \( n \) of the reactant at time \( t \) divided by its initial number of moles at time zero.

Substituting \( k \) from Equation (1) into Equation (2), we arrive at the following equation [23]:

\[ t = -\frac{1}{k_o} \ln(1-x) e^{\frac{E_a}{RT}} \]  

(3)

\[ \ln(t) = \frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A) \]  

(4)

The term \( A = -\frac{1}{k_o} \ln(1-x) \) is the oxidation coefficient of grease, which is a constant for every grease. In “Arrhenius Coordinates”, which has a reciprocal scale for temperature and a natural logarithmic scale for induction time, Equation (4) is a line with the slope \( \frac{E_a}{R} \). The line can be drawn between any two points.
with known induction times measured at two different temperatures. The activation energy can then be
 calculated from the slope of the drawn line.

Here we measure the induction times for Grease A at 200 °C and 220 °C using the PDSC instrument. Figures
8 and 9 show the heat flow curves and the calculated induction times (at the cross of the shown tangent
lines) for the temperatures. The blue curves are the derivatives of heat flow curves. These are used to locate
the tangent lines.

Fig 8. Induction time measurement of fresh Grease A at 200 °C
The induction time of Grease A was also measured at the temperature of 210 °C. Table 2 shows the measured induction times at different temperatures.

Table 2. Measured Induction times for Grease A

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Induction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473.15</td>
<td>30.59</td>
</tr>
<tr>
<td>483.15</td>
<td>13.8</td>
</tr>
<tr>
<td>493.15</td>
<td>6.24</td>
</tr>
</tbody>
</table>
Fig. 10 shows that the induction time plotted versus temperature yields a linear relationship in the Arrhenius coordinates system. It reveals that the oxidation of Grease A follows the first order kinetic equation. The activation energy of this grease is calculated from the slope of the line to be $E_a = 157.13 \text{ kJ mol}^{-1}$. The induction time measurements for fresh Grease B at two test temperatures of 225 °C and 210 °C are shown in Fig. 11 and Fig. 12, respectively. Table 3 shows the measured induction times for grease B.
Following a similar procedure, the activation energy of Grease B is calculated to be \( E_a = 149.7 \text{ kJ mol}^{-1} \). Although Grease B has a smaller activation energy than Grease A, its induction times are longer, which implies that this grease is more resistant to high temperatures.

### 3.2. Induction time monitoring during chemical degradation

The induction time of a fresh grease measured by the PDSC instrument is a measure of the level of antioxidant agents available in the grease [1]. Since the antioxidants postpone the oxidation reactions, a
A fresh grease with higher induction time is expected to last longer when subjected to high temperatures. This was the main concept used in the development of an oxidation stability test method for greases using a pressure differential scanning calorimeter introduced by Rhee [22], which was later developed as an ASTM D 5483 standard [20]. As indicated in the standard, the oxidation stability test is useful to compare the high-temperature stability of different greases but is not capable of predicting grease life.

In his later work, Rhee [23] correlated his induction time measurements to the actual grease life measured from the wheel bearing standard test method (ASTM D 3527 [24]). Fig. 13 shows his reported empirical correlation.

![Fig 13. Correlation between induction times and grease life from ASTM D 3527 test [23]](image)

According to Rhee, although the correlation showed good agreement for most of the tested greases, it was not accurate for greases having excessive oil separation or poor thermal stability [23]. The wheel-bearing standard test method, as described in ASTM D 3527, is a dynamic test and, therefore, it also includes mechanical degradation. Thus, the wheel-bearing test results cannot be accurately correlated with a purely chemical test such as the induction time measurement. Undoubtedly, a grease with low mechanical stability will fail mechanically through oil separation/bleeding and leakage before it fails chemically.

The induction times reported in Fig. 13 are for fresh greases. We now proceed to monitor the changes in the induction time of one fresh grease (Grease A) during a purely chemical degradation process when exposed to a high temperature in a heating chamber. As described in the heater setup test procedure (Section 2.3), grease samples were extracted from the heater for further testing. These greases were placed in the PDSC apparatus and their induction times were measured. Figures 14 and 15 show the heat flow curves measured at 200 °C by the PDSC instrument for two of the samples (one was taken after 2.6 hours preheating in the heating chamber at 140 °C and the other after 2 hours preheating at 165 °C) along with calculated induction times. As the grease samples experienced preheating in the heater setup, their induction times are less than that of the fresh grease (30.59 minutes). See Fig. 8.

Fig. 16 shows how the induction time changes for Grease A during the heating process at 140 °C and 165 °C. Note that the first point at time zero and the induction time of 30.59 min. is common between both results and shows the induction time of the fresh grease. Since the antioxidants tend to deplete during the heating process, the induction time of the grease tends to decrease as time progresses. This happens faster in high temperatures.
Fig 14. Grease induction time measurement of Grease A after 2.6 hours preheating in heater setup at 140°C measured by PDSC at 200 °C

Fig 15. Grease induction time measurement of Grease A after 2 hours preheating in heater setup at 165 °C measured by PDSC at 200 °C
Fig 16. Induction time change versus time for two preheating processes at temperatures of 140 °C and 165 °C for Grease A measured by PDSC at 200 °C

The same process for induction time monitoring was followed for Grease B. The induction times were measured using the PDSC at 210 °C. Fig. 17 shows the induction time change of Grease B during the heating process for two temperatures of 140 °C and 180 °C. Again, the first point at time zero and the induction time of 40.82 min. is common between both results and shows the induction time of fresh Grease B.

Fig 17. Induction time change versus time for two preheating processes at temperatures of 140 °C and 180 °C for Grease B measured by PDSC at 210 °C
3.3. Thermal energy absorption

Electrical energy consumption of the heater setup introduced in experimental Section 2.3 was measured at different temperatures. Fig. 18 shows the measured energy plotted as a function of time at different test temperatures for Grease A. A part of the consumed energy is lost from the heater and a part of it is absorbed by the grease. As described in test procedure, the heat loss was measured by running the empty chamber at each testing temperature. Table 4 shows the measured heat lost for all testing temperatures.

![Fig 18. Electrical energy consumed to maintain the temperature of the heater chamber at different test temperatures for Grease A](image)

Table 4. Measured heat loss in different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate of heat loss (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>8.55</td>
</tr>
<tr>
<td>110</td>
<td>14.37</td>
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<tr>
<td>125</td>
<td>17.10</td>
</tr>
<tr>
<td>140</td>
<td>19.95</td>
</tr>
<tr>
<td>165</td>
<td>24.80</td>
</tr>
<tr>
<td>180</td>
<td>27.48</td>
</tr>
<tr>
<td>210</td>
<td>32.00</td>
</tr>
</tbody>
</table>
The thermal energy absorbed by the grease sample is calculated after deducting the heat loss from the total consumed energy. Thermal energy absorption of Grease A is shown in Fig. 19 for all tested temperatures.

Examination of the results in Fig. 19 leads to the following observations. First, grease absorbs more energy in higher temperatures. Second, the energy absorption trend is almost linear at lower temperatures but exhibits nonlinearity at higher temperatures. Third, for the nonlinear curves, the rate of energy absorption (slope of the curves) decreases over time. Fig. 20 shows the curves-fit expressions at the lowest and highest temperatures. Interestingly, a power equation provides the best fit with high goodness of fit ($R^2 > 0.99$) for both the curves (lowest and highest temperatures) shown in Fig. 20. This is also valid for other temperatures.

Table 5 shows the curve fit results for all the test temperatures.
Table 5. Power equation ($a \cdot t^b$) parameters and goodness of fit for results of Fig. 19

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$a$</th>
<th>$b$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.859273</td>
<td>0.976393</td>
<td>0.999885</td>
</tr>
<tr>
<td>110</td>
<td>1.000489</td>
<td>0.972834</td>
<td>0.999271</td>
</tr>
<tr>
<td>125</td>
<td>1.622851</td>
<td>0.827506</td>
<td>0.999476</td>
</tr>
<tr>
<td>140</td>
<td>2.404413</td>
<td>0.657265</td>
<td>0.999386</td>
</tr>
<tr>
<td>165</td>
<td>3.882827</td>
<td>0.572494</td>
<td>0.998856</td>
</tr>
<tr>
<td>180</td>
<td>4.751787</td>
<td>0.531342</td>
<td>0.999705</td>
</tr>
<tr>
<td>210</td>
<td>5.673466</td>
<td>0.495141</td>
<td>0.999248</td>
</tr>
</tbody>
</table>

Fig. 21 shows the change of power equation parameters $a$ and $b$ versus temperature. Changes in parameters $a$ and $b$ are insignificant at temperatures lower than 110 °C. Physically, this implies that the oxidation reactions are slow in this temperature range for the tested grease (This is not surprising for Grease A as it is categorized as a high-temperature performance grease). Parameter $b$ is very close to one at low temperatures, which means the energy absorption versus time is almost linear for the temperatures below 110 °C. Upon increasing the temperature, the parameter $a$ increases almost linearly and parameter $b$ decreases exponentially.

The same behavior was also observed testing Grease B. Fig. 22 shows the energy absorbed by Grease B at three different temperatures. For this grease, also a power curve is the best-fitted equation with high goodness of fit ($R^2 > 0.99$). Table 6 shows the curve fit results for all the test temperatures.
Fig 21. Power equation parameters versus temperature for Grease A

Fig 22. Electrical energy absorbed by grease versus time for Grease B

Table 6. Power equation (\( at^b \)) parameters and goodness of fit for results of Fig. 22

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( a )</th>
<th>( b )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>140^\circ C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180^\circ C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>210^\circ C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 23 shows the change of power equation parameters $a$ and $b$ versus temperature for Grease B. These are similar to the trends observed for Grease A.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>1.40132</td>
<td>0.739090</td>
<td>0.99949</td>
</tr>
<tr>
<td>180</td>
<td>3.10642</td>
<td>0.590602</td>
<td>0.99876</td>
</tr>
<tr>
<td>210</td>
<td>4.29199</td>
<td>0.531197</td>
<td>0.99235</td>
</tr>
</tbody>
</table>

Fig 23. Power equation parameters versus temperature for Grease B

3.4. Relationship between thermal energy absorption and induction time

The procedure for monitoring of induction time during chemical degradation was described in Section 3.2. The reductions in the induction time of the fresh Grease A during 14 hours of heating at 140 °C and during 2 hours heating at 165 °C were presented in Fig. 16. The thermal absorbed energy by the same grease during the same heating processes was also calculated in Section 3.3 and was presented in Fig. 20. We now proceed to plot the induction times plotted as a function of the absorbed energy for the heating processes. The result is shown in Fig. 24.
Fig 24. Induction time vs absorbed energy for two preheating processes at temperatures of 140 °C and 165 °C for Grease A measured by PDSC at 200 °C

Interestingly, the induction time changes similarly for both temperatures plotted versus absorbed energy. This implies that the grease absorbs approximately the same amount of energy as it degrades regardless of the temperature and time. The energy absorption requires a longer time period when operating at a lower temperature and in a shorter time when operating at a higher temperature. This is also valid for Grease B. Fig. 25 shows the induction times versus absorbed energy for Grease B. The physical meaning and importance of absorbed energy is described in the next section.

Fig 25. Induction time vs absorbed energy for two preheating processes at temperatures of 140 °C and 180 °C for Grease B measured by PDSC at 210 °C
3.5. Maximum energy absorption theory

It was shown that the energy absorption follows this power equation:

\[ E(\text{energy absorption}) = a \cdot (\text{time})^b \]  \hspace{1cm} (5)

It was also shown that the exponent parameter \( b \) starts from one at low temperatures and decreases as temperature increases. The derivative of energy absorption can be written as:

\[ E' = a \cdot b \cdot t^{b-1} \]  \hspace{1cm} (6)

where \( t \) represents time. Since \( b \) is less than one, \( E' \) approaches to zero when time goes to infinity. This means that the energy absorption function approaches asymptotically to a maximum value as time approaches infinity. Assuming that the maximum value of the energy absorption is the same for a grease regardless of testing temperature, then all the curves in Fig. 20 should approach to the same value as time approaches to infinity and the difference between the curves should become nil. Having the power equation for each curve, the difference between each two curves can be calculated at any time. Therefore, the time that the difference between the two curves becomes very small can be evaluated. This is the time that energy absorption approaches to its maximum. Our assumption about having the same maximum energy absorption for all the temperatures can be verified if the same maximum value is calculated using any two combinations of the curves. For example, the maximum energy absorption of Grease A is calculated here using the power equations of 165 °C and 210°C. From Table 5 we have:

\[ E_{210°C} = 5.673466 \cdot t^{0.495141} \]
\[ E_{165°C} = 3.882827 \cdot t^{0.572494} \]
\[ E_{210°C} - E_{165°C} \leq 0.001 \text{ when } t \approx 134.65 \text{ hrs} \]

Therefore, Maximum Energy Absorption for Grease A \( \equiv 64.3 \) Watt-hours

The energy absorptions at 134.65 hours were also calculated for other temperatures and are listed in Table 7.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( A )</th>
<th>( b )</th>
<th>( E ) @ ( t=134.65 ) hr (Watt-hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>2.404413</td>
<td>0.657265</td>
<td>64.2844</td>
</tr>
<tr>
<td>165</td>
<td>3.882827</td>
<td>0.572494</td>
<td>64.2974</td>
</tr>
</tbody>
</table>
All the calculated energy absorptions are approaching to 64.3 Watt-hour. This is the maximum energy absorption for Grease A regardless of the oxidation temperature. The grease absorbs the same maximum energy at a longer time in lower temperature and at a shorter time in high temperatures. This phenomenon is demonstrated schematically in Fig. 26.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Power</th>
<th>Constant</th>
<th>Energy Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°C</td>
<td>4.751787</td>
<td>0.531342</td>
<td>64.2844</td>
</tr>
<tr>
<td>210°C</td>
<td>5.673466</td>
<td>0.495141</td>
<td>64.3201</td>
</tr>
</tbody>
</table>

Fig 26. Schematic of the difference between low and high temperate degradation

The maximum energy absorption can also be calculated for Grease B using its power equations of 180 °C and 210°C. From Table 6:

\[ E_{210^\circ C} = 4.29199 t^{0.531197} \]
\[ E_{180^\circ C} = 3.10642 t^{0.590602} \]

\( E_{210^\circ C} - E_{180^\circ C} \leq 0.001 \) when \( t \approx 230.9 \) hrs

Therefore, Maximum Energy Absorption for Grease B ≅ 77.3 Watt-hours

Using the grease power equation of 140 °C, it can be shown that the energy absorptions of the grease approach to the calculated maximum energy absorption after 230 hours degrading at 140 °C.

Physically, the maximum energy absorption can be considered as the total energy required for the grease to burn completely and degrade to its final state when all its chemical compounds are decomposed.
3.6. Maximum energy absorption versus activation energy

Referring to Section 3.1, the calculated activation energy of Grease A is \( E_a = 157.13 \, \text{kJ/mol} \). To gain further insight, it is worthwhile to calculate it for the whole grease sample (25 grams), convert its units to Watt-hour, and compare it with the maximum energy absorption. In order to do so, the molar mass (g/mole) of the grease is required. Since grease is a complex material and contains several chemical components and additives, it is not possible to calculate its molar mass analytically. The molar mass of Grease A can be estimated from ASTM D2502 standard [25], and it is found to be 520 g/mole using the values of the grease’s base oil viscosity of 220 cSt \((220 \times 10^{-6} \, \text{m}^2/\text{s})\) at 40 °C and 16 cSt \((16 \times 10^{-6} \, \text{m}^2/\text{s})\) at 100°C. Using the estimated molar mass, the activation energy for each gram of grease is calculated as:

\[
E_a = \left( \frac{157315 \, \text{J/mol}}{520 \, \text{g/mole}} \right) = 302.53 \, \text{J/g}
\]

For 25 grams of grease, the total value is:

\[
E_a = 7563.22 \, \text{J} = 2.1 \, \text{Watt hours}
\]

The calculated activation energy is very small compared to the calculated maximum energy absorption of 64.3 Watt-hours. Referring to Fig. 19, at high temperatures, the calculated activation energy (2.1 Watt-hours) is absorbed by the grease in a short period of time. This implies that in the chemical degradation process at high temperatures, the oxidation reactions initiate very rapidly (at least for the outer layer of grease exposed to oxygen). The rest of the maximum energy absorption is used to decompose the grease thickener and base oil by breaking down the chemical bonds of the grease component molecules. The following two interesting phenomena were observed in our experiments.

First, the grease color changes to black during the heating process in the heater setup. It happens much faster in higher temperatures and the discoloration process starts from the outer layer of the grease, which is directly exposed to oxygen and penetrates to inner layers as oxygen diffuses inside the grease. This means that the oxidation process is a gradual process and depends on the availability of oxygen and the diffusion speed of oxygen. Second, the blackened grease is still lubricious and contains oil even after 7 hours of degrading at 180 °C. Thus, the lubricating life of the grease is not completely diminished. It will be shown in the next section that the black grease can still lubricate a highly loaded contact for at least 18 hours.

4. Validation

The roller tester rig modified and utilized in [15] was used to chemically degrade several grease samples (by heating them in the rollers’ chamber) for different periods of time at different temperatures, and the remaining lubricating life of each grease sample was measured using the sample to lubricate the rollers. The traction behavior of the degraded grease was monitored to investigate the effectiveness of the grease. Failure is assumed when the traction curve experiences a rapid rise, which signifies the onset of damage to the rollers if the operation is allowed to continue. The results of the test are used to validate the theory.

4.1. Test procedure
Mechanical degradation of an EHL contact between two rollers was investigated using a roller tester machine that mimics the lubrication of gear teeth contact [7]. The rig is calibrated and aligned as described in [15]. Fig. 27 shows the grease chamber with the heating elements designed for this study. At the first stage of the test, the grease sample is chemically degraded inside the chamber at high temperature for a specific time (several hours) while the rollers are not touching each other and primarily serve as a “grease mixer”. During this period, the lowest possible shear rate (0.025 m/s rolling speed, zero slide-to-roll ratio and 3 mm gap between the rollers) was applied. Here, the grease sample is blended during the heating process to create oxygen exposure condition for the whole grease sample, and the shear rate is kept low to minimize the mechanical degradation inside the grease sample. After the heating process, the heating elements are turned off and enough time is provided in order for the grease to cool down to the room temperature.

At the second stage of the test, the degraded grease—which is still in the chamber—is used to lubricate the contact between rollers and its lubricating ability is tested to determine the grease’s remaining useful life. The rollers are loaded with a maximum Hertzian pressure of 0.7 GPa and the rollers are rotating with the rolling speed of 0.065 m/s with a slide-to-roll ratio of 1.3 at room temperature. The traction force between the rollers is monitored during the test. When the traction force increases dramatically, the test is terminated automatically by a built-in stopping mechanism that halts the motors to avoid damaging the rollers and the rig. This test was performed on Grease A at two temperatures of 180 °C and 210 °C. The heating period was 7 hours in both tests. Figures 28 and 29 show the traction force measurements in the second stage of the tests.
Comparing Figures 28 and 29, the first noticeable point is that by $30^\circ$C increase in the test temperature (from $180^\circ$C to $210^\circ$C), the lubricating life of the grease decreases by a factor of 8.3. This dramatic life reduction in high temperatures was reported by other researchers as grease life dropping in half for each 10 °C rise in the temperature [26]. The second point is that the change in the preheating temperature did not noticeably affect the grease traction (measured in room temperature in similar load and the slide-to-roll ratio, SR).
From visual observation, the degraded grease was black in color and dry but remained slippery. Slight vibration was observed in the rotation of the rollers during the lubrication life test. This vibration is reflected in Figures 28 and 29. The traction rises several times due to poor lubrication condition, but it returns back to its normal value. This trend continues up to the test termination point when the traction rises to a very high value and continuing the test could damage the rollers’ surfaces. As pointed out previously, the machine was programmed to automatically stop at this point prior to initiation of damage.

It is worthwhile to calculate and compare the absorption energy level of the greases after preheating process at the two temperatures tested. Using the value of power equation reported in Table 5, the absorption energy for Grease A after 7 hours heating is calculated as:

\[ E_{210^\circ C} = 5.673466 \times 10^{0.495141} = 14.87 \text{ Watt.hours} \]

\[ E_{180^\circ C} = 4.751787 \times 10^{0.531342} = 13.36 \text{ Watt.hours} \]

The time that it takes for a grease sample to reach to the same energy absorption level of \( E_{210^\circ C} = 14.87 \text{ Watt.hours} \) while it is being heated at \( 180 \, ^\circ C \) is calculated from:

\[ E_{180^\circ C} = 4.751787 (t) \times 10^{0.531342} \]

If \( E_{180^\circ C} = 14.87 \) yields \( t \approx 8.5 \) hours

Therefore, the grease sample absorbs the same amount of thermal energy (14.87 Watt-hours) either when it is heated for 8.5 hours at \( 180 \, ^\circ C \) or it is heated for 7 hours at \( 210 \, ^\circ C \). Fig. 30 shows the lubricating life test results after 8.5 hours of preheating the grease sample at \( 180 \, ^\circ C \). The measured lubricating life of the grease is 2.36 hours. This is close to the lubricating life of the grease after 7 hours preheating at \( 210 \, ^\circ C \) which was 2.23 hours.

Fig 30. Traction measurement of Grease A after 8.5 hours preheating at \( 180^\circ C \), \( U_r=0.065 \, \text{m/s}, \, SR=1.3, \) temperature =26 °C, maximum Hertzian pressure=0.7 GPa
5. Grease flow observations

Grease flow between the rollers was observed for fresh grease and reported in [15]. It was shown that the fresh grease experienced three successive phases: “Fully grease-covered rollers”, “Slippage and grease separation”, and “Formation of liquid lubricant reservoir”. The same type of experiments is performed in this investigation with the chemically degraded grease. The grease flow between the rollers is observed and captured for the degraded grease (preheated for 8.5 hours in the grease chamber at 180°C). The following are the descriptions of each phase with comparison with the same phase for fresh grease.

5.1. Phase 1: Fully grease covered rollers

Fig. 31 shows the first phase of grease flow for both chemically degraded grease (left picture) and fresh grease (right picture). From visual inspection, the degraded grease is darker and looks dried and non-uniform. The volume of the grease has also been decreased.

As described for the case of fresh grease in [15], in the first phase both the rollers are fully covered with the grease for the first several minutes of the test. Visual observation reveals that grease tends to attach itself to the rollers from the bottom of the chamber and is carried into the contact region by the rotation of the rollers. Some portion of the grease passes through the contact by forming a full film while the rest tends to go around the sides of the rollers, bypassing the contact area. The moving grease tends to return to the contact repetitively and the rollers remain fully covered by thick layers of grease until the end of this phase, which takes several minutes.

The following differences were observed for the first phase of degraded grease flow. The rollers are not fully covered with the grease at the beginning of the test, and the tendency of the degraded grease to attach itself to the rollers is less. The degraded grease looks dry at the first glance; however, because of the chemically broken thickener structure, it releases a large amount of base oil under high shear rate in the EHL contact. The released oil color is green, which is different from the blue color of the base oil of the fresh grease. The first phase ends after several seconds and grease slippage and separation (Phase 2) starts very soon due to the released base oil. The grease almost immediately turns to a mixture of separated degraded base oil and very soft broken degraded thickener.

![Fig 31. Phase 1: Fully grease covered rollers, comparison between chemically degraded grease (left picture) and fresh grease (right picture)](image)

5.2. Phase 2: Slippage and grease separation
According to [15], in the second phase, fresh grease suddenly separates itself from the rollers’ contacting surfaces. This first occurs in the roller with the larger diameter and soon extends to both rollers. Physically, the portion of the moving grease in contact with the roller surfaces begins to slide on the surface of the rollers without being carried into the contact area by the rollers’ rotation. During the second phase (which lasts almost 10 minutes in experiments with fresh grease [15]), the rolling surfaces may occasionally become partially covered by grease, but this process becomes less frequent as time passes.

For the chemically degraded grease, the second phase started sooner and lasted shorter. The separation happened on both rollers almost at the same time. Fig. 32 shows the second phase of grease flow for both chemically degraded grease (left picture) and fresh grease (right picture). From visual inspection, the degraded grease breaks to a very soft (with low consistency) material after passing through the contact.

![Image of grease flow comparison](image)

**Fig 32. Phase 2: Slippage and grease separation, comparison between chemically degraded grease (left picture) and fresh grease (right picture)**

### 5.3. Phase 3: Formation of liquid lubricant reservoir

During the final phase of fresh grease, no solid grease was observed on the rolling surfaces [7]. The rolling surfaces were covered by a very thin film of liquid lubricant which is highly mechanically degraded grease. It contains a mixture of base oil and destroyed thickener particles. Formed on either side of the rollers was a “solid grease wall” that constrained the thin liquid layer from leaving the contact—akin to a soft seal—and for a long period of time. Thus, a liquid lubricant reservoir was created between the solid grease and rollers’ surfaces that feeds the contact continuously. The importance of the solid grease walls/edges at the sides of the contact (to seal and keep the liquid lubricant in the contact) is emphasized in [15]. There it was shown that the solid grease walls/edges are subjected to low shear rate mechanical degradation which breaks their sealing effect after a long period of time (several years).

For the chemically degraded grease, the formation of liquid lubricant reservoir and grease walls/edges was also observed (Fig. 33).
Interestingly, since the degraded grease is softer than the fresh grease, at the exit of the contact when the edges are split, the grease edges are taller. The difference in the wall edges of degraded and fresh grease is shown in Fig. 34.

Fig 34. Grease edges, comparison between chemically degraded grease (left picture) and fresh grease (right picture)

Although the grease edges are taller in the degraded grease, they are unable to seal the contact. The consistency of the grease at the edges was measured using a rheometer as described in [2]. The net penetration measured was $\Delta = 1.01$, which implies that the grease at the edges is already degraded by dropping in the level of consistency from NLGI 2 to NLGI 1. In reference [15] it was calculated that when operating at room temperature, the grease edges are mechanically degraded to this level of consistency after 4.4 years. It is interesting that high temperature caused the same amount of degradation after only 8.5 hours. Since in our validation experiments (Section 4), the chemically degraded greases were used to lubricate the contact, the grease edges were not able to seal the lubricant oil at the contact from the beginning of the test. The base oil also was a degraded oil. Thus, the contact experienced poorer lubrication from the beginning of the tests. This explains the source of vibration observed in the rotation of the rollers and the resulting fluctuations in traction reflected in Figures. 28, 29 and 30. The contact became starved after a short period of time (2.3 hours as shown in Fig. 30) as a result of the broken sealing effect of grease edges and poor lubrication.

6. Conclusions
This paper is devoted to the determination of a correlation between the chemical degradation of lubricating grease and energy. Two different Li-complex greases are chemically degraded inside the heating chamber of the experimental setup, and their energy absorption during the heating process was accurately measured. A theory is introduced based on the acquired experimental results. It is shown that the level of absorbed energy can be used to determine the state of chemical degradation regardless of temperature and time. A grease absorbs the same amount of energy when is heated in a shorter time at a higher temperature or in a longer period of time at a lower temperature. It is shown that, for the tested greases, the plot of the energy absorption versus time always follows a power equation in the format of \( E(\text{energy absorption}) = a. (\text{time})^b \). The power curves are linear \( (b\approx 1) \) at lower temperatures and become nonlinear at higher temperatures. All the power curves are approaching to a maximum energy absorption value when time goes to infinity. Physically, the maximum energy absorption value can be considered as the total energy given to the grease for it to burn completely and degrade to its final state when all of its chemical compounds are decomposed. The maximum energy absorption values are calculated for tested greases and are compared to their measured activation energy. The predictions of the theory are verified using a roller tester rig. According to the power equations of Grease A, it absorbs the same amount of energy when is heated for 7 hours at 210 °C or is heated for 8.5 hours at 180 °C. The same remaining lubricating life is measured by testing the two grease samples heated for 7 hours at 210 °C and for 8.5 hours at 180 °C in a roller test rig operating in line-contact EHL. This concept is useful for estimating the chemical life of a grease at different temperatures. Since the experiments were done on two Li-complex greases, the validity of the theory for other types of grease needs to be studied.

7. References


