Changes in Ignition Behavior of Aged Fuels and Lubricants Behind Reflected Shock Waves

Raquel Juárez, Anette Lira, Matthew Abulail, and Eric L. Petersen
J. Mike Walker ’66 Department of Mechanical Engineering
Texas A&M University
College Station, TX, USA

1 Introduction

Improvements in engine technology and complexity increase the temperature, pressure, and shear conditions encountered by the fluids needed for normal operation [1-3]. Gas turbines especially exhibit high sump and hot-spot temperatures [3]. When lubricants are exposed to high surface temperatures, they undergo a degradation process—either oxidation or thermal breakdown—that changes their properties and causes solid by-products to form. When the oils are oxidized, the antioxidants in the lubricant are depleted, and the molecules react with oxygen in a series of reactions that may end in polymerization [4, 5]. The oxidation process eventually leads to an increase in viscosity and to the formation of sludge and varnish [1, 4, 5]. Lubricant oxidation may occur at relatively low temperatures but increases in speed as temperatures rise (>100°C) [4, 5]. No oxygen is needed for thermal breakdown to occur, but elevated temperatures (>300 or 400°C) are required for the thermal stability point to be exceeded, thermal cracking to occur, and by-products to form [4, 6, 7]. Thermal degradation results in decreasing viscosity and in the eventual formation of solid, carbonaceous coke deposits [4, 6]. As explained, both degradation pathways eventually result in changes in viscosity and in the formation of solid by-products.

Another issue that may arise from extremely high operating temperatures is the undesired ignition of turbine oils due to hot spots in the oil system, frictional heating, leakage of hot air into the sump, or leakage of the lubricant onto hot surfaces outside of the lubrication system [2, 8]. Lubricant flammability is one factor that may affect the likelihood of ignition, among other factors (like ignition source and duration, oil flow rate and temperature, leaked air flow rate and temperature, etc.) [8]. Oil system temperatures are expected to increase in the future, leading to higher oil degradation rates and increased risk of oil ignition [2]. Investigating the effect that lubricant degradation has on its flammability is therefore of interest. For example, Wirtz and Zeman [2] found that when carbonaceous deposits and volatile oil degradation components are added to aviation lubricants, their spontaneous ignition temperatures, determined using pressure differential scanning calorimetry, were lowered. In addition, Hameed [9] found that the kinematic viscosity, flash point, and fire point of a lubricant all decreased with increasing distance traveled in an automobile engine. Contamination with fuel is another way in which an engine’s lubricant’s flash point may decrease [4, 9].

Furthermore, in the case of jet engines that use regenerative cooling technology in which the combustor wall is cooled by the liquid fuel before it enters the combustion chamber, coking of the fuel

Correspondence to: epetersen@tamu.edu

entering the chamber may be an issue [10]. Hence, exploring the effect that the exposure of the fuel to high temperatures (to the point of coke formation) has on the ignition characteristics of the remaining fuel is also of interest.

2 Materials and Methods

Aging Process

The lubricants were aged using the experimental apparatus illustrated in Fig. 1(a). Before the process begins, 400 mL of lubricant are inserted into the reservoir, and the test section is preheated to the target set temperature. The test section consists of a stainless-steel with seven k-type thermocouples embedded into the surface. The readings from the central surface thermocouple are maintained constant during the coking test using a temperature controller. The system is purged with nitrogen before the oil is heated if studying the thermal breakdown is desired. If oxidation is of interest, air is introduced into the oil in the reservoir through a gas dispersion tube. Once the coking test and aging process begin, the lubricant is cycled through the heated test section and back into the reservoir at 10 mL/min. The bulk oil temperature is measured before and after it flows through the heated section. After a period of time, solid deposits start forming and accumulating on the inner wall of the test section. The accumulation of deposits results in a change in the axial temperature profile (in the case of pyrolysis tests) and in the drop of the outlet bulk oil temperature due to the increased resistance to heat transfer caused by the fouling.

The first lubricant in this study, Oil A, is a turbine lubricant made of a severely hydrotreated basestock. Oil A was tested for coking resistance and aged in both an oxidative and inert environment. Both tests lasted approximately 29 hours, and the time required for deposits to start accumulating was 238 minutes in the case of the pyrolysis test and 308 minutes in that of the oxidation test. Figure 1(b) shows the axial temperature distribution to which the oil was subjected. The oxidation test was conducted at surface temperatures approximately 200°C lower than the pyrolysis test to avoid bulk oil temperatures above the flash point due to the added risk of ignition. The pyrolysis test had an average outlet bulk oil temperature of 247°C, and the oxidation test had an outlet bulk oil temperature of about 137°C before it began to quickly drop due to deposit accumulation on the heated wall. In the case of the pyrolysis test, the axial temperature distribution changed once the coke deposits started accumulating in the test section which is also illustrated in Fig. 1(b). Both aging processes resulted in the formation of solid deposits. A sample of the aged oil was collected at the end of both coking tests. The pictures of the oil samples included in Fig. 2(a) show the drastic changes in appearance that resulted.

The ignition characteristics of a second lubricant, motor oil Castrol GTX 20W-50, were also studied. This motor oil was subjected to two rounds of heating in an inert environment in the same experimental apparatus (Fig. 1). The first round of heating lasted approximately 124 hours with surface temperatures between 344 and 445°C, and the second round of testing lasted 119 hours with surface temperatures between 290 and 512°C. A large amount of coke deposits and darkening of the oil resulted from this aging process as well.

The fuel samples were aged in a process that simulates fuel used in a jet engine that utilizes regenerative cooling technology and a “last-chance screen” to trap any deposits that may have formed as a result. A 55-gallon drum of JP-5 was cycled at 500 g/min through a 10-micron fuel filter followed by a heated section until it reached 204°C. The fuel is then passed through a screen that traps the resulting coke deposits. A differential pressure transducer is used to monitor the increase in differential pressure across the screen due to deposit buildup. The fuel is then cooled and returned to the reservoir. No oxygen was added to the system while heating. Figure 2(b) shows the aged fuel samples that were tested in the shock tube, supplied by Precision Combustion, Inc. (PCI) [11]. All three samples that were tested for combustion and are included in Fig. 2(b) proceeded from different fuel batches.

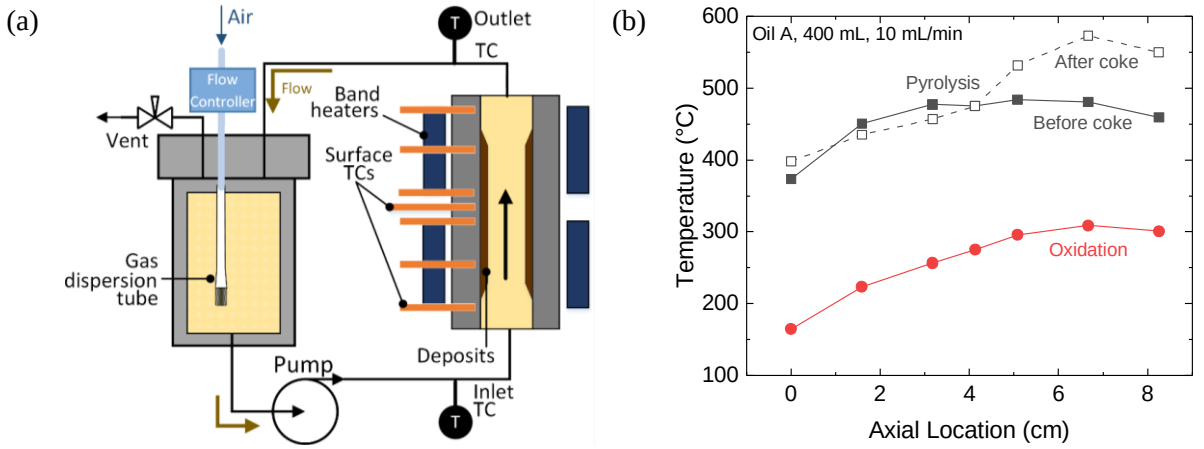

Figure 1: (a) Diagram of the experimental apparatus used to age the lubricants. Not to scale. (b) Axial surface temperature distribution in the test section during the aging processes of Oil A.

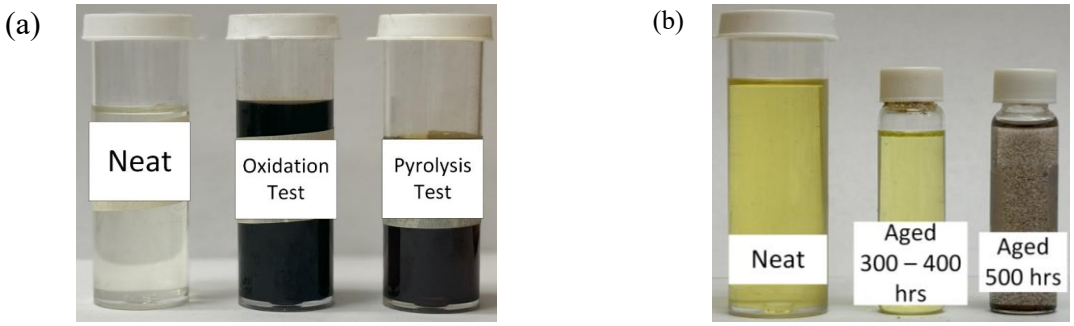

Figure 2: Neat and aged samples of (a) Oil A and (b) JP-5 (courtesy of PCI).

Injector Setup

In recent years, one of the shock tubes (the HPST) in the TEES Turbomachinery Laboratory at Texas A&M University has been adapted to allow for the study of heavy hydrocarbon lubricants and fuels [12, 13]. The method was developed to simulate gas-phase combustion of heavy lubricants and fuels despite the limitations caused by their high viscosity and low vapor pressure. The HPST is a pressure-driven shock tube. Its driven section is 4.92-m long with a 15.24 cm inner diameter. The driver section has an inner diameter of 7.62 cm and is 2.51 m long. Four piezoelectric pressure transducers are evenly distributed along the last 1.4 m of the shock tube with the final transducer being located 1.6 cm from the end wall. These transducers are used to determine the speed of the incident shock wave which is then used in conjunction with the normal shock relations to iteratively determine the post-reflected shock conditions (T_5 and P_5)[13].

For these experiments, an automobile injector is attached to the shock-tube endwall using a custom adapter and adhesive that allow it to hold a vacuum seal [13]. The injector is supplied with 275.8 kPa (40 psia) of air. A 0.2 mL droplet of the fuel to be studied is placed in front of the injector before every test. As the incident shock wave passes, an upstream pressure transducer signals a function generator which then closes a relay to provide power to the injector for 2 ms. The air introduced into the shock tube by the injector atomizes and disperses the liquid forward into the approaching incident wave. The incident wave causes the temperature and pressure to increase (to T_2 and P_2), breaks the droplets further and vaporizes them. Once the shock wave is reflected, the fuel-air mixture temperature and pressure increase further (to T_5 and P_5) which leads to the combustion of the fuel [13]. The timing of these events is such that the droplets are vaporized in time to ignite once the shockwave is reflected but are not introduced early enough for them to fall to the bottom of the shock tube [13].

A photomultiplier tube (PMT) is located 1.6 cm from the endwall to capture light emitted through a sidewall window port by excited OH molecules transitioning back to the base state through a 307±10

full width at half maximum filter. The OH* signal recorded with the PMT is used to determine the ignition delay time, as outlined in Fig. 3. The steepest slope in the OH* signal is used to calculate the sidewall OH* IDT. The reflected shock wave speed is used to calculate the time required for the wave to travel from the endwall to the sidewall measurement location (a 1.6-cm distance). The sidewall IDT is then corrected by this amount of time to obtain the actual IDT value. A more detailed description of the experimental setup and procedure may be found in the work of Abulail, Cooper, and Petersen [12, 13].

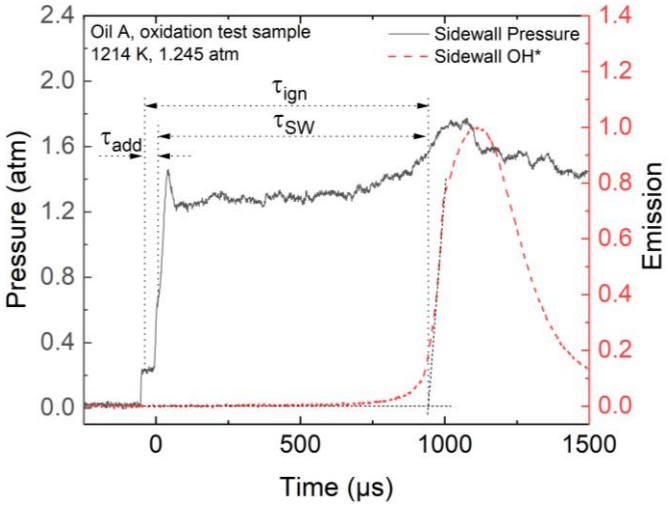

Figure 3: Definition of ignition delay time based on the steepest slope of the OH* chemiluminescence signal. An adjustment for time zero is made to account for the fact that the OH* and pressure signals are taken at the side wall. The reflected shock speed is used to calculate the time to be added (τ_{add}) to the sidewall IDT (τ_{SW}) to obtain the final IDT (τ_{ign}).

A few assumptions are made in the calculation of the stated equivalence ratio for these ignition experiments. First, it is assumed that all air in the driven section is compressed to the last 20 – 30 cm of the tube and is available for combustion. Second, the air introduced into the system by the injector is assumed to be negligible. Previous tests have supported this assumption based on the fact that the initial pressure in the driven section does not change after the injector is activated [13]. Third, the thermodynamic data of n-hexadecane are used as a surrogate for the lubricants since it is the highest-order hydrocarbon for which thermodynamic data are available and since the composition of most commercial lubricants is unknown to the public. In the case of the JP-5 experiments, the thermodynamic data for $C_{12}H_{22}$, the average composition, is used [14, 15]. The equivalence ratio is then determined by using the ideal gas law to calculate the molar amount of air in the driven section of known volume, temperature (T_1), and pressure (P_1); the known amount of fuel inserted into the shock tube with density given by the manufacturer; and the chemical composition and molecular weight of the surrogate used. The equivalence ratio is therefore varied between tests by changing the initial pressure in the driven section. While there is some inherent uncertainty in the local equivalence ratio, the value calculated for reference herein (and resulting IDTs) may still be used to compare the reactivity of the fuels and lubricants under the same experimental setup. Finally, according to previous work by Cooper [12], the uncertainties associated with this method of injecting the fuel from the shock-tube endwall are conservatively estimated to be 2.0%, 1.5%, and 30% for pressure, temperature, and IDT, respectively.

3 Results and Discussion

The resulting data for the neat and aged samples of Oil A, Castrol GTX 20W-50, and JP-5 are included in Figs. 4 (a), (b), and (c), respectively. Table 1 lists the values for the pre-exponential factor (A) and the activation energy (E_a) of the Arrhenius relation for all cases studied. The aging of the fuel

and lubricant samples did not result in a significant increase or decrease in the ignition delay times when the uncertainty in IDT is considered. A difference in the activation energy is seen, however. In all three cases, a decrease in the activation energy is observed in the samples that were aged in an inert environment (pyrolysis). The sample that resulted from the oxidation test of Oil A showed an increase in activation energy instead.

The aged Castrol GTX 20W-50 sample resulted in the most decreased activation energy when compared to that of the neat sample. This result may be because it is a motor oil (rather than a turbine oil) or because it was aged for significantly longer. The JP-5 samples, on the other hand, were cycled through the heated section 1.85 to 2.3 times more than the lubricant samples and yet resulted in the least-changed activation energies. This result suggests that the formation of deposits in fuels used for regenerative cooling technology does not necessarily affect the fuel's ignition characteristics. Further study is required to better understand the effect that cycling time, oil quantity, temperature, and other factors would have on the ignition characteristics of these hydrocarbons. Nevertheless, the aging cycle time and lubricant quantity of the tests completed with Oil A (Fig. 6(a)) were equal; and the amount of fuel aged among the JP-5 tests was also equal. Therefore, a comparison of the effect of aging within each group of fuel or lubricant may still be made.

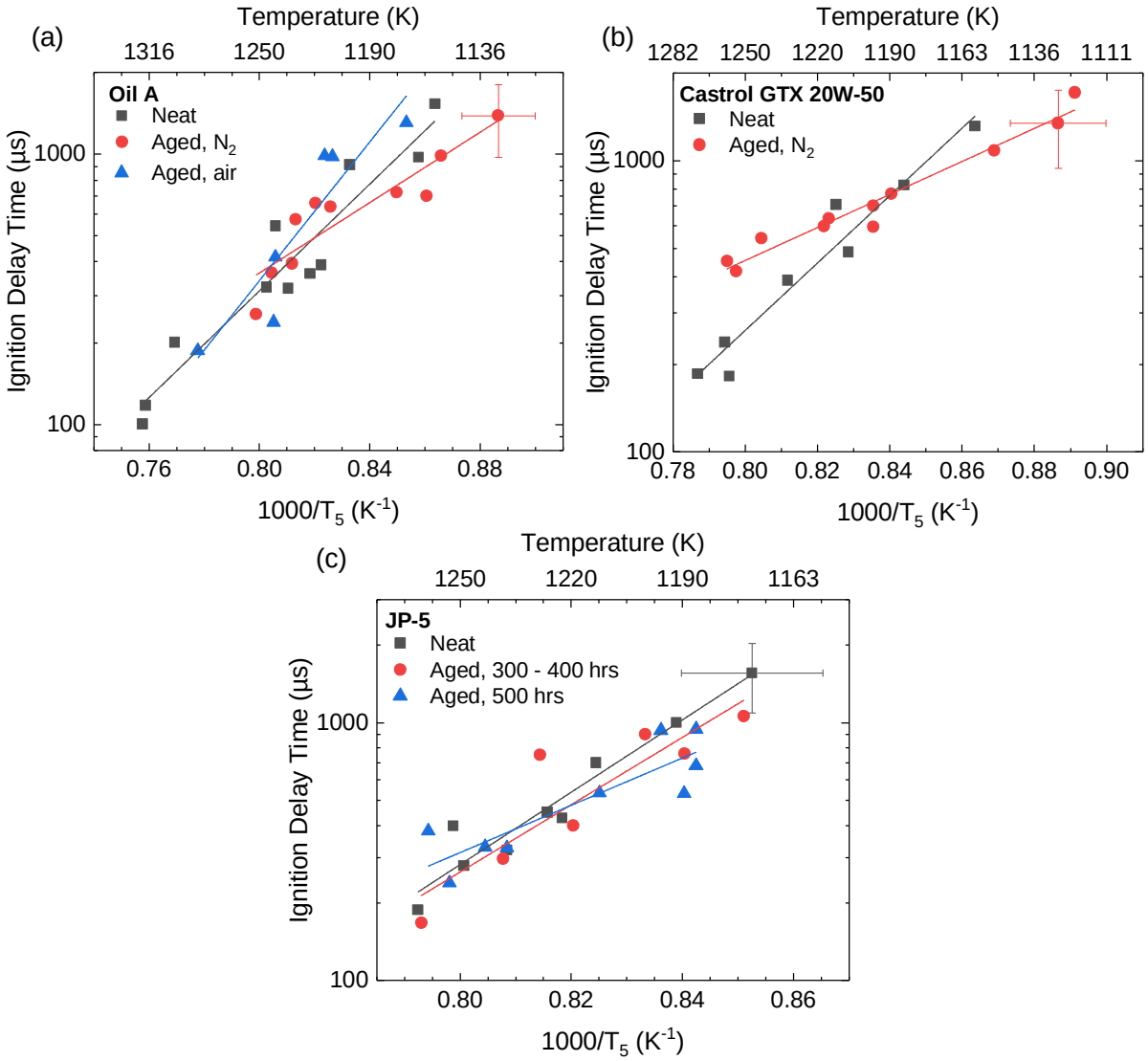

Figure 4: Ignition delay time data for neat and aged (a) Oil A, (b) Castrol GTX 20W-50, and (c) JP-5.

Table 1: Pre-exponential factor and activation energy for the Arrhenius relationship of the data collected.

Lubricant/Fuel		A (μs)	E_a (kcal/kmol)
Oil A	Neat	$3.97x10^{-6}$	45.2
	Pyrolysis	$2.26x10^{-3}$	29.8
	Oxidation	$1.85x10^{-8}$	58.7
Castrol GTX 20W-50	Neat	$1.43x10^{-7}$	53.0
	Pyrolysis	$1.32x10^{-2}$	26.0
JP-5	Neat	$1.65x10^{-9}$	64.2
	Aged, 300-400 hrs	$9.41x10^{-9}$	59.8
	Aged, 500 hrs	$1.43x10^{-5}$	42.0

References

[1] Wu N, Zong Z-M, Fei Y-W, Ma J. (2017). Studies on Thermal Oxidation Stability of Aviation Lubricating Oils. MATEC Web Conf. 114

[2] Wirtz RH, Zeman A. (1987). Spontaneous ignition temperatures of aviation turbine oils. Thermochimica Acta. 112: 2

[3] Novotny-Farkas F, Baumann K, Leimeter T. (2008). Optimizing the Thermo-Oxidation Stability of Gas Turbine Oils. Goriva i Maziva. 47: 3

[4] Mathura S. (2020). Lubrication Degradation Mechanisms: A Complete Guide. 1st ed. CRC Press. Boca Raton, FL.

[5] Gatto VJ, Moehle WE, Cobb TW, Schneller ER. (2006). Oxidation Fundamentals and Its Application to Turbine Oil Testing. J. ASTM Int. 3: 4

[6] Exxon Mobil Corporation. available at https://web.archive.org/web/20230609223051/ https://www.exxonmobil.com/en/aviation/knowledge-library/resources/engine-oil-coking.

[7] Kauffman RE, Feng AS, Karasek KR. (2000). Coke Formation from Aircraft Turbine Engine Oils: Part I - Deposit Analysis and Development of Laboratory Oil Coking Test. Tribol. Trans. 43: 4

[8] Loomis WR. (1976). Aircraft Engine Sump-Fire Studies. NASA Aircraft Safety and Operating Problems Conference. Hampton, VA, 19770011160.

[9] Hameed DK. (2021). Deterioration in Physical Engine Oil Properties after Different Trip Length. Kurd. J. Appl. Res. 6: 1

[10] Luo S, Xu D, Song J, Liu J. (2021). A review of regenerative cooling technologies for scramjets. Appl. Therm. Eng. 190

[11] Anderson A. in: Precision Combustion Inc. (Ed.).

[12] Cooper SP. (2022). High-Temperature Ignition Kinetics of Lubricating Oils. Ph.D. Dissertation, Texas A&M University. College Station, TX

[13] Abulail M, Cooper SP, Mohr DJ, Petersen EL. (2025). An improved endwall-injection technique for examining high-temperature ignition of lubricating oils in shock tubes. Rev. Sci. Inst. 96: 1

[14] Wang H, Xu R, Wang K, Bowman CT, Hanson RK, Davidson DF, Brezinsky K, Egolfopoulos FN. (2018). A physics-based approach to modeling real-fuel combustion chemistry - I. Evidence from experiments, and thermodynamic, chemical kinetic and statistical considerations. Combust. Flame. 193

[15] Xu R, Wang K, Banerjee S, Shao J, Parise T, Zhu Y, Wang S, Movaghar A, Lee DJ, Zhao R, Han X, Gao Y, Lu T, Brezinsky K, Egolfopoulos FN, Davidson DF, Hanson RK, Bowman CT, Wang H. (2018). A physics-based approach to modeling real-fuel combustion chemistry – II. Reaction kinetic models of jet and rocket fuels. Combust. Flame. 193