ABSTRACT

Assessment of MON-25/MMH Propellant System for Deep-Space Engines

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Hypergolic propellant system of oxidizer MON-25 and fuel MMH has been considered in propulsion trade studies for NASA science mission concepts. A propulsion system using this bi-propellant combination will be capable of operating at a lower temperature as compared to traditional MON-3/MMH for heater power reduction. Operation robustness can also be realized since such a propellant system is utilized under a wide range of temperatures.

Propulsion system designs and engine test programs for MON-25/MMH have been carried out since 2008. Several engine development programs have been conducted. The thrust classes of 22-Newton [5-lb_f] and 445-Newton [100-lb_f] were tested with the capability of a pulse mode operation for a wide range of duty cycles. Additional engine development tests are followed. Outcomes of the development efforts suggest that there is a balance of mission benefits and potential engine design and operation challenges, although the propellants can handle a low temperature.

This paper will report an assessment of using the MON-25/MMH system for deep-space application.

Nomenclature

AR	Aerojet Rocketdyne
^oC	Celsius, unit of temperature
EC	Europa Clippers, name of NASA mission studied
^oF	Fahrenheit, unit temperature
ILN	International Lunar Network, name of NASA mission studied
JPL	Jet Propulsion Laboratory
kPa	Kilo Pascal, unit of pressure
lb_f	Pound force, unit of force
MMH	Monomethyl Hydrazine
MON	Mixed oxides of nitrogen
NASA	National Aeronautics and Space Administration
NO	Nitric oxide
NTO	Nitrogen tetroxide
psia	Pound force per square inch, unit of pressure

Introduction

In the past decade, NASA has formulated science mission concepts with an anticipation of landing a spacecraft on the lunar surface, meteoroids, and other planets. Advancing thruster technology for spacecraft propulsion systems has been carried out with an intent of improving operation robustness and lowering system mass to maximize science payload.

Hypergolic bi-propellant nitrogen tetroxide (NTO) N_2O_4 and monomethyl hydrazine (MMH) $CH_3N_2H_3$ propulsion has been extensively used on enormous NASA programs - Apollo, Space Shuttle, and deep-space mission spacecraft. Such systems have been operated with nominal propellant temperature between ~15^{o}C [60^{o}F] and ~27^{o}C [80^{o}F], although they were designed for a slightly wider temperature range. The propulsion temperature is maintained with active thermal system required power. It should be noted that the freezing temperature of NTO is -11^{o}C [12^{o}F] while the one of MMH is around -52^{o}C [-62^{o}F]. Hence, depressing the freezing of oxidizer to the temperature similar to MMH would enable propulsion operation at low temperature. The benefits would not only relax the heater power requirement, but also provide capability of operating at a wider temperature range suitable for missions having a large temperature change.

For decades, from the 1940's up to the 1970's, a great deal of efforts(1, 2) was put into testing and characterizing the various mixture ratio of nitrogen tetroxide and nitric oxide, called mixed oxides of nitrogen (MON), including MON-25. Oxidizer MON-25 is a mixture of 75% nitrogen tetroxide, N_2O_4, and 25% nitric oxide, NO, in mass. In addition to that initial work completed, the Jet Propulsion Laboratory (JPL) in the 1990's funded work at Atlantic Research Corporation (now Moog)(3) and Kaiser Marquardt (now Aerojet Rocketdyne (AR))(4) testing existing MON-3/MMH thrusters with MON-25. Some performance losses were noted from these two test activities, but on the whole they were both largely successful in demonstrating the use of MON-25 in thrusters designed for MON-3. In more recent years, several engine development test programs as part of MON-25/MMH engine technology maturation, have been conducted by Rocketdyne (now AR)(5). The propellant system was considered for operating at wide range of temperatures, with design margin included, from 50°C (122°F) down to –30°C (–22 °F). The programs aimed to be lightweight and efficient in terms system volume and packaging. The thrust classes of 22-Newton [5-lb_f] and 445-Newton [100-lb_f] were tested with the capability of a pulse mode operation for a wide range of duty cycles. Though the test results and data are company proprietary, the overall results and lessons learned from their activities agree with what has been learned in the other programs.

Under NASA exploration roadmap(6) formulated in 2013, technology developments for precursor missions to advance the state of the art for eventual human missions to Mars were conducted. MON-25/MMH propulsion system was selected for a trade study for robotic Moon missions such as International Lunar Network(7) (ILN) and then Resource Prospector(8). The study concludes that using existing miniaturized MON-25/MMH thrusters for the lander stage of the vehicle would offer the lightest weight, and would reduced heater requirements. The missions would also provide an opportunity for demonstration of new technology for future missions. However, the thrusters may need to be re-qualified for in-space applications. It would be the first time such a MON-25/MMH system will be used in space with a wide range of temperature operations.

Other assessments of MON-25 and analyses have been performed for Europa Clipper[9] (EC) in recent years. Preliminary analyses were also performed to examine the impacts of the temperature extremes associated with the EC mission, assuming a Venus flyby. The results from those analyses confirmed that the high vapor pressure of MON-25 at elevated temperatures could have significant implications with respect to a number of mission and hardware requirements, including tank design and maximum design pressure of the system. Because the EC mission is currently designing for a potential Venus flyby prior to Jovian orbit insertion, and therefore must operate in both a warm and cold environment, this characteristic of MON-25 makes the design of the propulsion system much more challenging. Based on the information and data gathered for this assessment and others performed in the past by JPL[10], it was concluded that MON-25 is a potentially workable solution for the EC propulsion system. However, the adoption of MON-25 for EC will require the initiation of additional risk mitigation and design and development activities early on in the system design process.

As previously stated that there is a great interest of lowing the freezing of oxidizer to the temperature similar to the one of MMH. While both propellant systems, MON-3/MMH and MON-25/MMH, have similarities in propulsion system design, component hardware, and performance, the addition of NO to NTO results in the freezing point depression and in an increase in the vapor pressure compared to pure NTO with only a slight decrease in energy and density. This paper will primarily focus on the discussion of oxidizer MON-25.

Characteristics of MON-25 properties

Hypergolic propellants have been of great interest for in-space propulsion systems. Extensive research, tests, and data collection[1, 2] were conducted and documented with a lot of necessary information needed when it comes to propellant selection. Relationships for propellant properties were established. Tests for material compatibility were performed. A wealth of data on MON with various percentages of nitric oxide was compiled. Aside from its high vapor pressure, MON-25 is quite similar to NTO. The density, thermal and chemical properties of MON-25 are well characterized. Other unique properties - freezing point, vapor pressure, viscosity, and material compatibility can appeal for some applications and not for others. This paper will discuss these properties at length and highlight major effects of them in the propulsion design and operations.

Low freezing temperature:

Historically, nitric oxide was initially used as an inhibitor on nitrogen tetroxide propellant to resolve stress corrosion issues. Adding 1% and then 3% of NO to NTO, designated as MON-1 and MON-3, would reduce acceptable amount of iron nitrate in the oxidizer. As nitric oxide content is increased in the mixture, its freezing temperature also reduces. Increasing nitric oxide content to 10% (MON-10) and then 25% (MON-25) to depress the freezing point of the oxidizer were considered in several NASA programs. Using equations from a curve fit of test data[1], the freezing temperature as function of nitric oxide percentage in mass is plotted and presented in Figure 1. As seen from the plot, the freezing temperature is changed from -13^oC [9^oF] with 1% of NO added to the mixture down to -55^oC [-67^oF] when 25% of NO in the mixture. It should be noted that fuel MMH is frozen around -52^oC [-62^oF], similar to the one of MON-25. Hence, selection of MON-25 for its hypergolic fuel companion MMH would be easy in the thermal management respective and attractive for in-space propulsion application.

With respect to a concern of NTO crystallization at low temperature, experiments(2) of freezing MON-25 were carried out. It was observed that as temperatures approached -45^oC [-49^oF], NTO in MON-25 mixture would begin to crystallize. The results suggested that MON-25 should only be used in rocket engines at above -40^oC [-40^oF]. More recent testing and reports on this subject, along with feedback from both JPL and NASA White Sand Test Facility, suggest that those finding may have been inaccurate. During the time in which that report was published, the filtering requirements were much less stringent and therefore the quality of propellants was much lower than in the present day. The presence of particulate within the propellant used for that testing could have provided potential nucleation sites for premature N2O4 crystallization. In fact, it was noted in that report that the first test run had “many visible solids” present within the propellant sample, and the second test run used “filtered MON-25”. The inconsistencies between these reports suggest the lack of MON-25 property data at those extreme low temperatures. Regardless to the new finding, it may be appropriate to limit the temperature above -40^oC [-40^oF].

During a program planning exercise for ILN(5) (consideration of launching multiple lunar landing spacecraft capable to carry instrumentation payload weighted several kilograms), MON-25/MMH propulsion was selected at a baseline design. The outcomes of preliminary designs indicate that when propellants are loaded at the room temperature, the system temperature, with the propulsion only using a passive thermal protection, may be dropped down to -4^oF [-20^oC] at the time of the final lunar landing approach. Consequentially, the design does not need to accommodate an active heater system. Including the design margin, engine demonstration was planned with the propellant temperature range from 32^oC [90^oF] to -30^oC [-22^oF].

For Mars missions with consideration of the planet environments, the freezing point of MMH and MON-25 is below -40^oC [-40^oF] which approximates the diurnal average temperature on Mars. There has been a strong interest of using MON-25 for such missions. A propulsion team at JPL assessed engine injector design characteristics(11), including injection techniques, propellant atomization, etc. to address major concerns in regard to potential ignition delays. At -40^oC [-40^oF], MMH viscosity difference between the two propellants could possibly influence the atomization and breakup of the liquid sheet generated from MMH and MON-25 injection jet impingement. A result of any possible long ignition delays would lead to the combustion chamber over-pressurization which could have catastrophic mission failures. Ignition characteristics of MMH and MON-25 at propellant temperatures of 20^oC [68^oF] to -40^oC [-40^oF] were investigated. The hot fire test results showed that the rate of increase in ignition delay was much lower than anticipated. The ignition delay difference between the two hot fires at 20^oC [68^oF] to -40^oC [-40^oF] was about 3 msec. The study also discovered that as the propellant temperature and the thruster assembly initial temperature decreased, the accelerometer trace indicated a more quiet start.

It should be stated that there are a couple potential drawbacks of operating a propulsion system at low temperature. Most components used on existing hypergolic propulsion systems have not operated with low temperature. The components must be re-qualified or may need to be redesigned to accommodate for use in the low temperature environments. Because of the low temperature, more pressurant, such as helium, would be required to pressurize propellant tanks as compared to systems at higher temperature.

With the regard of using the oxidizer at elevated temperature, tests to characterize MON-25 up to 56ºC [133ºF] were performed[2]. The results indicate that the high temperature behavior of MON-25 shows no anomalies and no pressure hysteresis was observed. The diffusion rates of the vapors in the ullage space are rapid are enough to return into the liquid as temperature decreases.

Vaporization:

As it has been discussed, the primary benefit of mixing NO into N_2O_4 is to depress its freezing point. On the other hand, the addition of NO has a subsequent effect of increasing the vapor pressure of the MON mixture. Vapor pressure curves, generated from curve-fit equation[1], for several mixed oxides of nitrogen as function of temperature are shown in Figure 2. At room temperature, MON-1 can retain its liquid form under ambient atmospheric pressure around 103 kPa [15 psia], while keeping MON-25 in the liquid phase requires a pad pressure at around 452 kPa [66 psia]. Hence, instead of unloading or loading propellant, such as MON-1, to tanks at the atmospheric conditions, the process of transferring liquid MON-25 must be performed under a pad pressure above 452 kPa [66 psia] and maintain this pressure level all time during the storage at the room temperature.

To take an advantage of the increase of the vapor pressure as adding more NO into the oxidizer mixture, a study [12] was conducted to look into a development of rocket engine using oxidizer MON-30 while ammonia was selected as a fuel. Liquid ammonia has a relatively high vapor pressure compatible with MON-30. According to the study, the propellant combination has desirable reaction properties and relatively high performance. However, the combustion of the two propellants must require an ignition source. To be treated as hypergolic propellant system, lithium was used as an additive for liquid ammonia. A series of engine hot-fire tests under this study showed that the engine was able to start over a wide range of conditions.

With the regard of MON-25/MMH system for a given temperature condition, there would be a mismatch in the vapor pressure between MON-25 and MMH. Figure 3 shows a comparison of vapor pressure between MON-25 and MMH. Generally speaking, the vapor pressure mismatch can be accommodated through the system and component designs. For a mission that the temperature may fluctuate due to the change in the space environments, propulsion system of MON-25/MMH can be susceptible and operate at a wider temperature swing than NTO/MMH. This benefit is due to the fact of the low freezing temperatures of MON-25 and MMH. However, as shown in Figure 3, there is a drastic change of the vapor pressure of MON-25 from one temperature value to another as compared to its companion MMH. As temperature change from -38ºC to 80ºC, the vapor pressure of MMH increases approximately 7 kPa while the increase on MON-25 is up to 540 kPa. Significant increase in the vapor pressure of MON-25 at the elevated temperatures can have repercussions with respect to tank design and the maximum design pressure of the system. The EC mission is currently designing for a potential Venus flyby prior to Jovian orbit insertion, and therefore must operate in both a warm and cold environment, this characteristic of MON-25 makes the design of the propulsion system much more challenging. Based on the information and data gathered for this assessment and others performed in the past by JPL[10], it was concluded that MON-25 is a potentially workable solution for the EC propulsion system. However, the adoption of MON-25 for EC will require the initiation of additional risk mitigation and DDT&E (design, development, test and evaluation) activities early on in the system design process.

Per feedline system and engine design perspectives, as liquid MON-25 flows through sharp-curvature lines and abrupt geometries, such as forward or backward steps, cross-section expansion, etc., local flow-field pressure can be dropped below the propellant vapor pressure. Subsequently, isolated gaseous bubbles of MON-25 are formed. The bubbles can be collapsed as traveling downstream. This phenomena causes undesirable propellant flow oscillations that can lead to chamber pressure fluctuations. For certain conditions, especially in the engine injector manifold, the MON-25 bubbles can entrain through the injection orifices. This result in rough combustions. One way for reducing these issues is to design the flow geometry with less local pressure drop and also to operate the system at high pressure to ensure the local pressure drop to be above the vapor pressure.

Viscosity:

Dynamic viscosity of MON-25 and MMH plotted against temperature are shown in Figure 4. As it would be expected, the viscosity of the fluids would increase as the temperature reduces. The change in viscosity of MON-25 is gentle and behaves well. In contrast, the trend of MMH viscosity is similar to the one of MON-25 down to 0^oC [32^oF]. However, as can be seen from the plot, the rate of MMH viscosity drastically picks up when the temperature is below 0^oC [32^oF]. The exponential increase of MMH viscosity at the low temperature range would become challenging in system design when the temperature swing below 0^oC [32^oF] is anticipated. A propulsion system can be optimized for one condition, but would not be for another temperature.

From the engine performance perspective, drastic increase in viscosity from reducing temperature would cause a flow changing from turbulent regime to a laminar one through the injection orifices. Such a change in the flow conditions has strong effects on the propellant injection characteristics which have consequences in atomization, combustion performance, and behavior (chug, instability, etc.). To compensate for this undesirable situation, the system may need to run at high pressure and the temperature swing may be limited a certain range to avoid extreme low temperature.

Material compatibility:

It is well known that there has always remained corrosion-related problems due to the fact that NTO reacts with surfaces of stainless steels, such as on propellant tanks, tubing, valves, etc., formulating iron nitrate product[13]. If the propellant becomes saturated with the corrosion product, solid particles may precipitate from the liquid and could pose a threat to the operation of the propulsion system. Over the years, hypergolic bi-propellant propulsion designers have learned that by mixing some amount of NO to NTO, the iron becomes somewhat soluble. MON-1 and MON-3 (1% and 3% of NO in the mixture, respectively) have been used on actual propulsion systems. It is observed that the solubility of the iron in MON-3 is higher than MON-1. Although not aware of any further study on higher NO contents in the oxidizer, one can concludes that MON-25 has more benefits of reducing the corrosiveness of materials since more nitric oxide content on MON-25 would further reduce formulation of iron nitrate.

Summary

Assessments of using MON-25 as an oxidizer in propulsion systems for deep-space missions are reported. The assessments are based on literature surveys and collective understanding from system trade studies as well as some practical engine designs and tests. Pros and cons of MON-25 utilization in spacecraft application are summarized as follows:

Pros:

- Mixing additional NO into NTO, particularly with 25% of NO in mass, results low freezing point for the mixture. Subsequently, using MON-25 for in-space propulsion system would reduce heater power requirements and increase operation robustness.
- Propulsion system of MON-25/MMH is capably susceptible and operate at a wider temperature swing than NTO/MMH.
- Since both MON-25 and MMH have a similar freezing point around -50oC. With a concern of NTO crystallization at low temperature, MON-25 should only be used in rocket engines at above -40oC [-40oF].
- It was experimentally observed that engine has more quite [soft] start when the initial temperature of the engine and propellants are low.
- High temperature behavior of MON-25 shows no anomalies and no pressure hysteresis was observed. The diffusion rates of the vapors in the ullage space are rapid are enough to return into the liquid as temperature decreases.
- Liquid ammonia has a relatively high vapor pressure compatible with MON-30. Engine hot-fire tests show ammonia with lithium additives reacts hypergolically with MON-30.
- MON-25 may have more benefits of reducing the corrosiveness of materials than MON-3 since more NO content in the oxidizer would further reduce formulation of iron nitrate.

Cons:

- Significant increase in the vapor pressure of MON-25 at the elevated temperatures can have repercussions with respect to tank design and the maximum design pressure of the system.
- As liquid MON-25 flows through sharp-curvature lines and abrupt geometries, bubbles are formed due to local flow-field pressure is dropped below the propellant vapor pressure. This phenomena causes undesirable propellant flow oscillations that can lead to chamber pressure fluctuation.
- Hot-fire tests of engine indicates the ignition delay difference between 20oC [68oF] and -40oC [-40oF] is about 3 msec. It is much less than anticipated.

- Most existing propulsion components have been used at normal benign temperature. They may need to be re-qualified or redesigned to accommodate for use in the low temperature environments.
- Because of the low temperature, more pressurant, such as helium, would be required to pressurize propellant tanks as compared to systems at higher temperature
- Regarding MON-25/MMH system, a drastic increase of MMH viscosity when the temperature swing below 0oC [32oF] would become challenging in system design. Such a change in viscosity has strong effects on the propellant injection characteristics.

Conclusion

For deep-space missions, spacecraft often faces extreme temperature environments throughout its flight duration. In comparison with its MON family, such as widely used MON-1 and MON-3, oxidizer MON-25 can offer a capability of operating at lower temperature and a wider temperature range. Subsequently, MON-25 benefits the reduction of heater power requirement and robustness in operation.

High vapor pressure of MON-25 can hinder a desire of its use in a practical application, especially for a mission on which a large environmental temperature swing is anticipated. Although oxidizer MON-25 and its companion fuel MMH have a similar freezing point, an exponential increase in viscosity of MMH when reducing in temperature below 0oC [32oF] poses a unique challenging in propulsion system and engine designs. A way of overcoming these disadvantages is to operate the system at optimal pressure and to limit the temperature, particularly at the low end of the temperature.

Overall, a comprehensive trade study should be conducted when selecting MON-25 as a propellant for spacecraft. Depending missions, MON-25 can be attractive for certain missions while it may be not a great payoff for others.

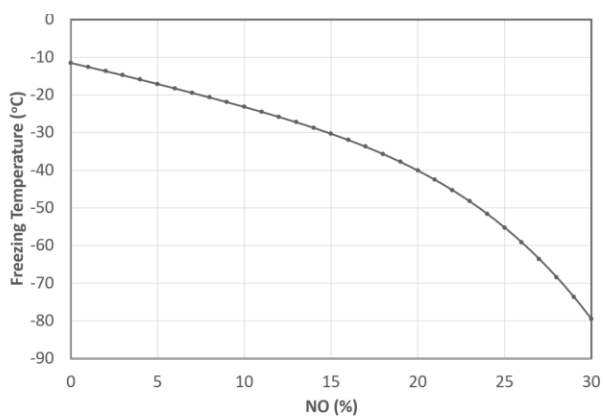

Figure 1: Freezing Temperature Reduction of MON with Increase of NO in the mixture

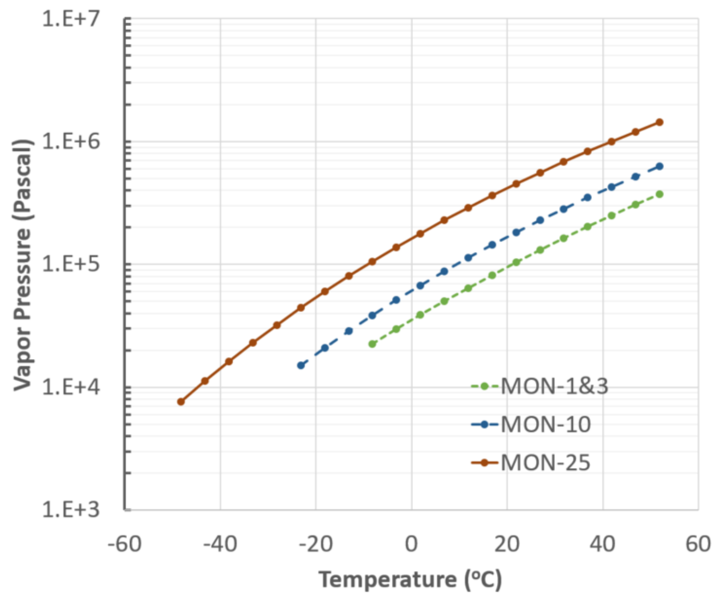

Figure 2: Vapor Pressures of Mixed Oxides of Nitrogen at Various Temperature

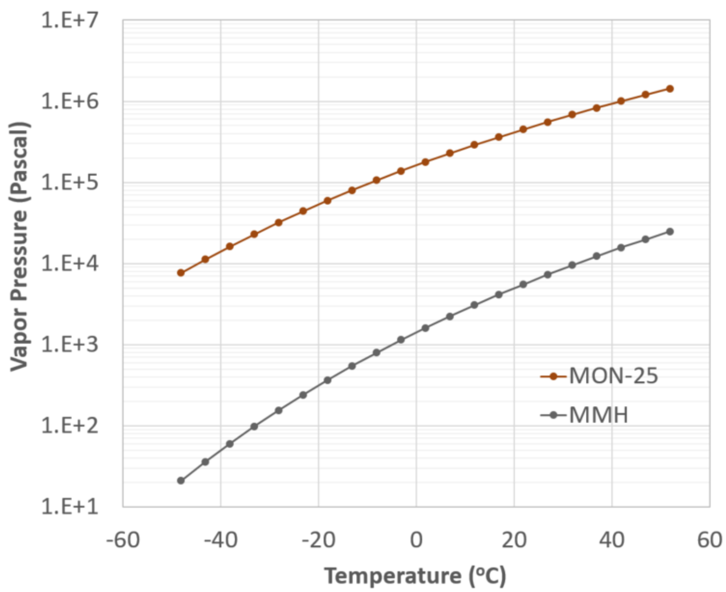

Figure 3: Comparison of Vapor Pressure of MON-25 and MMH

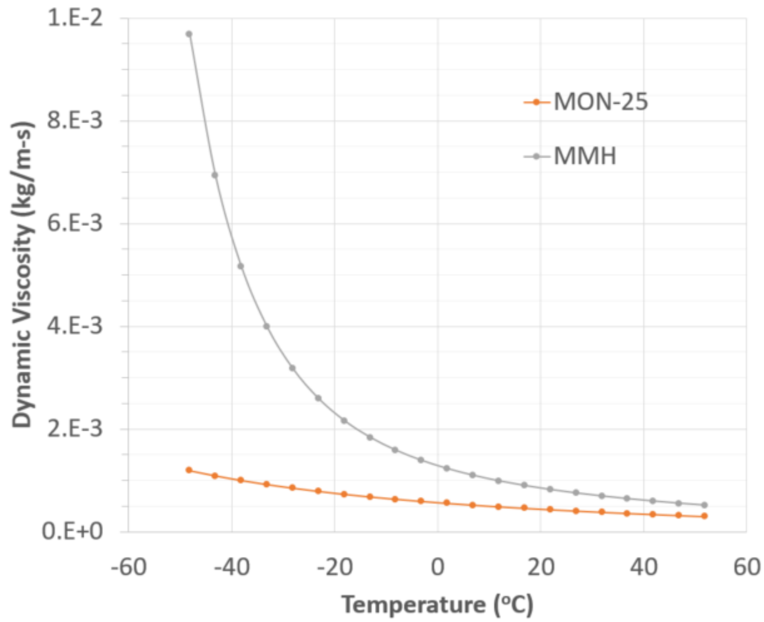

Figure 4: Comparison of Dynamic Viscosity of MON-25 and MMH

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