Project title: Enhancing Lubrication Characteristics of Soybean-Based Oils as a Multifunctional Biobased Lubricant

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Research Objectives: The primary objective of this proposed research is to establish soybean-based oil as a next-generation multifunctional bio-lubricant and a major substitute for mineral-based lubricants. The proposed research will build the framework for these goals by investigating the effects of novel chemical modification protocols to formulate high-performance lubricants from raw soybean oil and enhance its surface protection behavior by mixing it with select additives.

Completed Work: In this project two different types (regular and high oleic) of soybean oil have been procured. Necessary chemical compounds for chemical modification and ionic liquid (IL) additives have been arranged. A new sample holder for tribological testing has been designed and developed and test conditions for tribological testing have been finalized. Preliminary tribological tests using both regular and high oleic soybean oils have been conducted and wear tracks have been analyzed via profilometry and microscopy techniques. Protocols to additize soybean oils with ILs have been finalized and stabilization tests for IL additized soybean oils are currently under process. Parallelly, chemically modified high oleic soybean oils have been prepared and a group of physio-chemical and rheological tests have been performed.

Preliminary Results: Major research findings from the preliminary efforts are depicted below.

Materials: We are using raw soybean oil and high oleic soybean oil as our base oils. Two different ionic liquids (ILs) are procured to use as additive to soybean oil which are [P4444] [DEHP] (tetrabutylphosphonium bis (2-ethylhexyl) phosphate) and [P8888] [DEHP] (tetraoctylphosphonium bis(2-ethylhexyl) phosphate). AISI 52100 steel will be used as flat and slided against silicon nitride balls for friction and wear testing under controlled test conditions as depicted below.

Tribological process parameter design: Process parameters for the friction and wear testing have been finalized to simulate gear or bearing contacts for automotive components. The parameters are: applied load-75N, resulting Hertzian contact pressure 1.9 GPA, sliding velocity 0.1 m/s with stroke length 10 mm for a total sliding distance of 500m.

IL additization with soybean oil: We are using a hot plate magnetic stirrer for mixing IL with the soybean oil. At first, the weight of the beaker is measured with the help of a weighing machine. Then the oil is poured into the beaker. Afterwards, a certain weight percentage of IL is mixed into the beaker. The beaker is kept in the hot plate magnetic stirrer and covered up with a lid. Finally, the mixture is stirred for 30 min at 70º C temperature. As of now we prepared three different IL additized solutions with weight percent of 1,3 and 10%.

Design and development of small-scale sample holder: It is necessary to have capability run tribological tests using smaller quantity of lubricants for research purpose because we have limited amount of ILs and we can't prepare huge amount of chemically modified oil based on funding resource as of now. Keeping that in mind, a sample holder has been designed (Figure 1) where only 10 ml of lubricant is needed to run one tribological test as compared to 35 ml required lubricant in normal sample holder. The final version was made with A36 Alloy Steel which can allow us to run tests at higher temperature (100ºC).

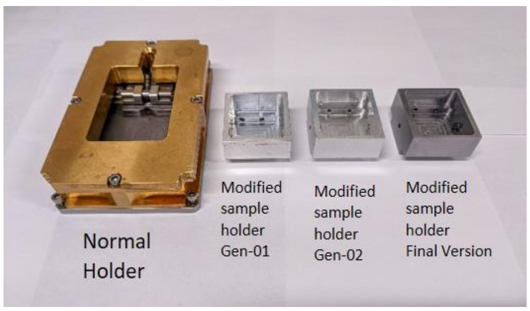

Figure 1: Sample holder development for tribo-tests

Once the sample holder is modified, it is necessary to conduct tribological tests using both normal and small-scale holder to make sure that the sample holder modification did not impact the friction and wear characteristics. Tribological tests under soybean oil lubricated conditions were conducted and we observed comparable friction and wear behavior under both sample holder conditions confirming usability of the newly developed small size holders for future tribo tests. The friction and wear behavior of the confirmation tests are presented in Figure 2.

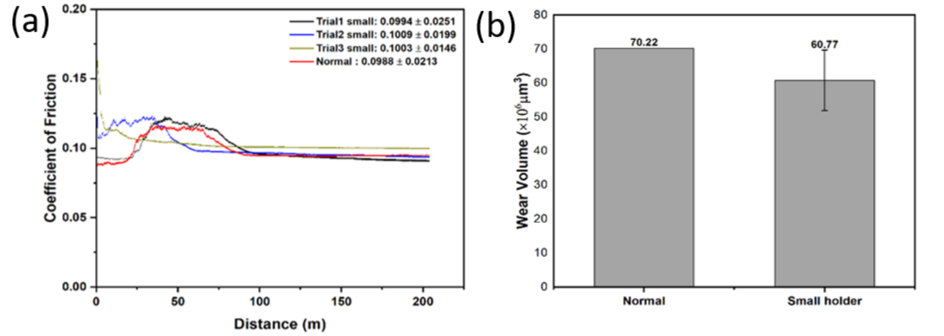

Figure 2: Comparative friction and wear behavior from tests using fabricated small sample holder and normal holder (a) Coefficient of Friction (b) wear volume. Tests were carried out for 200m sliding distance, 50N load and 5 Hz sliding frequency in soybean oil lubricated conditions.

Tribological behavior of raw soybean oil: Friction and were tests were conducted in Dr. Roy's lab with raw and high oleic soybean oil under controlled test conditions as mentioned before. Two repeat tests on each case were performed and high oleic soybean oil resulted slight decreased friction coefficient and enhanced wear resistance as compared to raw soybean oil. The friction and wear behavior for raw and high oleic lubricated soybean oils are presented in Figure 3 and 4 respectively. For each tribological tests, instantaneous normal load and resulting lateral loads were captured and coefficient of friction is calculated. Post experiment, the wear tracks were analyzed using white light interferometry technique to measure the wear track depth and wear volumes in each case. The wear track volume was slightly deeper in raw soybean oil (depth 11 µm) case as compared to that of high oleic soybean oil (approximate depth 10 µm) which is consistent with the wear volume measurements. The two-dimensional wear track depth profiles in each case is presented in Figure 5.

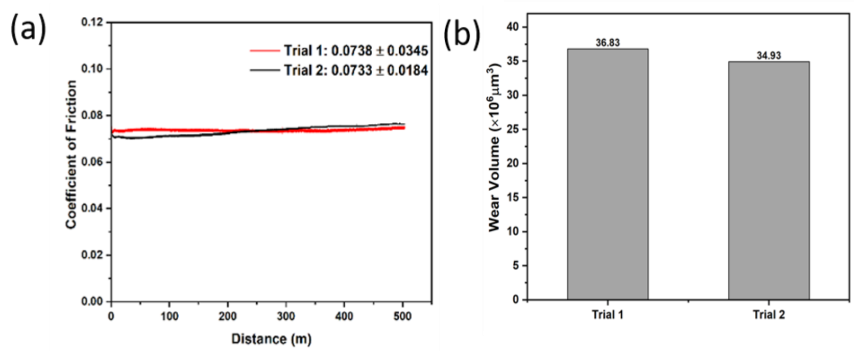

Figure 3: Preliminary tribo test results using raw soybean oil (a) Coefficient of friction (b) wear volume.

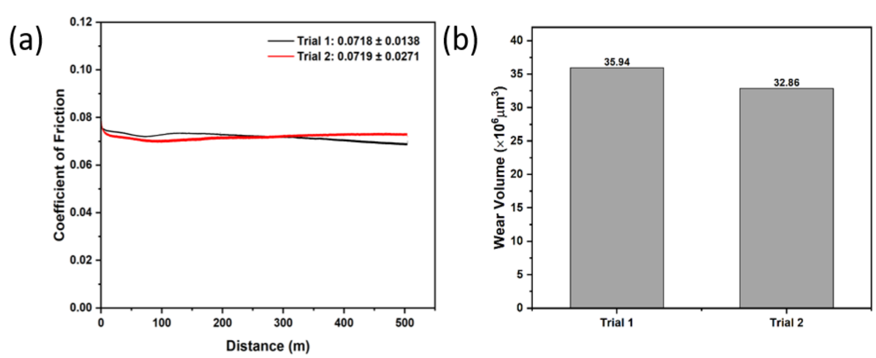

Figure 4: Preliminary tribo test results using high oleic soybean oil (a) Coefficient of friction (b) wear volume.

We are currently observing the stability of IL additized oils to make sure the additives are properly mixed with the base oils (regular and high oleic). Next, we will conduct tribological tests to observe if there is any benefit from frictional behavior or wear resistance due to addition of ionic liquids with the soybean oils. On a separate approach, we are collaborating with Agricultural Research Service, USDA laboratory to chemically modify the soybean oil in order to develop high performance lubricant. This involves chemical modification, physio-chemical property analysis of chemically modified oils and tribological testing. In that route, high oleic soybean oil only has been selected for chemical modification based on its chemical structure and ability to enhance high temperature thermo-oxidative behavior. After chemical modification, a group of physio-chemical and rheological analysis were conducted. In future, we will conduct remaining property analysis along with tribological tests to compare the friction and wear behavior of chemically modified high oleic soybean oil as compared raw high oleic soybean oil. The completed research activities in this route are depicted below.

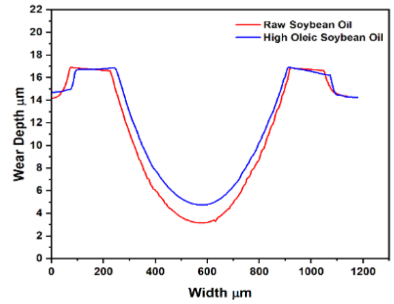

Figure 5: Comparison of the wear depth measured after tribology test using raw soybean oil and high oleic soybean oil

Analysis of fatty acid chain in regular (RSOY) and high oleic soybean oils (HOSOY): GC-MS analysis was carried out to determine the fatty acid composition of RSOY and HOSOY. According to the GC-MS analysis (spectra are not provided) the compositions of RSOY and HOSOY are as follows:

RSOY:	Palmitic acid:	10.9%
	Stearic acid:	3.4%
	Oleic acid:	22.6%
	Linoleic acid:	56.4%
	Linolenic acid:	6.5%
HOSOY:	Palmitic acid:	6.4%
	Stearic acid:	3.7%
	Oleic acid:	83.5%
	Linoleic acid:	6.3%

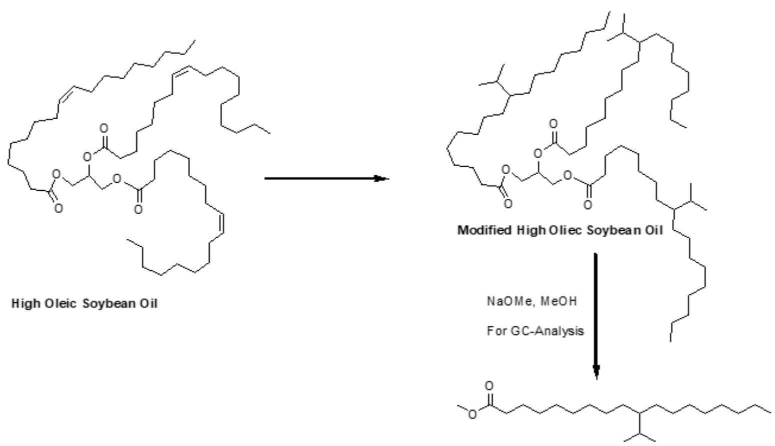

Figure 6: Iso-propylation of HOSOY and formation of fatty acid methyl esters for GC-MS analysis.

Chemical modification of HOSOY: Based on the analysis of fatty acids on both regular and high oleic versions, high oleic soybean oil was selected for chemical modification. The synthesis of chemically modified HOSOY or iso propyl branched HOSOY (BHOSOY) from HOSOY is shown in Figure 6. The major objective of this chemical modification is to break C-C double bonds to single bond which may enhance the thermo-oxidative behavior of branched HOSOY (or BHOSOY).

Structural Characterization of BHOSOY

NMR Analysis: ^{1}H spectra was obtained in deuterated chloroform ($CDCl_3$) on 600 MHz NMR spectrometers (Bruker Corporation, Billerica, MA, USA) equipped with 5-mm BBO probe. Chemical shifts are reported in parts per million (ppm) from

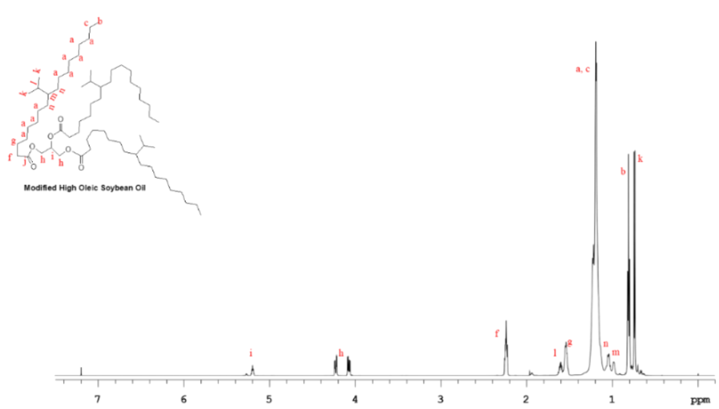

Figure 7: ^{1}H NMR of BHOSOY. Spectral peaks of BHOSOY are assigned with their corresponding protons in letters.

tetramethylsilane in Figure 7 and 8 for ^{1}H NMR NMR data clearly shows the structural configuration of the product as expected.

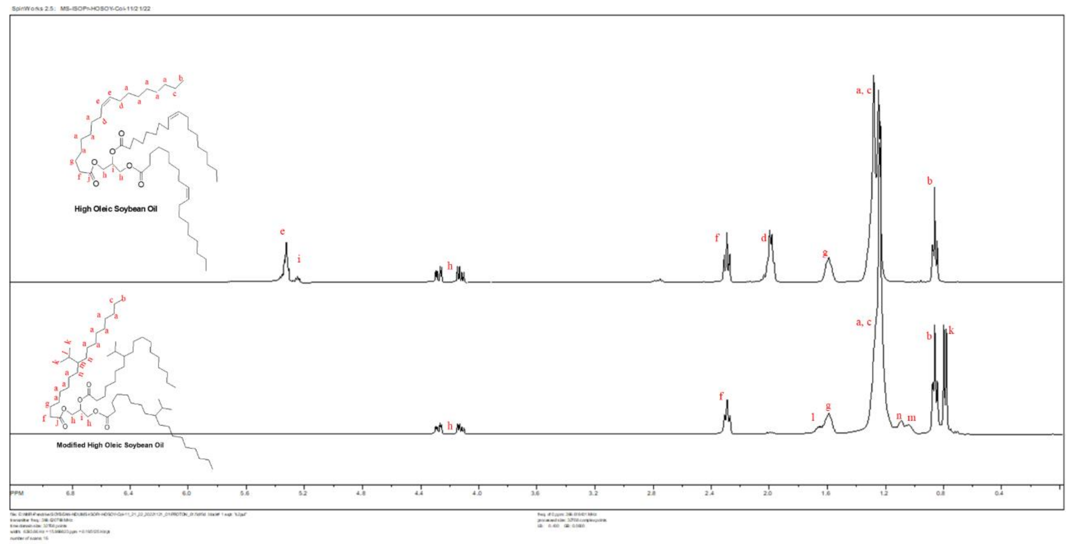

Figure 8: Comparison between the ^{1}H NMRs of HOSOY and BHOSOY. Spectral peaks are assigned with their corresponding protons in letters.

Property analysis of regular, high oleic and chemically modified oils: Major property analysis results on three different sets of oils are tabulated below (Table 1). We could successfully increase the viscosity of chemically modified HOSOY significantly which can help enhancing friction and wear behavior during tribo tests.

Table 1: Measured rheological and physical properties of different sets of soybean oils

	Temp, °C	RSOY	HOSOY	BHOSOY
Density (g/cm3)	40	0.9066	0.8993	0.8965
	100	0.8668	0.8596	0.8573
Kinematic viscosity (mm2/s)	40	30.69	38.93	142.13
	100	7.53	8.49	19.39
Dynamic viscosity (mPa/s)	40	27.83	35.02	127.42
	100	6.53	7.30	16.62
Viscosity Index		228.3	203.6	155.9

Work to be completed: As mentioned earlier, we would like to conduct tribological tests to understand the friction and wear behavior of IL additized and chemically modifies soybean oils to establish our novel approaches in order to enhance the lubrication characteristics of raw soybean oil. A couple of chemical analysis in particular ^{13}C NMR and Heteronuclear Single Quantum Coherence (HSQC) spectra will be captured on BHOSOY for further identification of the chemically modified product. GC-MS chemical analysis on both HOSOY and BHOSOY will be conducted to compare the molecular weight and chemical changes. High temperature thermo-oxidative behavior will be captured on these oils using PDSC testing. Pour point and cloud point temperature will reveal the low temperature characteristics of these oils. Finally, after tribological tests, the wear tracks and counter specimens will be analyzed using scanning electron microscopy and energy dispersive X-ray spectroscopy to understand the changes in wear mechanisms under different lubricating oil types. The overall findings will be captured in a technical report and presented to ND Soybean Council at the end of this project period.