MSU-NORTHERN BIO-ENERGY CENTER OF EXCELLENCE

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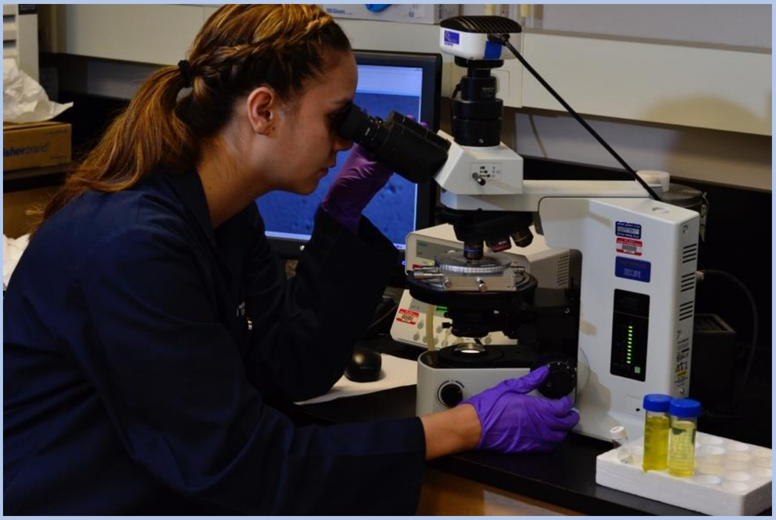

Greg Kegel
Chancellor, Principal Investigator
Montana State University Northern

Jessica Windy Boy
Director
Bio-Energy Center

Randy L. Maglinao, PhD
Senior Research Scientist
Bio-Energy Center

Md. Joynal Abedin, PhD
Senior Research Scientist
Bio-Energy Center

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MSU-Northern
Bio-Energy Center

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EXECUTIVE SUMMARY

The goal of this project was to establish the Bio-Energy Center (the Center) of Montana State University Northern (MSUN) as a Regional Research Center of Excellence in research, product development, and commercialization of non-food biomass for the bio-energy industry. A three-step approach, namely, (1) enhance the Center's research and testing capabilities, (2) develop advanced biofuels from locally grown agricultural crops, and (3) educate the community through outreach programs for public understanding and acceptance of new technologies was identified to achieve this goal. The research activities aimed to address the obstacles concerning the production of biofuels and other bio-based fuel additives considering feedstock quality, conversion process, economic viability, and public awareness.

First and foremost in enhancing the capabilities of the Center is the improvement of its laboratories and other physical facilities for investigating new biomass conversion technologies and the development of its manpower complement with expertise in chemistry, engineering, biology, and energy. MSUN renovated its Auto Diagnostics building and updated its mechanical and electrical systems necessary to house the state-of-the-art 525kW (704 hp) A/C Dynamometer. The newly renovated building was designated as the Advanced Fuels Building. Two laboratories, namely Biomass Conversion lab and Wet Chemistry lab were also added to the Center's facilities. The Biomass Conversion lab was for research on the production of advanced biofuels including bio-jet fuel and bio-based fuel additives while the Wet Chemistry lab was used to conduct catalyst research. Necessary equipment and machines, such as gas chromatograph-mass spectrometry, were purchased and installed to help in research and testing.

With the enhanced capabilities of the Center, research and testing activities were very much facilitated and more precise. New biofuels derived from *Camelina sativa* (camelina), a locally-grown oilseed crop was developed through a chemical process for converting the oil extracted into jet fuel. Promising methods of synthesizing heterogeneous metal complex catalyst that support the chemical conversion process were likewise developed. Breaking-down lignin to valuable chemicals using a metal complex catalyst was also investigated. Lignin is an organic polymer that binds around cellulose and hemicellulose fibers which strengthen cell walls in woody biomass. Test results showed promise and could lead to further exploration of using lignin for fuels and fuel additives. These findings could create another value-added product from lignin that can be sourced from beetle kill trees and product residues from cellulose ethanol plants. Coupled with these research discoveries was the provision of technical support to businesses in terms of product development and commercialization of bio-based products. This in turn opened new avenues for advancing the bio-energy industry in the region and helped support the regional agricultural-based economy through developing biofuels derived from feedstock that are grown locally. It assisted in developing biofuels that reduce exhaust emissions and improve engine performance.

The growth of the bio-energy industry in the region is also dependent on the creation of a market for biodiesel in North Central Montana. The region is a very conservative region with an aging population and the culture of the community generally resists change and use new products, bringing a tough market for biodiesel and biodiesel blends. Local biodiesel producers worked for several years to get local fuel distributors to carry a 5% or greater blend of biodiesel only to be repetitively turned down. The strategy for biodiesel to penetrate the market is to educate the community about the benefits of using biodiesel, the third step of the approach. Fleet tests with local businesses that are recognized and respected in the community were run. If companies endorsed the use of biodiesel blends, the community would also be convinced of their use. The Center partnered with Opportunity Link and the North Central Transit to test the use of a 5-20% biodiesel blend in the Transit bus fleet. Opportunity Link assisted in the community promotion and support. The transit ran the biodiesel blend for over a year with no operation problems, including the effect of extreme cold winter months.

After the transit fleet test, a year-long study using a B20, blend of 20% by volume biodiesel was conducted with the Burlington Northern Santa Fe Railroad (BNSF). This test was the first of its kind for BNSF and the first locomotive fleet test conducted under the region's climate. The test was comprehensive and considered the effects of biodiesel on fuel filters, fuel consumption, and fuel injector wear. Two engines, hooked-up together, were used for the entire test. One engine used a regular diesel while the other used a B20 blend. Two sets of fuel injectors were pulled every three months and sent to the manufacturer for evaluation. BNSF did not experience any significant operability problems during the entire test. All the biodiesel used in the test was produced from Montana grown crops. The success of these tests gave confidence to fuel distributors and opened the market for B5, blend of 5% by volume biodiesel, with a local fleet fuel provider. Several fleets were exclusively fueled with the biodiesel blend in the summer including the Havre Public School System.

Emission effects of using "off-spec" biodiesel, biodiesel that failed one or more fuel performance properties required by the American Society of Testing and Materials (ASTM) were also investigated. The U.S. Environmental Protection Agency (EPA) requires all biodiesel producers to certify their fuel according to ASTM D 6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. Using a 2007 Cummins ISL diesel engine, diesel, canola biodiesel, canola biodiesel contaminated with methanol or oil, and aged canola biodiesel with high free fatty acid were tested and their exhaust emissions analyzed. Test results showed that canola biodiesel with 5% by mass of methanol had higher carbon monoxide emission than with canola biodiesel that passed ASTM D6751. Particulate matter (PM) emissions, also known as soot emissions, were high with canola biodiesel with methanol and with high free fatty acids. However, even with the relatively high exhaust emissions, the values from the "off-spec" biodiesel was significantly lower than a No. 2 ultra low sulfur diesel (ULSD).

ABOUT THE REPORT

This revised final report to the United States Department of Energy contains the outcomes resulting from the implementation of the *"MSU-Northern Bio-Energy Center of Excellence"* project from 2010 to 2014. The project team was composed of staff from the Bio-Energy Center, Montana State University Northern. The people listed below were the major personnel involved in this project.

1. Greg Kegel
2. Jessica Windy Boy
3. Dr. Nestor Soriano, PhD
4. Dr. Randy L. Maglinao, PhD
5. Dr. Md. Joynal Abedin, PhD
6. Akash Narani
7. Taylor Lyon
8. Keith Richardson

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1. PROJECT SUMMARY

Table 1 summarizes the goal, tasks, and accomplishments of the project in the form of a grid. The project's overall goal was to establish Montana State University Northern's Bio-Energy Center (the Center) as a Regional Research Center of Excellence in research, product development, and commercialization of non-food biomass for the bio-energy industry. To achieve this goal, the Center used a three-step approach, namely, (1) enhance the Center's research and testing capabilities, (2) develop advanced biofuels from locally grown agricultural crops, and (3) educate the community through outreach programs for public understanding and acceptance of new technologies. Major tasks were identified to support these three approaches.

Table 1. Goal, tasks, and accomplishments grid.

Project Goal: Establish Montana State University Northern's Bio-Energy Center (the Center) as a Regional Research Center of Excellence in research, product development, and commercialization of non-food biomass for the bio-energy industry.		
Tasks	**Objectives**	**Accomplishments**
1. Site Development of Bio-Energy Research Center	Renovate an old laboratory space to provide upgrades necessary for installation of equipment that would comprise the heavy-duty diesel engine performance test cell, biodiesel processing lab, and oil press lab.	Three laboratories namely, Biomass Conversion lab, Wet Chemistry/Synthesis lab, and Advance Heavy-Duty Engine Test lab, were established. **SUCCESSFUL**
2. Development of Alternative Bio-based Aviation Fuel	Explore a new platform to produce bio-jet fuel derived from lignin.	Lignin was separated using catalyst but was unsuccessful. An alternative approach was used and test results showed promise, although the Center was unable to produce a fuel from the lignin.
3. Development of Camelina Oil-derived Fuel for Naval Applications	Explore the development of a process technology based on alkene metathesis to produce fuel derived from non-food source intended for naval applications.	The Center discovered and patented a new process that converts camelina oil to jet fuel as well as other fuel types such as diesel, and navel fuel. **SUCCESSFUL**

4. Viability of Using Straight Plant Oils in Agricultural Operations	Establish a viable method of using straight plant oils as an alternative fuel in off-road diesel engines based on chemical, performance, and exhaust emission testing.	Successfully pressed different oilseeds grown in Montana including camelina, safflower (2 varieties), and canola. Investigated different refining and purifying techniques to improve the quality of oil for fuel applications. The techniques researched included chemical degumming, filter pressing, bleaching, and centrifugation. Ran different refined oils in a Caterpillar CAT 3176 diesel engine to evaluate how each oil performed in industrial diesel engines. Investigated using Waste Vegetable Oil (WVO) on a 2007 Cummins ISL diesel engine but the runs were unsuccessful. It was observed that the ECM of the engine was getting erroneous calculations and readings when operated at higher loads. This forced the ECM to shut down the engine as safety feature programmed in the engine. **SUCCESSFUL**
5. Performance of Locomotive Engine Fueled with Biodiesel Blend	Increase public awareness in the benefits of using locally produced biodiesel at the local railroad company.	Performed a year-long study with BNSF train engines in Havre, MT rail yard. **SUCCESSFUL**
6. Engine Exhaust Emissions of “Off-Spec” Biodiesel	Assess the possible environmental and health hazards associated with burning “off-spec” biodiesel in heavy duty highway diesel engines by collecting exhaust emission data.	Compared engine performance and exhaust emissions of diesel, canola biodiesel, contaminated biodiesel, and aged biodiesel on a 2007 Cummins ISL diesel engine. **SUCCESSFUL**
7. Out-Reach and Education to Support	Provide education and outreach to the community to encourage the	Due to movement in funding priorities within the project, the

Developing “Green” Industry in Montana	development and support of the bio-product industry in Montana.	scope was scaled back to focus on college classes and public education. Center developed curriculum for Advance Research Class NSCI 450. Center also performed several workshops around the state for different groups from K-12 up to Senior Citizen level. Conducted workshop for mechanics in partnership with National Biodiesel Board (NBB). **SUCCESSFUL**
8. Technical Assistance to Montana and North Central Regional Bio-based companies	Support the development of a bio-based product market in Montana and surrounding region by providing technical assistance to companies that are in the process of bringing a bio-based product to market.	The Center successfully assisted three companies with product testing for research and development. **SUCCESSFUL**
9. Administration	(Not applicable)	General grant administration.

2. ENHANCEMENT OF THE CENTER'S RESEARCH AND TESTING FACILITIES

2.1. Site Development of Bio-Energy Research Center

Through this project, MSUN established three important laboratories to transform the Center as a proof-of-concept center for biofuels and additives used in heavy duty diesel engine. The Biomass Conversion laboratory would be used for research on developing new biofuels including bio-jet fuel and bio-based fuel additives. The Wet Chemistry/Synthesis laboratory with instrumentation was also added to assist in synthesizing new chemicals such as heterogeneous metal complex catalysts essential in producing advanced fuels from lignin. Lignin is an organic polymer that binds around cellulose and hemicellulose fibers which strengthen cell walls in woody biomass.

MSUN also renovated its Auto Diagnostics building to include the installation of new and updated equipment and upgrading the mechanical and electrical systems necessary to house the new 704 hp AVL (Anstalt für Verbrennungskraftmaschinen List, Graz, Austria) DynoRoad A/C Dynamometer, AVL SESAM-FTIR Emission Analyzer, and AVL 483 Microsoot Sensor Measuring Unit (Figure 1). The building previously had an old eddy current chassis dynamometer which was removed several years ago. The renovations also included proper ventilation and fire rating for pilot-scale biofuel processing units. The renovated building meets all the new code requirements of Montana State for energy efficiency.

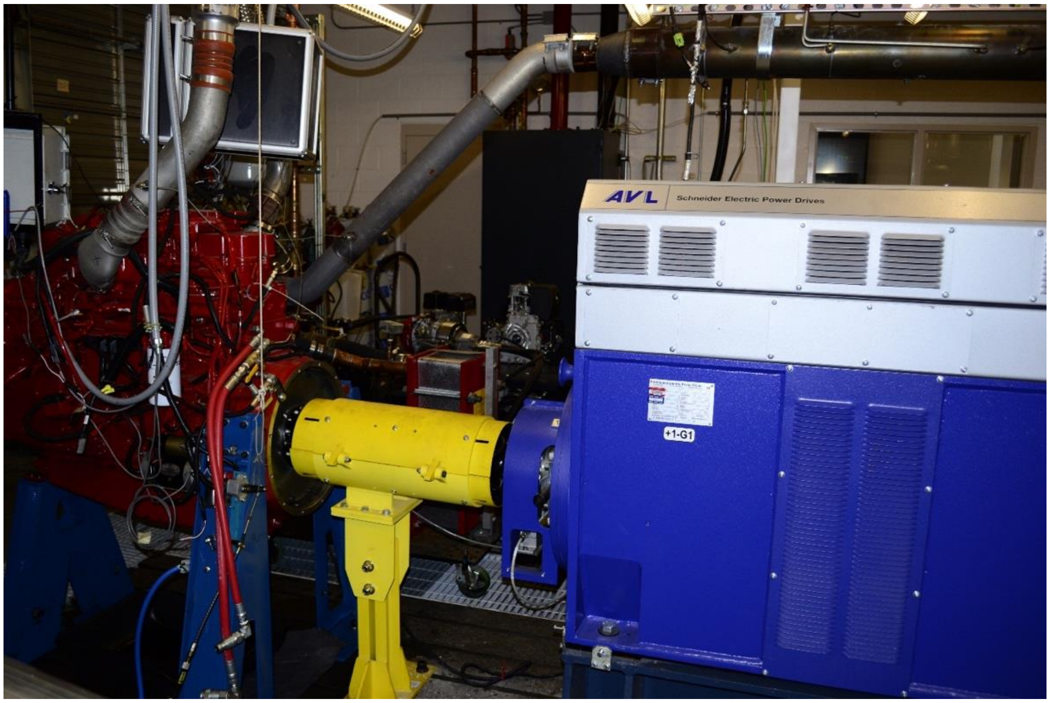


Figure 1. The 704 hp AVL DynoRoad A/C Dynamometer coupled with an 8.9L Cummins ISL compression-ignition engine.

Renovations in the building also included an OSHA approved room for the pilot-scale biofuel processing reactor, an oil processing laboratory, and a conference/control room (Figure 2). The building was commissioned in June 2013 and designated as MSUN's Advanced Fuels Building, although renovation was completed in June 2014.

Figure 2. The oil processing laboratory *(top right)*, reactor room *(left)*, and conference/control room *(bottom right)* in the Advanced Fuels Building.

3. ADVANCED BIOFUELS RESEARCH AND DEVELOPMENT

3.1. Development of Alternative Bio-based Aviation Fuel

Lead Investigators: Nestor Soriano, PhD and Md. Joynal Abedin, PhD

Lignin is a polymer that consists of a network of aromatic compounds. Lignin varies in structure depending on the biomass source and the bonds that link the aromatic compounds which are very strong carbon-oxygen bonds. A method that can successfully break these strong bonds could lead to valuable chemicals and aromatic rich biofuels. Bio-oil may be produced from lignin by catalytically breaking the bonds that connect its monomer units together.

Methyltrioxorhenium (VII) ($MeReO_3$, MTO) in combination with hydrogen peroxide (H_2O_2) creates a potential route to oxidatively break lignin. Several experiments on oxidatively cleaving Kraft lignin using H_2O_2 and MTO were conducted. Reactions conducted at room temperature (25°C) yielded no products (e.g. phenolic compounds). Adding acetic acid to the solution also had similar results. Increasing the reaction temperature to 70°C and 100°C did not break the bonds of lignin as well, although side-chain oxidation of the aliphatic moieties were observed at 100°C. These results were consistent with the fact that lignin is recalcitrant to oxidative cleavage due to significant amount of strong C-C and C-O bonds. To cleave these bonds, higher temperatures and elevated pressures would be needed and a robust catalyst that can tolerate these reaction conditions would be necessary to selectively break lignin into its aromatic units. To test this hypothesis, Kraft lignin in H_2O_2 solution was reacted at 300°C and 500 kPa and using MTO as the catalyst. Results from the gas chromatograph mass spectrometer (GC-MS) showed that the C-O bonds in the lignin cleaved into phenols. Phenols are class of organic compounds with a hydroxyl group bonded with an aromatic hydrocarbon.

The next step of the process was to remove the oxygen atoms from, or deoxygenate, the phenols produced in the first step. Nickel-based catalysts are known to both hydrogenate as well deoxygenate phenols. A silica supported, Ni(COD)-NHC catalyst was developed to crack as well as hydrogenate lignin (Figure 3). Ni(COD) and NHC stands for cyclooctadiene nickel and N-heterocyclic carbene, respectively. The hypothesis is that by covalently bonding the nickel complex to a silica would create a robust catalyst that can handle elevated temperatures and pressures while retaining the catalyst's selectivity. The complex was formed *in-situ* with the addition of a silica-supported NHC and $Ni(COD)_2$ in the presence of high boiling point solvents to cleave and remove the oxygen from the C-O bonds of lignin (Scheme 1). Catalyst precursors were confirmed but no aromatic fuels were successfully produced.

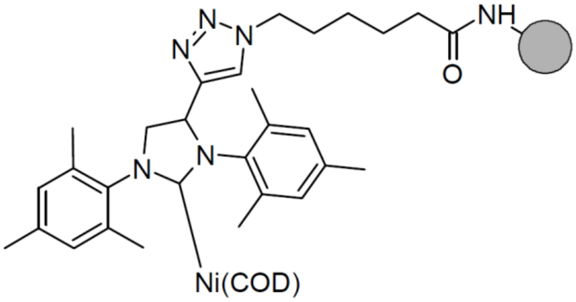
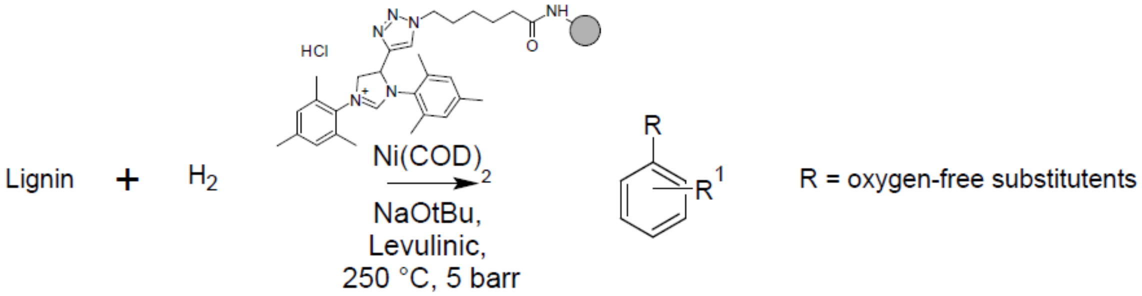


Figure 3. Ni-NHC catalyst on silica support.



Scheme 1. Deoxygenation of lignin.

3.2. Development of Camelina Oil-Derived Fuel for Advance Transportation Fuels

Lead Investigators: Nestor Soriano, PhD and Randy L. Maglinao, PhD

The increasing use of fossil fuels has been blamed for the catastrophic effects of climate change. As the population and human and industrial activities increase, the use of biofuels appears to be inevitable. For instance, in the transportation sector, like the aviation industry, both the global traffic and fuel usage has grown significantly from 2000 to 2005.[1] In the United States, despite the world-changing events in the early 2000s and the global financial crisis of 2007-2008, the general trend of the fuel usage of the aviation industry is increasing.[2] Considering these situations, the development and use of alternative sources of fuels become a very big challenge.

Biomass can be converted into alternative fuels which when used could minimize the detrimental impact on the environment. However, not all in the transportation sector can use first generation biofuels, such as bio-ethanol and biodiesel. The aviation industry, which is closely regulated by Federal Aviation Administration (FAA), is currently allowing alternative fuels containing only hydrocarbons. The U.S. Air Force and other commercial airlines in the U.S., Europe, and Asia had conducted several successful demonstration flights on the use of alternative jet fuel since 2007.[3,4] The fuels used varied from synthetic paraffinic kerosene (SPK) produced via Fischer-Tropsch (FT) process or hydroprocessed esters and fatty acids (HEFA) produced from hydrotreating of natural oils such as animal fat, jatropha, algae, and camelina. Both HEFA and SPK are composed of only hydrocarbons. To mitigate some of the anticipated operational problems associated with

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[1] Lee, D. S.; Fahey, D. W.; Forster, P. M.; Newton, P. J.; Wit, R. C.; Lim, L. L.; Owen, B.; Sausen, R. Aviation and global climate change in the 21st century. *Atmospheric Environment* **2009**, *43*(22), 3520-3537.

[2] Davis, S. C.; Diegel, S. W. and Boundy, R. G. 2013. Transportation Energy Data Book: Edition 32. U.S. Department of Energy. cta.ornl.gov/data (accessed July 10, 2014).

[3] Moses, C. A. Comparative Evaluation of Semi Synthetic Jet Fuels; CRC: 2008.

[4] Blakey, S.; Rye, L.; Wilson, C. W., Aviation gas turbine alternative fuels: A review. *Proceedings of the Combustion Institute* **2011**, *33* (2), 2863-2885.

the use of renewable fuels, a maximum blend of 50% with conventional jet fuel was employed during these demonstrations.

SPK and HEFA, however, present challenges in the production and economic stand point. As of 2014, none of the commercial scale FT facilities are in the U.S. The four commercially viable technologies based on FT process located in South Africa, the Middle East and Asia use coal and natural gas as feedstock. Moreover, both SPK and HEFA are produced under a high energy intensive process requiring relatively higher temperatures and pressures to achieve a reasonable conversion.

The Center proposed a pathway for producing high value chemicals and transportation fuels from camelina oil. The production involves three general processes, namely, (a) alkene metathesis of camelina oil, (b) "aromatization" and hydrogenation, and (3) separation through distillation. Unlike the conventional thermocatalytic conversion such as hydrotreatment, this process may take place at significantly lower temperature and pressure resulting in lower energy input. This study aimed to (a) understand the chemistry involved in alkene metathesis of fatty acid methyl esters (FAME) with ethylene, (b) demonstrate the conversion of camelina oil into fuel, and (c) propose a scale-up production facility.

3.2.1. Chemistry of Alkene Metathesis

Alkene metathesis is a well-known process of producing industrially important chemicals both in the oleochemical and petrochemical industries. The transformation involves a metal-catalyzed rearrangement of carbon-carbon double bonds according to the generally accepted mechanism proposed by Chauvin and Herisson in 1970.[5] The Philips triolefin process and the Shell Higher Olefins Process (SHOP) are among the early applications of alkene metathesis in the petrochemical industry.[6,7] In both technologies, the target compounds are longer-chain alkenes for polymer and detergent applications. The self-metathesis of natural oils and their fatty acid methyl derivatives as well as the alkene metathesis of these compounds with ethylene, most commonly known as ethenolysis, had also been reported and demonstrated.[8,9]

This study demonstrated that ethenolysis of camelina biodiesel under mild temperature conditions (20 – 100°C) using Ruthenium-based catalysts can take place. The products of the camelina biodiesel metathesis consist of a variety of aliphatic and cyclic monoalkenes and dienes. (Table

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[5] Vougioukalakis, G. C.; Grubbs, R. H. Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts. *Chemical Reviews* **2010**, *110* (3), 1746-87.

[6] Mol, J. C. Application of olefin metathesis in oleochemistry: an example of green chemistry. *Green Chemistry* **2002**, *4* (1), 5-13.

[7] Skupinska, J. Oligomerization of alpha-olefins to higher oligomers. *Chemical Reviews* **1991**, *91* (4), 613-648.

[8] Behr, A.; Krema, S. Metathesis applied to unsaturated lipid compounds. *Lipid Technology* **2011**, *23* (7), 156-157.

[9] Behr, A.; Westfechtel, A.; Perez Gomes, J. Catalytic Processes for the Technical Use of Natural Fats and Oils. *Chemical Engineering & Technology* **2008**, *31* (5), 700-714.

2). It was observed that direct ethenolysis of camelina biodiesel produces mostly terminal alkenes (α – olefins), such as 1-decene and 1-heptene. These terminal alkenes are the direct result of ethenolysis of oleic acid methyl ester and linoleic acid methyl ester. It is noted that camelina biodiesel contains 10 – 12%, 37 – 40%, and 48 – 50% by mass of saturated, monounsaturated, and polyunsaturated fatty acid methyl esters (FAMEs), respectively. The monounsaturated FAMEs are primarily oleic (C18:1), and eicosanoic (C20:1) comprising about 24% and 13% of the total FAMEs in camelina biodiesel, respectively. The presence of 1,4-cyclohexadiene in the product could be explained by the ring closure metathesis of 1,4,7-octatriene, which is produced from the ethenolysis of linolenic methyl ester (C18:3).

Table 2. Summary of products after ethenolysis of camelina biodiesel.

	Products[b]		
		Further Metathesis	
FAME[a]	**Ethenolysis**	**Cross-metathesis[c]**	**RCM[d]**
Oleic acid, methyl ester (C18:1)	• 9-decenoic acid, methyl ester • 1-decene	• 9-octadecene[e]	n/a
Linoleic acid, methyl ester (18:2)	• 9-decenoic acid, methyl ester • 1,4-decadiene • 9,12-tridecadienoic acid, methyl ester • 1-heptene	n/a	n/a
Linolenic acid, methyl ester (C18:3)	• 9-decenoic acid, methyl ester • 1,4,7-decatriene • 1-butene • 1-4-pentadiene • 1-4 heptene	• 9-dodecenoic acid, methyl ester • 1,4-tridecadiene	• 1,4-cyclohexadiene

Note: The metathesis reaction was conducted at 20 – 100°C and at 482 – 5,172 kPa of ethylene.

Legend: [a] – list of the major unsaturated fatty acid methyl esters found in camelina biodiesel, [b] – products were grouped based on the type of reaction and the fatty acid methyl ester it was produced from, [c] – cross-metathesis reaction excluding cross-metathesis with ethylene, [d] – ring closing metathesis reaction, and [e] – 9-octadecene was produced by metathesis of two 1-decene compounds.

Most of the unsaturated fatty acids were converted to decenoic acid methyl esters (C10:1), with carbon-carbon double bond at position 9 (terminal alkene) resulting from ethenolysis (Table 2). The 10 – 12% saturated components, which are mainly palmitic (C16:0; 7%) and stearic (C18:0; 2%) remained unreacted.

3.2.2. Production of Advanced Transportation Fuel from Camelina Oil

One of the challenges of using camelina biodiesel in alkene metathesis is that the product contains fatty acid methyl esters which have boiling points close to the hydrocarbons produced during reaction. This becomes an issue during downstream processing, specifically separating hydrocarbons from fatty acid methyl esters. Chromatogram results confirmed that medium-chain fatty acid methyl esters, such as decanoic methyl esters (C10), are distilled with the hydrocarbon fraction during distillation. It is noted that the products, collected after camelina biodiesel alkene metathesis, were hydrogenated using a nickel-based catalyst and vacuum distilled to separate the hydrocarbons from the biodiesel. Hydrogenation converts alkenes to alkanes, like decene to decane, and unsaturated fatty acid methyl esters to saturated, such as decenoic methyl esters to decanoic methyl esters.

As of the report period, biodiesel, also known as fatty acid methyl esters, has not been approved by U.S. Federal Aviation Administration (FAA) for commercial and military aviation engines. Thus, a fuel containing fatty acid methyl esters could not be accepted as an alternative jet fuel. To address this concern, the Center investigated the alkene metathesis of camelina oil, instead of its biodiesel, to produce advanced transportation fuels. The hypothesis is that the fatty acids moieties in the triglycerides will remain intact after alkene metathesis and the same hydrocarbons would still be produced. Since triglycerides have higher boiling point than biodiesel, hydrocarbons can be separated easily by using distillation.

For this study, a 500-mL batch pressure reactor with 1000L high pressure syringe pump was used. Camelina oil was reacted with ethylene gas using a ruthenium-based catalyst. Using the high pressure syringe pump, a constant reactor pressure of ethylene was maintained during the alkene metathesis reaction. After the reaction, the dissolved catalyst was removed from the liquid product by adding a bleaching clay and mixing the slurry for 30 minutes. The slurry was then centrifuged and the purified liquid product was collected. The purified liquid product was then mixed with 4.0% by mass of a hydrogenation catalyst (nickel-based catalyst). Hydrogen gas was supplied and maintained at 482 hPa and reacted for one hour at 80°C. At this stage of the process, α-olefins and polyunsaturated olefins were hydrogenated into straight-chain paraffins. The liquid product was separated from the catalyst using a centrifuge. The refined liquid product was vacuum distilled. Typically, the cooling liquid of the condenser used in the distillation was at –5°C to avoid losses of low boiling point components. GC-MS results of the distillate collected at MH runs showed that only the hydrocarbons were collected (Table 3). The distillated product was mostly composed of medium-chain aliphatic hydrocarbons, such as cyclohexane, decane and dodecane. Less than 2% by wt. were long-chain hydrocarbons (C16-C22) and aromatics.

Table 3. Distillate composition after processing camelina oil.

	Percent Composition [a], % wt.	
Description	**MH**[b]	**MAH**[c]
Aliphatic hydrocarbons (C6-C15)	98.7 ± 0.7	73.6 ± 1.0
Aliphatic hydrocarbons (C16-C22)	0.6 ± 0.2	0.6 ± 0.5
Aromatics (C6-C8)	0.7 ± 0.7	25.8 ± 1.5
Mono-, di- and triglycerides	N.D.[d]	N.D.

Note: The hydrocarbon fraction was separated from the oil product using a vacuum distillation setup. [a] – computed relative amounts of compounds based on peak areas of the chromatogram. [b] – camelina oil which underwent ethenolysis and hydrogenation using a nickel-based hydrogenation catalyst. [c] – camelina oil which underwent ethenolysis, aromatization (reaction with a nickel-based catalyst in the absence of hydrogen) and then hydrogenation. [d] – not detected by GC/MS.

The aromatics found in the MAH runs confirmed the hypothesis that the absence of hydrogen would lead to removal of hydrogen atoms from 1,4-cyclohexadiene and formation of alkylated benzenes. This step was designated as the “aromatization” step. As discussed earlier, 1,4-cyclohexadiene, which was formed via ring closing metathesis of linolenic acid (C18:3), presents a route in producing biofuels containing aromatics. Results showed that adding the “aromatization” step during processing produces a distillate with 25.8 ±1.5 % wt. aromatics (Table 3). The aromatics components in the distillate were composed mainly of benzene and a minimal amount of ethylbenzene.

To better understand the formation of aromatics, model compounds where used in various steps of the process. Pure 1,4-cylcohexadiene were used in “aromatization” and hydrogenation experiments. Two solutions were prepared, 1,4-cyclohexadiene with and without 1-dodecene. Nickel catalyst and hydrocarbon solvent (i.e. heptane) were used. Successive “aromatization” and hydrogenation of 1,4-cyclohexadiene in the presence of 1-dodecene produced benzene and dodecane. Minor amounts of 4-dodecene and 5-dodecene were observed from isomerization of 1-dodecene (Table 4). As expected, only benzene was observed after “aromatization” and hydrogenation of 1,4-cyclohexadiene without 1-dodecene. This confirmed the hypothesis that aromatics are formed from 1,4-cyclohexadiene without the aid of other alkenes. It was also confirmed that the formation of benzene from 1,4-cyclohexdiene was only possible during “aromatization” step and not during hydrogenation. Direct hydrogenation of 1,4-cylcohexadiene in the presence of 1-dodecene did not produce benzene; quantitative conversion of 1,4-cyclohexadiene to cyclohexane was observed (Table 4).

Table 4. Conversion and selectivity to benzene and alkanes during "aromatization" and hydrogenation steps.

MODEL COMPOUND	Successive "aromatization" and hydrogenation with 1-dodecene	Successive "aromatization" and hydrogenation without 1-dodecene	"Aromatization" only with 1-dodecene	Hydrogenation only with 1-dodecene
	REACTION PARAMETERS			
1. 1,4-cyclohexadiene				
Conversion, % by mass	>99.9	>99.9	88.9	>99.9
Aromatization				
benzene	Major	Major	Major	Not detected
Hydrogenation				
cyclohexane	Not detected	Not detected	Not detected	Major
2. 1- dodecene				
Conversion, % by mass	>99.9	----	20.2	>99.9
Hydrogenation				
dodecane	Major	----	Not detected	Major
Isomerization				
4-dodecene	Minor	----	Major	Minor
5-dodecene	Minor	----	Major	Minor

The fuel performance characteristics of the hydrocarbon distillate were also investigated. Table 5 summarizes the results of the tests. MSUN BioJet refers to the hydrocarbon distillate collected after processing camelina oil. The MSUN BioJet exhibited comparable cloud point, carbon residue and sulfur content with commercial Jet A fuel. Rapid Small Scale Oxidative Test (RSSOT) results showed that the MSUN BioJet was more stable against oxidation compared to the Jet A sample used in the study (Table 5). RSSOT was performed in a PetroOxy unit from PetroTest using ASTM D7545, Standard Test Method for Oxidation Stability of Middle Distillate Fuels.

Table 5. Properties of the neat commercial Jet A fuel and MSUN Biojet fuel.

Fuel Properties	ASTM Method	Jet A	MSUN BioJet
Cloud point, °C	D2500	Less than –32	Less than –32
Carbon residue, %	D4530	0	0
Sulfur, ppm	D5453	2.05	1.97
RSSOT, min	D7545	64	181

Using a Grabner IROX Diesel Analyzer, cetane number, distillation characteristics, and density of the MSUN BioJet blend were determined. The MSUN BioJet blend was a mixture of 50% by volume of MSUN BioJet and 50% of Jet A mixed at room temperature. Jet A was purchased at Havre Airport (Havre, MT). Results showed that the MSUN BioJet blend had a higher cetane number and cetane index compared to Jet A (Table 6). The higher value was because MSUN BioJet is mostly composed of straight-chain paraffins. Straight-chain paraffins, such as decane and octadecane have higher cetane values compared to branched paraffins. The lower distillation temperature of the MSUN Biojet blend at T90, T95, and density relative to Jet A suggests the presence of higher amounts of shorter-chain hydrocarbons in the mixture.

Table 6. Fuel properties of commercial Jet A fuel and its 50/50 blend with MSUN Biojet fuel determined by IROX Diesel Analyzer.

Fuel Properties	**Jet A Fuel**	**MSUN BioJet blend (50%)**
Cetane number	44.0	53.9
Cetane index	37.5	61.7
T90, °C	341	213
T95, °C	371	223
Density, g/m^3 (at 30°C)	0.813	0.772

Based on the experimental results and the types of catalysts available, the Center proposed a pilot-scale production facility with a stirred tank vessel for the alkene metathesis step and a continuous tubular reactor for the "aromatization" and hydrogenation step. A stirred tank vessel was chosen over a continuous tubular reactor in the metathesis step because the currently available metathesis catalyst is a homogeneous type. Moreover, the metathesis reaction takes 4 – 6 hours to achieve reasonable conversions and yield. For a 10 L/h (63 gal/d) production facility, an eighty-gallon capacity stirred tank and a continuous tubular reactor at 1 h^{-1} liquid hourly space velocity, respectively, could be proposed. To produce 60 gallons of fuel and chemicals per day, a total of 304 tons of camelina seed is needed to be processed annually. Thus, the total area of farm land required was estimated at 553 acres with the assumption that the crop yield is at 1,100 pounds of camelina seed per acre.

In conclusion, production of advanced alternative fuels and bio-based chemicals from camelina oil via ethenolysis is possible. The inherent properties of camelina oil, such as containing 85% unsaturated fatty acids, makes it the ideal feedstock for the process. Moreover, specialty chemicals, such as 1,4-cyclohexadiene, were also produced because of the unique fatty acid profile of camelina oil.

3.3. Viability of Pure Plant Oils as an Alternative Fuel in Diesel Engines

Lead Investigators: Taylor Lyon, Randy Maglinao, PhD, and Nestor Soriano, PhD

The feasibility of using straight vegetable oil (SVO) as a fuel for agricultural production (primarily tractors used during planting and harvesting crops) was assessed based on: (1) virgin oil processing techniques, (2) ASTM and EIN fuel quality, and (3) heavy duty engine bench testing. The study was limited only to on oilseeds produced in Montana such as canola, linoleic safflower, high-oleic safflower, camelina, and waste vegetable oil (WVO).

Various oilseeds were procured from local Montana producers and pressed them at the Center's oil pressing lab. Extracting the oil on-site gave the investigators control of the entire process during the study. All fuel processing techniques were developed by the Center. The quality of the oils extracted and processed was evaluated at the Center's Fuel Analysis lab. The fuel performance of each oil was determined using a Caterpillar CAT 3176 diesel engine coupled on a water-brake dynamometer.

3.3.1. Feedstock (SVO and WVO) Preparation

When dealing with unconventional feedstock like vegetable oils, it is important to know its qualities and the necessary pretreatment steps before using it in diesel engines. Water (both free and bound) and insolubles (sediments and particulates) are the common contaminants found in both virgin oils and waste vegetable oils. Water and sediments can be removed through physical processes, such as filtration, settling, and centrifugation. The oil specifications, listed in Table 7, are the recommended limits to ensure trouble-free engine operation.

To remove water and insolubles from waste vegetable oils, a multi-step system of filtration and centrifugation can be used. Figure 4 illustrates a possible low-capital setup for this purpose. The following sections describe each step.

Table 7. Proposed oil specifications.

Description	**Target Value or Specification**	**Test Method**
Water content	≤ 750 ppm	Karl Fischer
Water & sediment	≤ 0.05% vol.	ASTM D2709
Acid Number	≤ 2.0 mg KOH/g (for SVO)	ASTM D664
Carbon Residue	≤ 0.40 % mass	ASTM D4530
Kinematic Viscosity @ 40°C	≤ 36 cSt	ASTM D445
Oxidative Stability at 110°C	≥ 6.0 h	EN 14112

Note: The Center still recommends meeting all the tests in EIN V51605, except for the iodine number. To remove suspended solids and very fine particulates in the oil, it is recommended to filter the oil below 1µm.

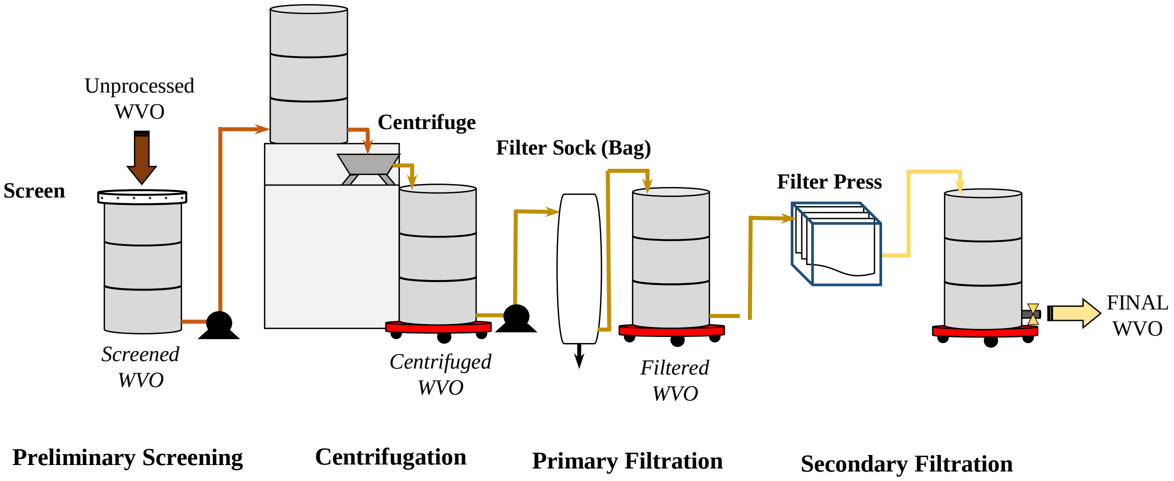

Figure 4. A schematic diagram for a low-capital pretreatment setup for refining WVO.

3.3.1.1. Preliminary Screening

WVO usually contains large solids that could damage and clog fuel lines and appurtenances. To remove these solids from the oil, very fine screens with opening sizes of 0.04 to 0.06 inches (1.0 – 1.4 mm) can be used (Figure 5). To improve flow and screening capture, it is recommended that the screens are cleaned regularly.

Figure 5. Preliminary screening of waste vegetable oil.

3.3.1.2. Centrifugation

Centrifugation uses centrifugal force to separate solid particles from a liquid, in this case, oil. Centrifugal force can be much greater force than gravity allowing even very small particulate matter and components slightly denser than the fluid to settle. Therefore, centrifugation is usually more efficient in removing solids than gravity settling. The Bio-Energy Center uses a centrifuge with a preheater to improve the flow of waste vegetable oil through the equipment and simultaneously remove water thru evaporation (Figures 6 and 7). Results of the experiment conducted by the Bio-Energy Center showed that there was a significant reduction both in water and sediment content after centrifuging waste vegetable oil (Table 8).

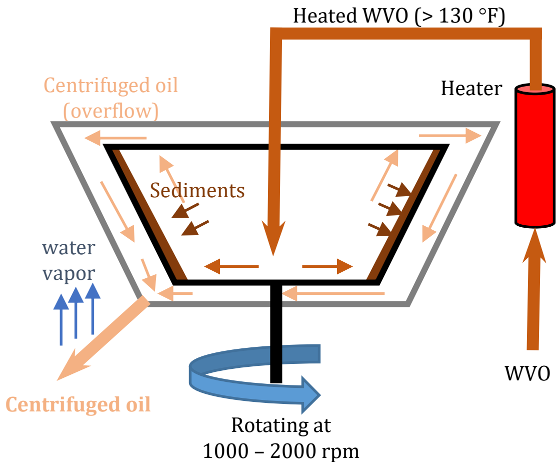

Figure 6. Simple illustration of how a centrifuge works.

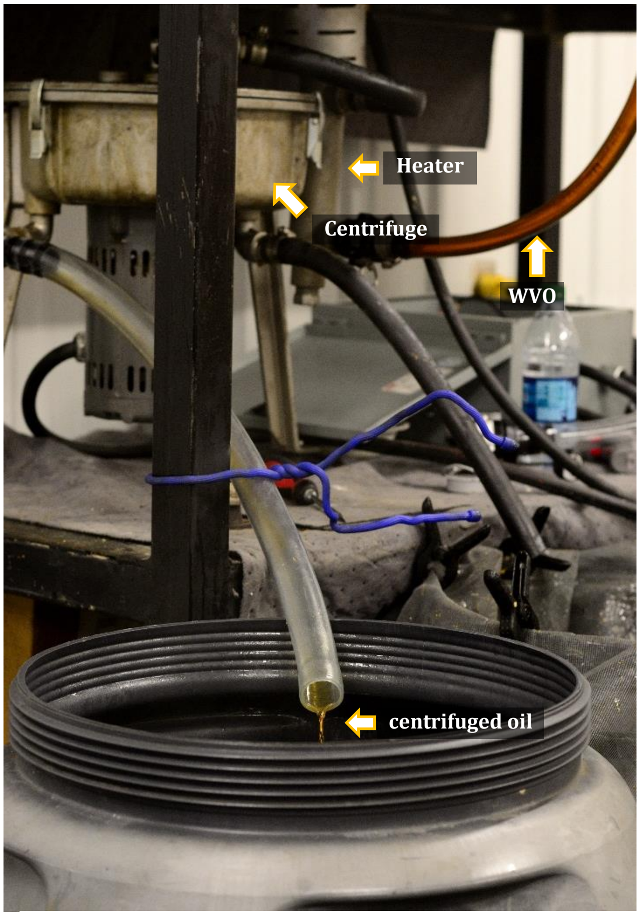

Figure 7. Centrifugation of waste vegetable oil.

Table 8. Percent removed after centrifugation.

	Percentage amount of contaminant removed after centrifugation	
Contaminant	**Oil pre-heated to 55°C[a]**	**Oil at room temperature**
Free water and sediments	69.05 ± 10.91%	14.29 ± 14.29%
Total water content (free & bound)	87.42 ± 6.82%	65.16 ± 3.00%

Note: [a] – The centrifuged oil contains less than 0.05% by volume of water and sediments.

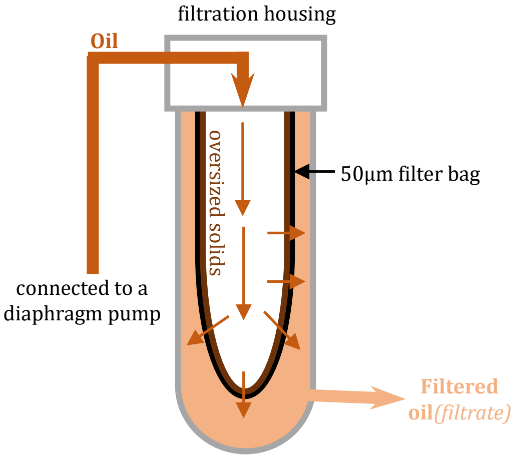

Figure 8. Primary filtration unit. (a) *Left photo:* Bio-Energy Center's primary filtration setup with a 50µm polyester filter bag inside. (b) *Top photo:* Schematic illustration on how solids are removed from an oil during filtration.

Figure 9. Filter press unit. (a) *Left photo:* Schematic illustration on how solids are removed from an oil in a filter press. (b) *Right photo:* Bio-Energy Center's filter press unit.

3.3.1.3. Primary and Secondary Filtration

The filtration process uses a porous material to separate particles of different sizes. Although centrifugation is capable of removing most of the solid particles in an oil, very fine and suspended particles could remain. These very fine particles can accumulate and clog fuel filters, resulting in unscheduled filter replacement. Filtering the oil with a filter bag with an opening of 50 µm or less can remove these particles. The Center uses a polyester filter bag with a 50 µm opening size. A completely sealed filtration housing was used to let the pressure build up inside and push the oil through the filter bag (Figure **8-b**). A diaphragm pump was used to push the oil to the filtration unit. One advantage of using this type of filtration housing is that the interior of the housing remains clean even after the bag is removed. This reduces downtime during filter bag clean up.

For farmers and SVO users who want to use waste vegetable oils to fuel their operations, it is necessary to completely remove all insolubles in the oil. Passing the filtered oil through a filter press can be an option to achieve this (Figure **9**). Filter presses use the fluid’s (e.g. WVO) own sediments to form a cake which will act as a filter. If done correctly, filter presses can remove very fine particles as small as 1µm. In a typical startup operation, a filter aid, typically a diatomaceous earth, is added to a crude oil (unprocessed) to form a precoat. The precoat prevents the formation of gelatinous layer that plugs filter presses. Once the cake is formed between the filter press’ plates, centrifuged and filtered waste vegetable oil can be processed.

3.3.2. SVO and WVO Performance Evaluation

The Center also explored different techniques for processing extracted oils by mechanical press. Methods to remove sediment and phospholipids and gums present in cold pressed oils, oils that are mechanically extracted without the addition of heat, were evaluated. Oil purification by settling and filter sock filtration, chemical degumming, and filter press filtration were studied. Engine performance tests with oil from each purification method were planned but early in the research, it was observed that oils that were filtered via chemical degumming or filter sock/settling method did not meet fuel quality standards listed in Table **7**. Therefore, only filter pressed oils were used in engine evaluation.

Tables **9** and **10** lists the engine speeds and loads of the two test cycles used in the engine performance and exhaust emission analysis. These test cycles were developed in consultation with farmers, clients, and the Center’s performance engineer, Keith Richardson. A Caterpillar CAT 3176 diesel engine coupled with a water break dynamometer was used. The physical and chemical properties of filter pressed oils used to fuel the engine are summarized in Table **11**. Canola and safflower (hi-oleic) oil were found to be suitable oil for Montana. It is noted that canola oil had better properties than safflower, especially its kinematic viscosity. Camelina oil, due to its high ω-3 fatty acid content, was likely to build up more carbon deposits in the engine, e.g. fuel injectors. This was supported by the high carbon residue of camelina oil (Table **11**).

Table 9. Custom 3-mode constant speed test cycle.

STEP	Engine Speed	Engine Load, N-m	Time
1	1600	825	600
2	1600	1250	600
3	1600	985	600

Table 10. Custom 3-mode test cycle.

STEP	Engine Speed, rpm	Engine Load, N-m	Time, s
1	1400	475	600
2	1475	900	600
3	1775	1000	600

Table 11. Fuel properties of plant oils used in the evaluation.

	OIL TESTED		
Fuel Property	**Safflower Oil♣**	**Canola Oil**	**Camelina Oil**
Viscosity @ 40°C	37.2 ± 1.2[a]	35.4 ± 1.0[a]	31.2 ± 0.1[b]
Cloud Point, °C	–15.8 ± 1.3[a]	–12.7 ± 1.5[a]	–8.5 ± 0.7[b]
Pour Point, °C	–18.8 ± 2.2[a]	–23.0 ±1.7[b]	–16.0 ± 4.2[a,b]
Carbon Residue, ppm	0.23 ± 0.01[a]	0.27 ± 0.01[a,b]	0.55 ± 0.03[b]
Sulfur Content, ppm	0.4 ± 0.2[a]	1.6 ± 0.4[a,b]	1.6 ± 0.3[b]
Acid Number, mg KOH/g	1.4 ± 1.8[a]	0.6 ± 0.3[a]	0.7 ± 0.1[a]
Oxidative Stability Index, h	15.0 ± 6.4[a]	10.7 ± 1.8[a]	4.2 ± 0.8[b]
RSSOT, min	48.3 ± 8.3[a]	39.3 ± 4.2[a]	18.6 ± 1.0[b]

Note: ♣ - Hi-oleic variety of safflower oil was used in this study. Within a row, values followed by the same letter are NOT significantly different (95% confidence limit). Average values are presented followed by the standard deviation.

Results of the engine performance and exhaust emission analysis are summarized in Figures 10 through 16. Average values and standard errors of each step are itemized in Table A-1 in the Appendix section. Set points (i.e., engine speed and engine load) were attained for all the fuels used in this study as shown in Tables A-1 and A-2 (Appendix). The brake specific fuel consumption (BSFC) was generally higher in SVO than in diesel (Figure 10). The possible reason for this is the diesel has higher specific energy (amount of energy per unit mass) than SVO. Diesel composes of hydrocarbons in which all its bonds (i.e., C-C and C-H) releases energy during combustion. Unlike oxygenated fuels such as vegetable oils and biodiesel, C-O bonds do not give as much energy as C-H and C-C bonds during combustion. Exhaust emission analysis showed that exhaust emissions from SVO contained lower concentrations of carbon monoxide, soot, and formaldehyde than the exhaust emission from diesel (Figures 13, 14, and 16). In contrast, oxides of nitrogen (NOx) emissions were generally higher in concentration with SVO. It is hypothesized that exhaust temperature affected the thermal NOx formation in which higher combustion temperatures favored the formation of NOx emissions. Table A-1 shows that exhaust temperatures of SVO were higher than diesel which is more apparent at step 1 of the custom 3-mode constant speed test cycle in Table 9.

The engine performance and exhaust emission tests using the WVO was conducted at the Advanced Fuels Building that houses the ALV DynoRoad A/C Dynamometer. The emission analysis units, namely, AVL SESAM-FTIR Emission Analyzer and AVL 483 Microsoot Sensor Measuring Unit emission analyzer were also moved and installed to the new building. A newer model engine, specifically, 2007 8.9L ISL Cummins diesel engine was used. The engine was operated over a custom 8-mode test cycle based on AVL's 8-Mode Test Cycle instead of the test cycles in Tables 9 and 10. AVL's 8-mode test cycle is designed for testing industrial diesel engines and NOx emissions. Grade no. 2 ultra low sulfur diesel (ULSD) was used as the control. The WVO was refined using the setup discussed in Figure 4 to protect the engine from contaminants. During testing the WVO, the engine unexpectedly shut down at step 4 of the test cycle. Even with several attempts, the engine shut down at step 4. After analyzing the data in the Engine Control Module (ECM), it was concluded that during steps with high load settings, the engine's ECM gives incorrect output readings. Load readings of more than 100% were recorded even the actual load was just at 60%. It was assumed that the engine's ECM forced the engine to shut down once the load readings reached more than 100%. Because the algorithms stored in the ECM are proprietary of the manufacturer, the investigators did not know how the load was calculated or read by the ECM.

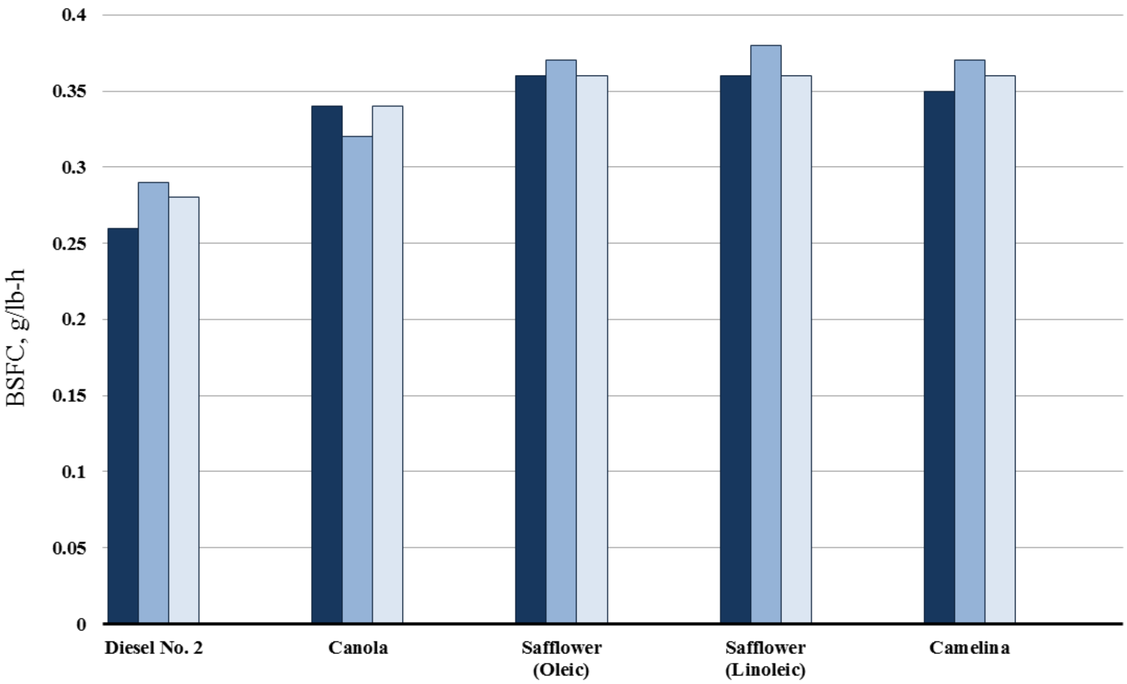

Figure 10. Average brake specific fuel consumption of diesel engine using different fuels.
Legend: The bars represent the following: ■ – Step 1, ▨ – Step 2, □ – Step 3.

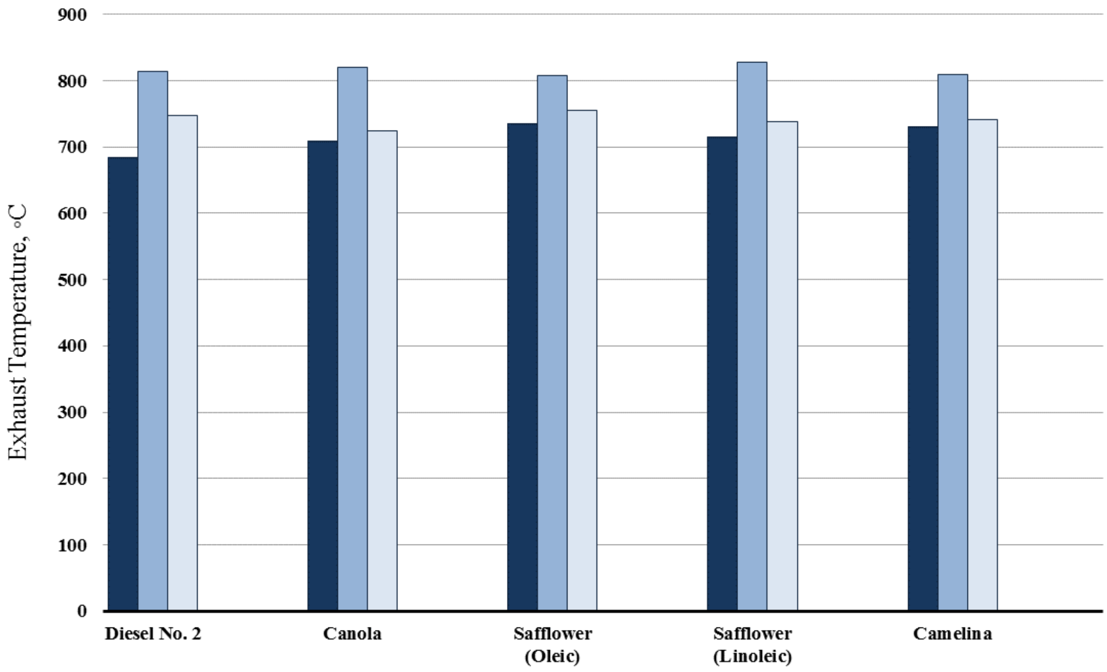

Figure 11. Exhaust temperature of diesel engine using different fuels.
Legend: The bars represent the following: ■ – Step 1, ▨ – Step 2, □ – Step 3.

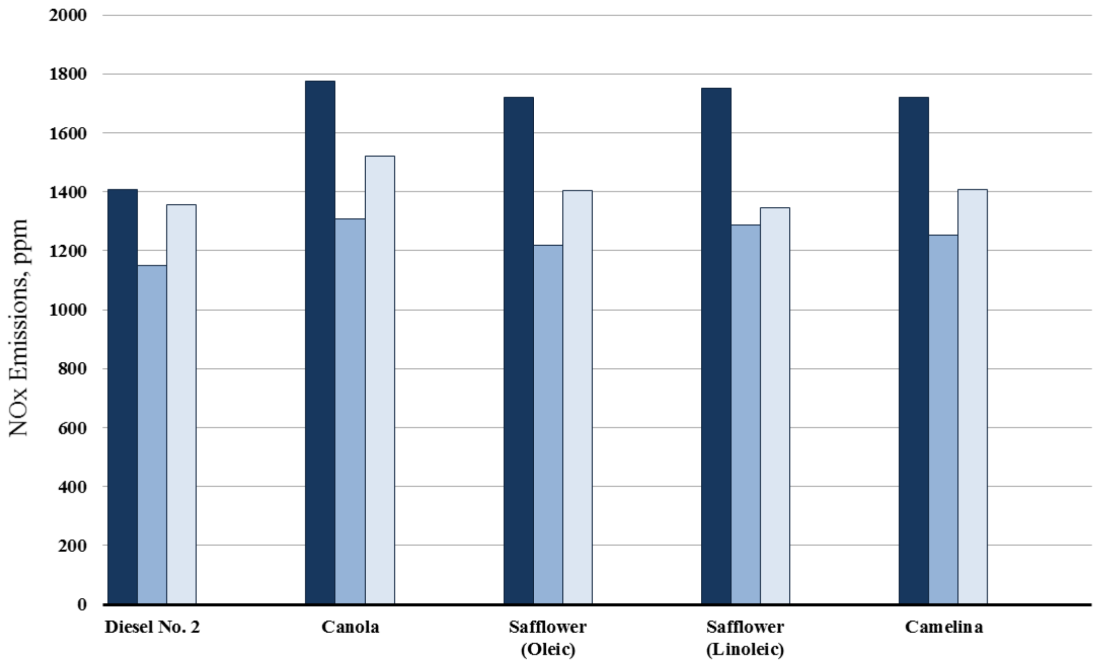

Figure 12. Nitrogen oxides engine exhaust emission concentration using different fuels. Legend: The bars represent the following: ■ – Step 1, ▨ – Step 2, □ – Step 3.

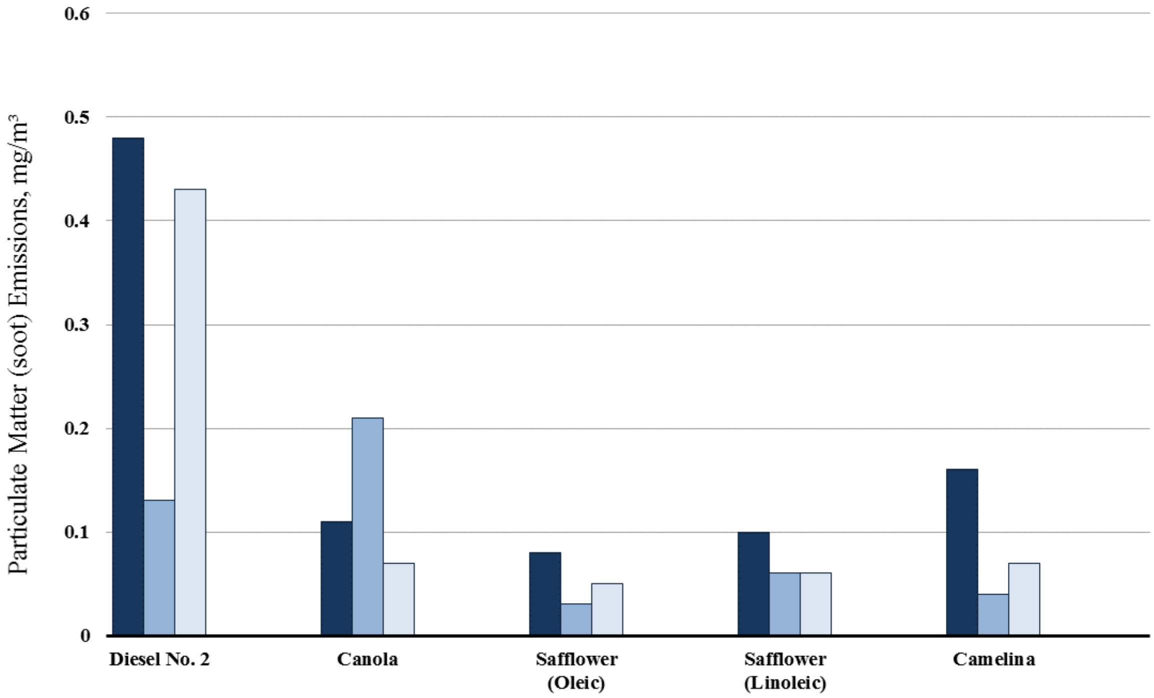

Figure 13. Particulate matter engine exhaust emission concentration using different fuels. Legend: The bars represent the following: ■ – Step 1, ▨ – Step 2, □ – Step 3.

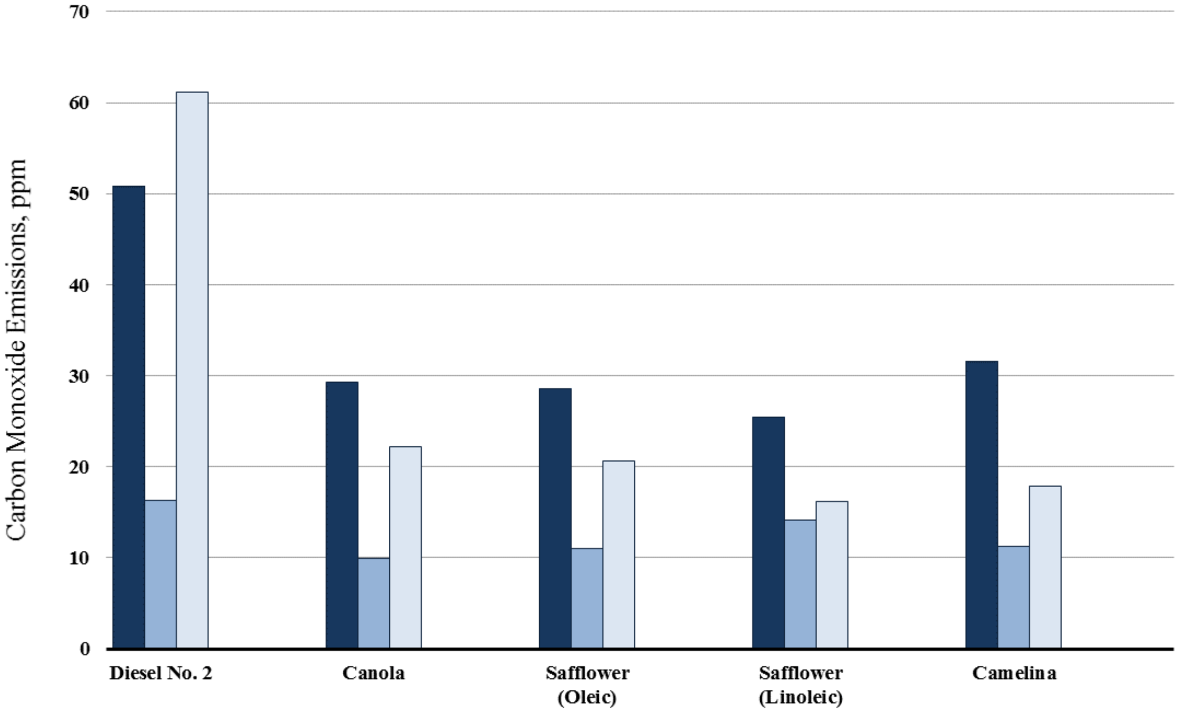

Figure 14. Carbon monoxide engine exhaust emission concentration using different fuels. Legend: The bars represent the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.

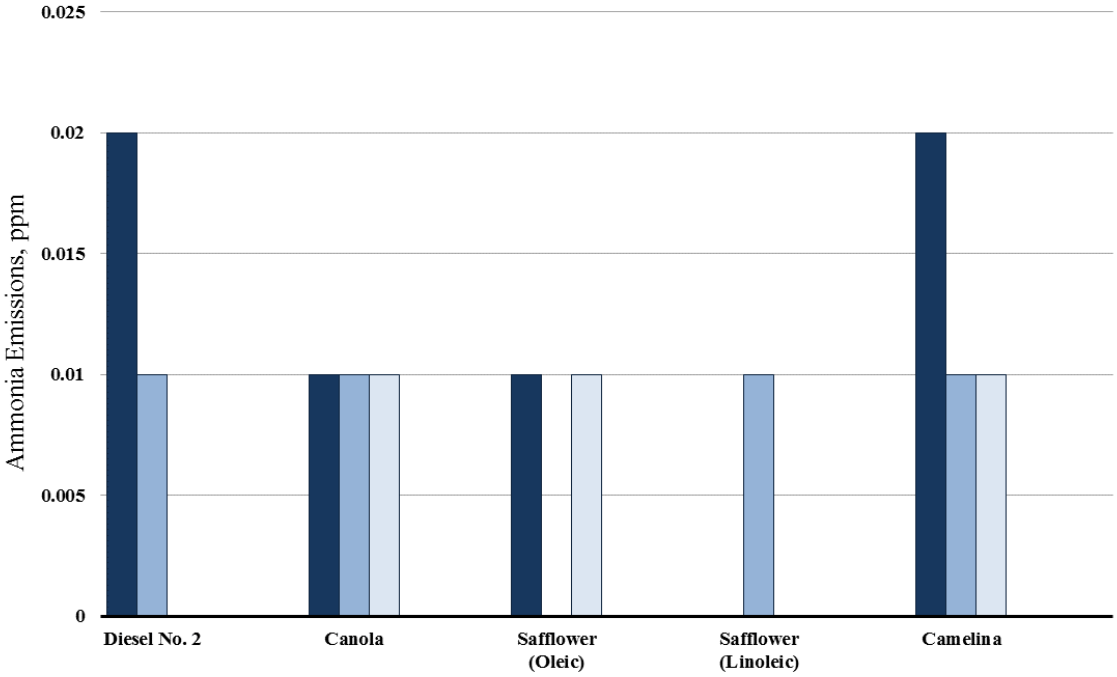

Figure 15. Ammonia engine exhaust emission concentration using different fuels. Legend: The bars represent the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

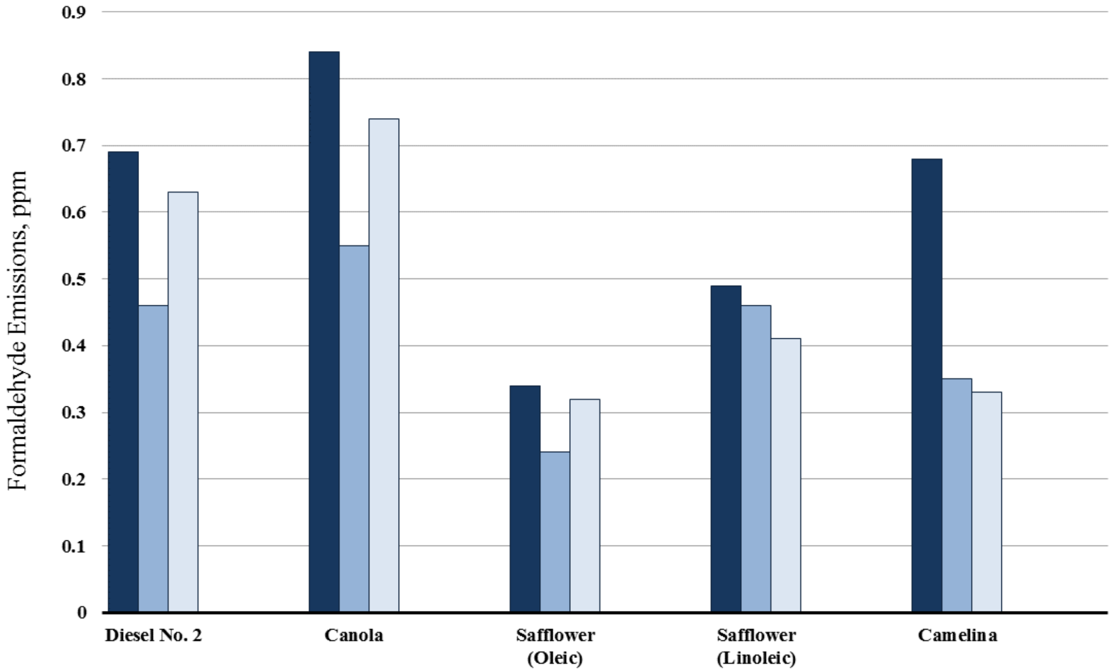

Figure 16. Formaldehyde engine exhaust emission concentration using different fuels. Legend: The bars represent the following: ■ − Step 1, ▨ − Step 2, □ − Step 3

3.4. Effects of Contaminants in Canola Biodiesel to Diesel Engine Exhaust Emissions

Lead Investigator: Randy L. Maglinao, PhD

Biodiesel, a biomass-based fuel composed of mono-alkyl esters of long-chain fatty acids, is an excellent alternative and renewable source of fuel for diesel engines. Biodiesel positively affects the lubricity of diesel and significantly lower harmful exhaust emissions, like particulate matter and unburned hydrocarbons, compared to diesel. Poor processing and refining practices during production, however, could lead to a fuel with deficient properties and could result to engine problems. Fernando and his co-workers[10] observed that the presence of unconverted triacylglycerides (TAG) in the biodiesel affects the cetane number, cloud point, viscosity, and the carbon residue properties. Cetane number, defined as the measure of the ignition performance of a fuel during compression-ignition, of biodiesel decreased as the amount of unconverted TAG increased. Similarly, the carbon residue increased as more TAG was in a biodiesel. They also observed that the soybean biodiesel with 15% wt. or more of TAG failed to meet ASTM D6751 specification for both cetane number and carbon residue.

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[10] Fernando, S.; Karra, P.; Hernandez, R.; Jha, S. K. Effect of Incompletely Converted Soybean Oil on Biodiesel Quality. *Energy* **2007**, *32* (5), 844-851.

ASTM D6751, also known as the “Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels”, lists the required properties of the biodiesel for use as a blend component of a diesel fuel. It is the investigator’s understanding that ASTM D6751 rational are to ensure a good quality fuel blend stock is sold to consumers, to warrant successful operation of engines using the fuel, and to protect engines from damage and premature wear and tear. ASTM standards are developed for OEM (Original Equipment Manufacturing) acceptance of fuels, both fossil-based and alternative but, it is not necessary for meeting the emission standards. It is still not clear if a biodiesel that does not meet the standard properties in the ASTM would result in poor engine emissions. This is a major concern for the environment which targets small biodiesel producers who do not sell their product to the market but instead use the biodiesel to run their own operations. Most of the time, small biodiesel producers do not have complex production and refining facilities that can efficiently convert TAG to biodiesel and remove contaminants, like methanol, from biodiesel. It is important to know if using “off-spec” biodiesel will harm the environment due to emissions rather than help it. Currently, there is no in-depth research in the literature on the emissions of biodiesel not meeting ASTM D6751 standard. Thus, this task aimed to investigate the emissions of biodiesel containing high TAG, methanol and free fatty acids and compare it with Grade No. 2 ultra-low-sulfur diesel and good quality biodiesel.

Canola seeds were purchased from several local farmers near Havre, MT and converted to biodiesel at the Center’s biodiesel facility using a 55-gallon batch biodiesel processor. The biodiesel was contaminated with known amounts of methanol, free fatty acids, and canola oil. Clean and contaminated biodiesels were characterized in accordance with ASTM D6751. The total and free glycerin, acid number, flash point, kinematic viscosity, sulfur content, cloud point, vacuum distillation, oxidative stability, and carbon residue properties of biodiesel were measured. Similarly, Grade No. 2 ultra-low-sulfur diesel (ULSD) was used as the baseline fuel and was also characterized using the tests mentioned before except for total and free glycerin, oxidative stability and vacuum distillation.

ULSD, biodiesel, and contaminated biodiesels were evaluated using an 8.9L 2007 model year Cummins ISL compression-ignition engine connected to a 704 hp AVL DynoRoad A/C Dynamometer. Performance and test parameters such as engine power, engine speed, engine load, and oil temperature and pressure were monitored or controlled by AVL BOBCAT, an integrated engine testing automation system. For the evaluation of the changes in exhaust emissions, the engine was operated over an 8-step test cycle based on eight-mode test cycle according to Code of Federal Regulations Title 40 Part 89 Subpart E, a steady state test procedure designed for non-road heavy-duty engines.

Results of the fuel characterization of the different fuels showed that the addition of contaminants affected some of the properties like, increased viscosity in samples contaminated with unconverted oils and significant decrease in both fuel viscosity and flash point for biodiesel with methanol. For the exhaust emissions, biodiesel resulted in significant reduction in particulate matter and carbon monoxide exhaust emissions in comparison with ULSD (Table 12 and Figure 17). Carbon monoxide exhaust emission was statistically higher in biodiesel contaminated with methanol compared to the biodiesel meeting ASTM specification. Particulate matter emissions were also higher in biodiesel contaminated with methanol and free fatty acids, although, the increase in the exhaust emissions for the contaminated biodiesels was small. In comparison with ULSD, the carbon monoxide and particulate matter exhaust emissions for all contaminated biodiesel tested were still significantly lower.

Table 12. Exhaust emissions of ULSD and different biodiesels.

FUEL	**Emission Species Concentration, g/bhp-h**			
	Nitrogen oxides (NO_x)	**Carbon Monoxide (CO)**	**Carbon Dioxide (CO_2)**	**Particulate Matter (PM)**
ULSD	$1.96^{a} \pm 0.02$	$0.135^{a} \pm 0.001$	$292.67^{a} \pm 0.49$	$0.0169^{a} \pm 0.0008$
Canola B100	$2.33^{b} \pm 0.03$	$0.086^{b} \pm 0.000$	$299.20^{b} \pm 0.69$	$0.0022^{b} \pm 0.0001$
CBD-TAG	$2.33^{b} \pm 0.03$	$0.091^{b} \pm 0.003$	$308.14^{c} \pm 1.96$	$0.0025^{b} \pm 0.0002$
CBD-MEO	$2.29^{b} \pm 0.01$	$0.100^{c} \pm 0.001$	$293.91^{ab} \pm 3.09$	$0.0018^{c} \pm 0.0001$
CBD-FFA	$2.40^{b} \pm 0.15$	$0.085^{b} \pm 0.005$	$301.13^{b} \pm 3.94$	$0.0014^{d} \pm 0.0001$

Note: The test cycle used in this study was not the heavy-duty transient cycle used in federal test procedure and the exhaust emissions were collected before the DPF of the engine. Therefore, NOx was higher than normally seen with this engine. Within a column, values followed by the same letter are not statistically different ($\alpha = 0.05$). Average values are presented followed by standard deviation.

As common to biodiesel, this reduction resulted in a tradeoff whereby NOx exhaust emissions were significantly higher for biodiesel and contaminated biodiesel than for ULSD (Table 12). It is worth to note that there were no significant changes in NOx emissions among the different biodiesel tested.

Based on the results of the study, small biofuel producers which uses 100% canola biodiesel with specifications slightly outside the ASTM D6751 standards, specifically total glycerin, methanol content and acid number, would unlikely produce more harmful emissions than using diesel.

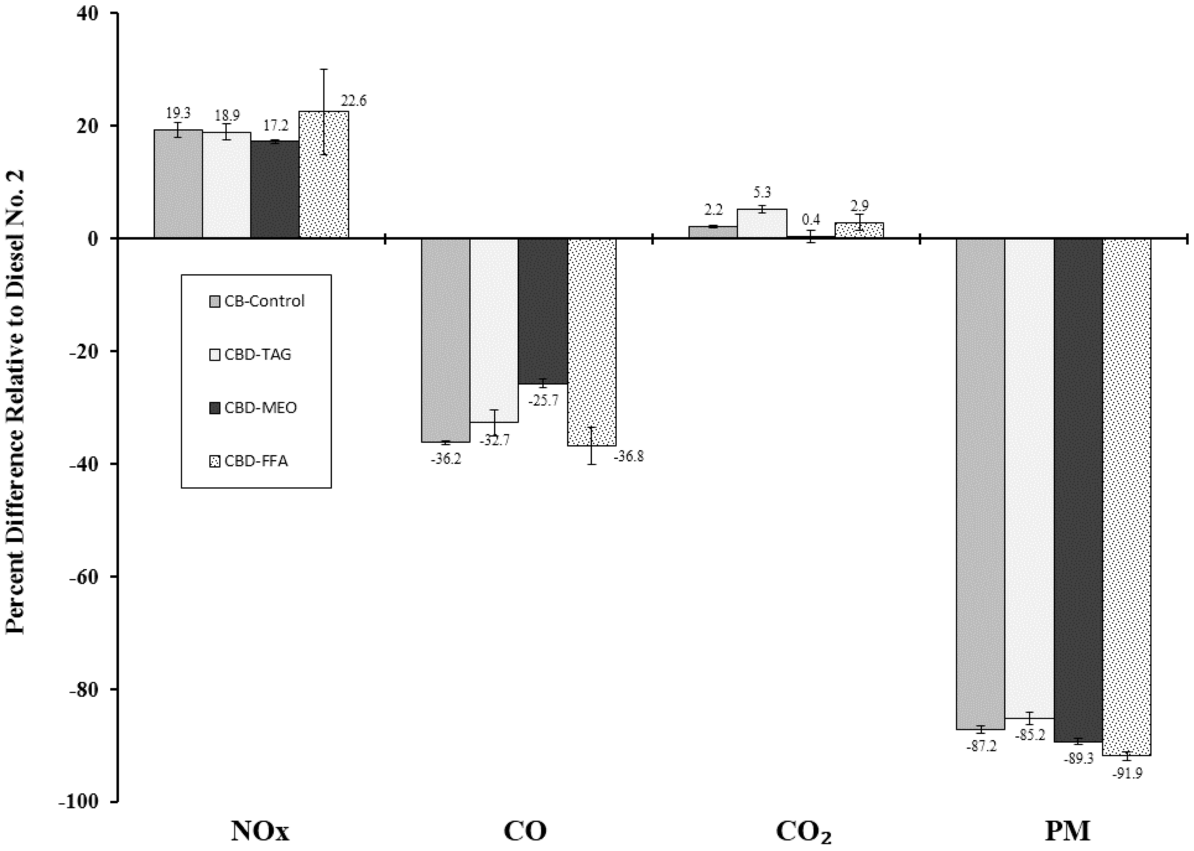

Figure 17. Changes in exhaust emissions for biodiesel and contaminated fuels relative to results for ULSD. Note: CB-Control – refined canola biodiesel; CBD-TAG – canola biodiesel contaminated with 5% volume of canola oil; CBD-MEO – canola biodiesel contaminated with 5% volume of methanol; CBD-FFA – canola biodiesel with out of specification acid number (high free fatty acid content).

4. RESEARCH, EDUCATION, AND OUTREACH ACTIVITIES FOR EXPANDING MONTANA BIODIESEL'S MARKET

4.1. Locomotive Engine Performance and Market Demonstration

Opportunity Link, together with the Bio-Energy Center and the Havre Diesel Shop of BNSF Railways worked on developing markets for Montana biodiesel from 2010 to 2012 with funding from the Montana Department of Environmental Quality's *Alternative Energy Development Grant Program*. The Center and its partners also received support from Bear Paw Development Corporation, Earl Fisher Biofuels, Ezzie's Wholesale, Montana Department of Agriculture's *Growth Through Agriculture Program*, Interstate-McBee, and the National Biodiesel Board.

The objectives of this task were two-fold. The first, was to pilot the use of biodiesel as an alternative fuel for Montana's railway industry – successfully demonstrating both the long-term environmental and economic benefits that this renewable fuel holds for the industry and local communities. The second was to prepare local oilseed producers, refineries, government and other stakeholders to anticipate and realize the potential of increased biodiesel production in the region.

The Center and its partners monitored two BNSF-owned EMD SD 40-2 locomotive with a 16-cylinder turbo charged Tier O engine equipped with Wireless Monitoring Device. One of the locomotives, a 1928, was fueled with B20 blend (20% biodiesel blend) while the other used BNSF's bulk diesel fuel. Both locomotives were monitored for a one-year period starting July 1, 2010. The biodiesel used in the project came from two sources, canola and safflower biodiesels produced by the Bio-Energy Center and biodiesel purchased from Earl Fisher Biofuels (Chester, MT). In both cases, oilseeds grown in Montana were used to produce the biodiesel. The fuel blending station set-up and financed by BNSF Havre Diesel Shop was used to blend diesel and biodiesel to make B20 blend. The diesel, biodiesel, and B20 blend used in the study were tested and analyzed in accordance with ASTM methods. These tests were done at the Bio-Energy Center's Fuels Chemistry lab and the BNSF's analysis laboratory in Topeka, KS. Throughout the demonstration, a wireless monitoring device placed onboard for each locomotive recorded real-time engine parameters and fuel consumption. A standard 92-day maintenance schedule that included injector evaluation, filter evaluation, and oil analysis during the demonstration was followed. Two fuel injectors from each locomotive were removed and replaced following maintenance schedule and sent to the manufacturer, Interstate-McBee, for evaluation. Upon the completion of the demonstration, locomotive exhaust emission tests were conducted using an 11-mode test cycle. Exhaust emissions were measured using a Portable Emissions Analyzer Sensor SEMTECH-DS (PEMS), borrowed from the National Renewable Energy Laboratory, which is capable of measuring CO, CO_2, O_2, NO, NO_2, and total hydrocarbons. The project was presented to BNSF executive staff in November 2011 and then to the Havre Diesel Shop Superintendent.

The Center, with the help of its partners, successfully setup a system to sell Montana's biodiesel in Havre. Ezzie's Wholesale in its Havre CENEX station, started selling B5 blend (5% by volume of biodiesel) using biodiesel produced by Earl Fisher Biofuels. The B5 blend was sold at the same price as the regular diesel. Profits gained from using biodiesel were set aside to purchase more biodiesel. This system would ensure the continuity of biodiesel blend use and sales in Havre. To educate the public on the benefits and deficiencies of biodiesel as well as misconceptions of using biodiesel, the Center and its partners with the help from the National Biodiesel Board through its Diesel Technician Training Program, successfully held a biodiesel workshop for diesel technicians at MSUN. Results and outcomes of this task were also presented to a variety of audiences.

The Center and its partners continued to educate the public and biodiesel stakeholders (e.g., farmers, producers, users, and policy-makers) on the viability and potential of a community-based oilseed and biodiesel production model for the region. The Center was also successful in getting funding and support to continue planning and execution of this community-based model.

4.1.1. Long-Term Environmental Benefits of using B20 Blend

The Center and Earl Fisher Biofuels produced 1,073 gallons and 14,431 gallons of biodiesel, respectively, for this project. This was matched by BNSF Railways which provided 77,524 gallons of diesel. One significant outcome of this study was that Earl Fisher Biofuels, operated and owned by third-generation farmers, Brett Earl and Logan Fisher, became a trusted vendor of the BNSF Fuel Department. It created a direct network between Earl Fisher Biofuels and Rocky Elgie of BNSF's fuel department head. With this network established, Earl Fisher Biofuels was now able to negotiate with BNSF for future biodiesel sales. The project also demonstrated the capacity of BNSF's Havre Diesel Shop to receive bulk biodiesel for making B20 blend and comply with ASTM 7467, Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20).

Results of the emissions testing showed a general decrease in NO (2 to 6%), NO_2 (2 to 14%), CO (2 to 16%), and total hydrocarbons (5 to 13%) emissions for B20 blend compared to diesel. The decrease in concentration of emission species (e.g. NO, NO_2, and CO) for B20 blend was affected by the mode the locomotive was running. In general, there was an overall reduction in emissions at mode 1, the warm-up mode. Reduction in NO and NO_2 emissions for B20 blend were mostly observed at modes using mid-range power notches. Meanwhile CO and total hydrocarbon emissions for B20 blend were lower compared to diesel at modes with lower power.

At the end of the demonstration, BNSF released their initial assessment on the impacts of biodiesel use on locomotive performance and maintenance. The following were their assessment:

a) Currently use up to 5% biodiesel "B5" as part of ASTM D975 diesel fuel specification,
b) "B20" test at Havre, MT to evaluate maintenance and reliability impacts,
c) Initial plugging of fuel filters due to fuel system "clean-up", no subsequent issues,
d) Fuel injector teardown inspection, no issues, and
e) Extreme winter operations, no issues.

During the last quarter of the maintenance schedule, deposits or "gums" were observed on the fuel injectors. Several factors and reasons could have caused the formation of 'gums" on the fuel injectors but none of the reasons had proven detrimental to continued use of biodiesel blends.

The results of this study demonstrated the environmental benefits of using good quality B20 blend for railroad locomotive engines with no significant loss in performance. This demonstration concurred with Amtrak's findings from its year-long Heartland Flyer B20 trial in 2011.[11] In that study, it was observed that B20 blend emissions were lower than the emission limits set by EPA. In essence, B20 blend was a reliable fuel causing minimal and engine wear.

4.1.2. Long-term Economic Benefits of Using B20 Blend

BNSF has been exploring the use of alternative fuel and energy sources for its fleet. In 2010-2011, BNSF conducted an in-service test of a hydrogen fuel cell hybrid in Commerce, CA with updates that increased fuel cell power and hydrogen storage capacity. BNSF has also conducted extensive testing and use of liquefied natural gas (LNG), through Refrigerated Liquid Methane (RLM), from 1987 – 1995 that posed up to 30% loss in horsepower, loss in efficiency and safety issues. BNSF has also experienced reliability issues and escalating fuel cost on LNG fueled MK Rail locomotives leased by BNSF from 1993 to 2012. Unlike the alternative energy sources discussed above, use of biodiesel does not require engine modification for BNSF locomotives, does not present issues in its use, and does not contribute to significant power loss. The ease of switching an entire fleet of locomotive engines to biodiesel without any engine modification makes biodiesel the best option among other alternatives.

Due to biodiesel's excellent lubricity, low toxicity, and high flash point, it is safer to handle compared to diesel and it is beneficial to the environment. These properties of biodiesel could easily outweigh the additional cost of biodiesel in the longer term. Though the price of biodiesel in Montana is still cost-prohibitive, biodiesel in other states are being sold at equal or close to the cost of diesel fuel. A different set of market conditions, not one conditioned by overseas petroleum supply, would be at play in biodiesel pricing.

Another way that the Center and its partners addressed the long-term cost of biodiesel was through the Center's project on developing a closed-loop, community-based oilseed production model that was funded through the Western Sustainable Agriculture Research and Education Grant Program (Western SARE). The project successfully demonstrated how Montana farmers would be able to attain 10% energy independence using these steps: (1) allocating a portion of their land to growing oilseeds, (2) extracting and processing the oil to food-grade culinary oil, then (3) collecting back the used oil to fuel their farming operations. This system of marketing oil as a high-grade cooking oil and reprocessing the used oil to make fuel provides value-added product that makes growing oilseeds competitive and advantageous against growing wheat.

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[11] Sims, B. Amtrak presents details on year-long Heartland Flyer B20 trial. *Biodiesel Magazine* [Online] Posted November 7, 2011. http://www.biodieselmagazine.com/articles/8156/amtrak-presents-details-on-year-long-heartland-flyer-b20-trial (accessed August 11, 2014).

4.1.3. Markets for Montana Biodiesel

Another significant outcome of the project, besides opening the railway industry market to Montana biodiesel, was the successful execution of making Montana biodiesel available for public utilization. This broadened the market for Montana biodiesel. Over a hundred community residents, stakeholders, partners, and technicians attended when Ezzie's owner, Lary Poulton, opened the Montana B5 blend pump to the public. Local newspapers and television news covered the event, increasing public awareness for both the project and biodiesel availability in the region. On the same week of the grand opening, the Center hosted a diesel technician training conducted by the National Biodiesel Board. Over sixty diesel technicians, diesel instructors and diesel tech students in Montana completed the training and are now able to provide solutions to common engine problems usually attributed to biodiesel use. The participation of National Biodiesel Board in carrying out the training improved the community's confidence in using Montana biodiesel.

4.1.4. Oilseed and Biodiesel Development Plan

The Center and its partners were successful in expanding the development of oilseed and biodiesel production in Montana. The Center's partners are aware of the breadth and scale of planning and partnerships needed to establish an oilseed and biodiesel industry in Montana. Two regional planning grants, supporting this goal, were submitted and successfully awarded.

The Economic Development Administration awarded the Center a project to expand and enhance the region's existing research and development of bio-energy (bio-fuels) and foster technology transfer of renewable energy and energy efficiency technologies into the private sector. This grant award would lead to the scale-up of the Bio-Energy research projects and the identification of other valuable co-products. The grant aimed to further develop the research outcomes of this project into new opportunities for the region's agricultural sector. The grant award also provided support for technical assistance for businesses, technology transfer, and collaborative research with public and private sector.

Opportunity Link, one of the Center's partners, was recently awarded a HUD-EPA-DOT Sustainable Communities Regional on behalf of Northcentral Montana communities. With this grant award, Northcentral Montana communities would have resources to facilitate planning for sustainable development and to develop a 20-year regional, coordinated plan. The planning would help address farmer-producer risks and develop new market opportunities in the agricultural energy, oil & gas, and biofuel sectors. With Biomass Crop Assistance Program (BCAP) of the U.S. Department of Agriculture, and EPA's new target goals for using biodiesel and sustainable aviation fuel, demand for oilseeds would be expected to increase. However, with no secure market in sight, Montana farmer-producers struggle to understand and mitigate oilseed crop risks. These grant awards aimed to produce and disseminate information.

5. CONCLUSIONS

Through the project, the research and testing capabilities of the Bio-Energy Center of Montana State University Northern (MSUN), were enhanced to make it a Regional Research Center of Excellence to address the obstacles concerning biofuels, feedstock, quality, conversion process, economic viability, and public awareness. Three laboratories equipped with the needed instrumentation were established to facilitate research on and testing of advanced biofuels derived from locally grown agricultural crops and synthesis of value-added chemicals from waste products such as lignin. The enhanced capabilities of the center also helped to demonstrate model systems that create the market for Montana biofuels and educate the community on the benefits of using biofuels. New advanced biofuels (e.g. bio-jet fuel with aromatics) and value-added chemicals were produced from camelina, potentially expanding Montana’s oilseed market. The Center was also successful in demonstrating the feasibility of using B20 blend in locomotive engines, increasing public awareness on the benefits of using biodiesel, and collecting information on the practicality, advantages, and challenges of using straight vegetable oils (SVO), waste vegetable oils (WVO), and “off-spec” biodiesel for farming operations.

APPENDIX

Tables A-1 and A-2 summarize the average and standard errors of BSFC, brake power, exhaust temperature, and exhaust emission concentration (in ppm). There are two test cycles used in evaluating diesel and different SVOs. Table A-1 lists the engine performance and emission analysis results obtained from operating CAT C15 diesel using a custom 3-mode constant speed test cycle as summarized in Tables 9. Table A-2, on the other hand, are results from operating the engine using a custom 3-mode test cycle as described in Table 10. In both test cycles, the CAT C15 diesel engine used in the study was coupled with a water break dynamometer.

Table A-1. Engine performance and emission analysis results using a custom 3-mode constant speed test cycle.

TEST/STEP		**Diesel No. 2**	**Canola**	**Safflower♣ (Oleic)**	**Safflower♣♣(Linoleic)**	**Camelina**
BSFC, g/bhp-h	1	0.26 ± 0.01	0.34 ± 0.01	0.36 ± 0.00	0.36 ± 0.00	0.35 ± 0.00
	2	0.29 ± 0.00	0.32 ± 0.04	0.37 ± 0.00	0.38 ± 0.00	0.37 ± 0.00
	3	0.28 ± 0.01	0.34 ± 0.00	0.36 ± 0.00	0.36 ± 0.00	0.36 ± 0.00
Power, hp	1	251.83 ± 0.62	251.36 ± 0.03	251.33 ± 0.07	251.30 ± 0.03	251.44 ± 0.02
	2	380.61 ± 0.39	372.60 ± 14.25	365.62 ± 0.06	380.22 ± 0.29	365.54 ± 0.05
	3	300.24 ± 0.15	300.07 ± 0.04	300.15 ± 0.07	300.16 ± 0.08	300.11 ± 0.05
Burn Rate, lbs/h	1	63.88 ± 2.45	85.37 ± 1.04	90.56 ± 0.17	90.47 ± 0.35	90.63 ± 0.12
	2	108.35 ± 0.43	126.70 ± 14.07	134.55 ± 0.29	142.60 ± 0.43	134.55 ± 0.45
	3	82.59 ± 1.96	102.31 ± 0.52	108.19 ± 0.28	108.45 ± 0.93	107.46 ± 0.24
Exhaust Temp., °C	1	683.55 ± 15.95	708.27 ± 13.22	735.31 ± 2.52	714.67 ± 2.00	730.65 ± 7.89
	2	813.52 ± 30.67	820.67 ± 38.00	807.89 ± 5.54	828.53 ± 1.40	808.85 ± 6.36
	3	747.95 ± 37.15	725.15 ± 9.41	755.65 ± 5.83	738.39 ± 3.74	741.07 ± 3.74
NOx, ppm	1	1406.77 ± 23.08	1773.52 ± 3.98	1719.86 ± 27.98	1752.30 ± 26.78	1721.33 ± 32.06
	2	1149.45 ± 168.75	1307.80 ± 76.30	1219.84 ± 8.71	1288.38 ± 106.74	1252.79 ± 20.92
	3	1357.65 ± 208.02	1519.86 ± 18.30	1402.62 ± 70.19	1344.69 ± 39.38	1406.81 ± 39.19
CO_2 , %	1	6.48 ± 0.14	6.96 ± 0.04	7.08 ± 0.01	6.97 ± 0.01	7.20 ± 0.04
	2	7.24 ± 0.13	7.94 ± 0.69	7.58 ± 0.03	7.62 ± 0.36	7.69 ± 0.03
	3	7.05 ± 0.30	7.19 ± 0.01	7.28 ± 0.03	7.14 ± 0.00	7.21 ± 0.04
CO, pp	1	50.78 ± 4.30	29.32 ± 1.25	28.55 ± 0.88	25.42 ± 0.80	31.54 ± 1.95

TEST/STEP		Diesel No. 2	Canola	Safflower♣ (Oleic)	Safflower♣♣(Linoleic)	Camelina
	2	16.36 ± 1.02	458.41 ± 776.80	11.03 ± 0.03	14.08 ± 3.36	11.31 ± 0.29
	3	61.11 ± 29.46	22.15 ± 1.51	20.59 ± 1.23	16.23 ± 0.17	17.89 ± 0.84
SO_2 , ppm	1	0.74 ± 0.10	0.50 ± 0.09	0.64 ± 0.02	0.47 ± 0.01	0.30 ± 0.11
	2	0.94 ± 0.02	0.78 ± 0.08	0.80 ± 0.01	0.67 ± 0.04	0.74 ± 0.10
	3	0.82 ± 0.13	0.59 ± 0.12	0.68 ± 0.08	0.67 ± 0.00	0.70 ± 0.12
NO , ppm	1	1364.91 ± 21.09	1736.88 ± 1.49	1678.11 ± 27.37	1710.88 ± 26.55	1689.24 ± 36.77
	2	1117.35 ± 167.41	1278.38 ± 75.05	1190.93 ± 7.89	1259.64 ± 103.21	1226.52 ± 20.51
	3	1318.59 ± 203.10	1488.75 ± 21.79	1368.87 ± 69.60	1313.19 ± 39.30	1373.55 ± 39.07
N_2O , ppm	1	0.45 ± 0.14	0.42 ± 0.01	0.47 ± 0.00	0.52 ± 0.01	0.53 ± 0.01
	2	0.34 ± 0.17	0.35 ± 0.00	0.41 ± 0.00	0.46 ± 0.04	0.28 ± 0.00
	3	0.41 ± 0.18	0.48 ± 0.01	0.44 ± 0.00	0.49 ± 0.00	0.32 ± 0.01
NH3 , ppm	1	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.02 ± 0.01
	2	0.01 ± 0.00	0.01 ± 0.01	0.00 ± 0.00	0.01 ± 0.01	0.01 ± 0.01
	3	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00
HCHO , ppm	1	0.69 ± 0.54	0.84 ± 0.21	0.34 ± 0.05	0.49 ± 0.02	0.68 ± 0.19
	2	0.46 ± 0.23	0.55 ± 0.04	0.24 ± 0.02	0.46 ± 0.03	0.35 ± 0.06
	3	0.63 ± 0.18	0.74 ± 0.18	0.32 ± 0.01	0.41 ± 0.04	0.33 ± 0.02
PM, mg/m3	1	0.48 ± 0.06	0.11 ± 0.03	0.08 ± 0.00	0.10 ± 0.00	0.16 ± 0.06
	2	0.13 ± 0.01	0.21 ± 0.30	0.03 ± 0.01	0.06 ± 0.01	0.04 ± 0.01
	3	0.43 ± 0.21	0.07 ± 0.01	0.05 ± 0.00	0.06 ± 0.00	0.07 ± 0.01
THC, ppm	1	14.60 ± 0.72	N/A	9.96 ± 0.16	9.60 ± 0.02	N/A
	2	13.47 ± 0.65	N/A	10.15 ± 0.02	8.94 ± 0.11	N/A
	3	14.26 ± 0.98	N/A	9.83 ± 0.05	8.94 ± 0.09	N/A

Notes:♣ - Hi-oleic variety of safflower oil was used; ♣♣ - hi-linoleic variety of safflower oil was used. Average values are presented followed by the standard deviation. N/A - not applicable since no data was collected during testing due to instrument error or malfunction.

Table A-2. Engine performance and emission analysis results using a custom 3-mode test cycle.

TEST/STEP		Canola	Safflower♣ (Oleic)	Safflower♣♣ (Linoleic)	Camelina
BSFC, g/bhp-h	1	0.36 ± 0.01	0.38 ± 0.01	0.37 ± 0.02	0.38 ± 0.00
	2	0.34 ± 0.01	0.36 ± 0.01	0.36 ± 0.00	0.36 ± 0.00
	3	0.36 ± 0.00	0.37 ± 0.00	0.37 ± 0.00	0.37 ± 0.00
Power, hp	1	126.60 ± 0.06	126.61 ± 0.02	126.57 ± 0.06	126.59 ± 0.13
	2	252.70 ± 0.12	252.77 ± 0.01	252.80 ± 0.06	252.78 ± 0.04
	3	337.87 ± 0.07	337.95 ± 0.06	337.91 ± 0.11	338.02 ± 0.11
Burn Rate, lbs/h	1	45.17 ± 0.03	47.76 ± 0.36	47.71 ± 0.14	48.52 ± 0.10
	2	85.60 ± 0.23	91.10 ± 0.22	90.77 ± 0.39	91.11 ± 0.44
	3	120.45 ± 0.56	124.72 ± 0.43	124.06 ± 0.41	124.65 ± 0.47
Exhaust Temp., °C	1	623.34 ± 5.49	660.68 ± 17.22	638.51 ± 6.99	676.95 ± 1.08
	2	752.78 ± 6.31	778.48 ± 0.96	754.15 ± 4.39	771.57 ± 2.65
	3	731.88 ± 1.66	770.23 ± 2.77	751.28 ± 3.92	770.86 ± 2.67
NOx, ppm	1	2026.08 ± 10.13	2112.19 ± 7.77	1927.18 ± 211.20	2128.84 ± 27.47
	2	1809.51 ± 30.86	1577.32 ± 18.75	1832.81 ± 232.27	1600.26 ± 72.20
	3	1308.44 ± 31.13	1278.48 ± 21.87	1449.98 ± 205.55	1284.92 ± 35.88
CO_2 , %	1	6.23 ± 0.02	6.40 ± 0.02	6.62 ± 0.30	6.70 ± 0.04
	2	7.48 ± 0.03	7.54 ± 0.02	7.08 ± 0.58	7.61 ± 0.03
	3	7.00 ± 0.05	7.24 ± 0.02	7.24 ± 0.16	7.37 ± 0.03
CO, ppm	1	48.39 ± 3.40	41.70 ± 0.07	44.74 ± 17.70	41.12 ± 1.42
	2	35.67 ± 1.36	38.11 ± 0.64	35.13 ± 7.94	38.04 ± 0.74
	3	14.91 ± 0.82	17.13 ± 0.32	20.34 ± 8.65	16.90 ± 0.14
SO_2 , ppm	1	0.41 ± 0.06	0.26 ± 0.06	0.38 ± 0.13	0.32 ± 0.03
	2	0.58 ± 0.01	0.67 ± 0.04	0.50 ± 0.12	0.47 ± 0.04
	3	0.65 ± 0.05	0.68 ± 0.02	0.57 ± 0.03	0.42 ± 0.06
NO , ppm	1	1971.51 ± 11.00	2062.99 ± 9.46	1880.48 ± 204.94	2077.91 ± 26.76
	2	1773.19 ± 27.56	1541.07 ± 18.63	1792.62 ± 221.62	1565.15 ± 70.51
	3	1274.05 ± 30.78	1244.70 ± 21.26	1416.68 ± 203.64	1254.39 ± 35.79
N_2O , ppm	1	0.48 ± 0.01	0.46 ± 0.00	0.59 ± 0.07	0.57 ± 0.01
	2	0.41 ± 0.00	0.47 ± 0.01	0.53 ± 0.05	0.51 ± 0.01
	3	0.41 ± 0.00	0.46 ± 0.00	0.50 ± 0.01	0.50 ± 0.01
NH3 , ppm	1	0.02 ± 0.00	0.02 ± 0.00	0.01 ± 0.01	0.02 ± 0.00
	2	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
	3	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00
HCHO , ppm	1	1.00 ± 0.11	0.63 ± 0.00	0.97 ± 0.50	0.46 ± 0.03
	2	0.70 ± 0.10	0.38 ± 0.06	0.63 ± 0.15	0.41 ± 0.02
	3	0.62 ± 0.05	0.39 ± 0.01	0.47 ± 0.04	0.45 ± 0.04
PM, m	1	0.30 ± 0.22	0.11 ± 0.00	0.73 ± 0.46	0.14 ± 0.02

TEST/STEP		Canola	Safflower♣ (Oleic)	Safflower♣♣ (Linoleic)	Camelina
	2	0.09 ± 0.00	0.08 ± 0.00	0.10 ± 0.00	0.12 ± 0.00
	3	0.05 ± 0.00	0.05 ± 0.00	0.06 ± 0.00	0.07 ± 0.00
THC, ppm	1	N/A	10.53 ± 0.04	N/A	N/A
	2	N/A	9.38 ± 0.20	N/A	N/A
	3	N/A	8.91 ± 0.16	N/A	N/A

Notes:♣ *- Hi-oleic variety of safflower oil was used;* ♣♣ *- hi-linoleic variety of safflower oil was used. Average values are presented followed by the standard deviation. N/A - not applicable since no data was collected during testing due to instrument error or malfunction.*