MSU-NORTHERN

BIO-ENERGY CENTER

OF EXCELLENCE

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ABSTRACT

MSU-Northern set out to build the Bio-Energy Center as a Regional Research Center of Excellence to address the obstacles concerning biofuels, feedstock, quality, conversion process, economic viability and public awareness. The Bio-Energy Center built its laboratories and expertise in order to research and support product development and commercialization for the bio-energy industry in the Montana.

Greg Kegel, Principle Investigator
Jessica Windy Boy, Director
Dr. Md. Joynal Abedin
Dr. Randy Maglinao

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EXECUTIVE SUMMARY.

MSU-Northern established the Bio-Energy Center (the Center) into a Regional Research Center of Excellence to address the obstacles concerning biofuels, feedstock, quality, conversion process, economic viability and public awareness. The Center built its laboratories and expertise in order to research and support product development and commercialization for the bio-energy industry in our region. The Center wanted to support the regional agricultural based economy by researching biofuels based on feedstock's that can be grown in our region in an environmentally responsible manner. We were also interested in any technology that will improve the emissions and fuel economy performance of heavy duty diesel engines. The Center had a three step approach to accomplish these goals:

1. Enhance the Center's research and testing capabilities
2. Develop advanced biofuels from locally grown agricultural crops.
3. Educate and outreach for public understanding and acceptance of new technology.

The Center was very successful in completing the tasks as outlined in the project plan. Key successes include discovering and patenting a new chemical conversion process for converting camelina oil to jet fuel, as well as promise in developing a heterogeneous Grubs catalyst to support the new chemical conversion process. The Center also successfully fragmented and deoxygenated naturally occurring lignin with a Ni-NHC catalyst, showing promise for further exploration of using lignin for fuels and fuel additives. This would create another value-added product for lignin that can be sourced from beetle kill trees or waste products from cellulose ethanol fuel facilities.

Another important research component for this project was to create a market for biodiesel in North Central Montana. North Central Montana is a very conservative region with an aging population. The culture in our region rejects new products and change, making selling biodiesel or even a biodiesel blend a tough market. Our local biodiesel producer worked for several years trying to get a local fuel distributor to carry a 5% or greater blend of biodiesel. They were repetitively turned down. To better educate our population and support in order to create a local market for biofuels, the Center developed a strategy to run fleet tests with local businesses that are recognized and respected in our community. The theory is that if the companies' endorsed using biodiesel blends, the community would accept biodiesel blends. The Center partnered with Opportunity Link and the North Central Transit to use a 5-20% biodiesel blend in the Transit bus fleet for the first test. Opportunity Link assisted with the community promotion and support. The transit ran the biodiesel blend for over a year with no operability problems, including the extreme cold winter months.

After concluding the transit fleet test, the Center approached Burlington Northern Santa Fe Railroad (BNSF) about conducting a yearlong study using a biodiesel 20% blend. This test was the first of its kind for BNSF and the first locomotive fleet test conducted in our climate. The test was comprehensive and considered effects on fuel filters, fuel consumption and injector wear. Two sets of injectors were pulled every three (3) months and sent to the manufacture for evaluation. The test was also comparative. Two engines were hooked together for the entire test. One engine did not use biodiesel where the other engine used a 20% blend. The project completed and was very successful. BNSF did not experience any significant operability problems during the test. All biodiesel used in the test was Montana grown and produced. These successful tests opened the market for biodiesel 5% blend with a local fleet fuel provider. They have several fleets that are exclusively fueled with the biodiesel blend in the summer including the Havre Public School System.

The Center also investigated the emissions effects of using off-spec biodiesel. The Environmental Protection Agency requires all biodiesel producers to certify and test their fuel according to ASTM D 6798 standards. The average cost for full ASTM D6798 fuel testing is $1100 per sample. This cost is very prohibitive for the small biodiesel producer wanting to make enough fuel for self-use. The Center felt that the EPA policy is not in line with actual risk for damage to the environment. The ASTM standard is establish to ensure fuel quality and consumer protection. Environmental protections are not considered in the ASTM fuel standards. To explore the effects of burning off-spec biodiesel at 100% blend the Center performed a series of engine performance testing on a Cummins ISL, 2007 compliant. The fuels were tainted with the following imperfections:

- Unconverted oils 5%
- Methanol 5%
- Free Fatty Acids

We were only testing for changes in the emissions in comparison to good quality biodiesel, B100. The results included the following: in the methanol 5% blend, carbon monoxide raised considerably. The PM increased for both the methanol and free fatty acid fuels. However, even with the increases in carbon monoxide and PM, the emissions from the off-spec 100% biodiesel was significantly decreased in comparison to ultra-low sulfur #2 clear diesel.

Two major tasks assisted the Bio-Energy Center in becoming a proof of concept center for bio-based heavy duty diesel engine products. To accomplish this goal, the Center needed to build out three important labs. The first lab was the biomass conversion lab, used to research advanced fuels including jet fuel and fuel additives. The Center also added a wet chemistry lab that including a chemical synthesis lab, necessary for catalyst research. Both of these labs are very key in supporting our biofuels research. The Center has remodeled our old Auto-Diagnostic lab to install a new 750kW A/C dynamometer, emissions benches and created safe OSHA approved room for the biofuel processing reactor. This building, renamed “The Advance Fuels Building” required major mechanical and electrical upgrades to accommodate the new equipment. The Advance Fuels Building was finished in in June 2014, however it was commissioned in June 2013.

GOALS AND OBJECTIVES ACCOMPLISHMENTS GRID

Goal: To establish Montana State University-Northern Bio-Energy Center of Excellence that will perform research on non-food biomass conversion and optimization studies for biomass.	
Objective	**Accomplishment**
Site Development of Bio-Energy Research Center:	Three labs were established: biomass conversion lab, wet chemistry/synthesis lab and advance heavy duty engine test lab. **SUCCESSFUL**
Development of Alternative Bio-based Aviation Fuel	Lignan was separated using catalyst, unsuccessful in first approach. The second approached shows promise, although the Center was unable to produce a fuel from the lignin.
Development of Camelina Oil-derived Fuel for Naval Applications	The Center developed and patented a new process to convert camelina oil to jet fuel as well as other fuel types such as diesel and navel fuel using a Grubbs catalyst approach. **SUCCESSFUL**
Viability of Using Straight Plant Oils in Agricultural Operations	Successfully pressed different oilseeds produced in MT including camelina, safflower (2 types), and canola. Researched purifying techniques for organic oils to include degumming from filter press, chemical, and centrifuge. Ran different processed oils in CAT 3176 for engine performance. Tried to run last trial of Waste Vegetable Oil in newer 2007 Cummins ISL engine, failed. New engines will not allow the “hotter” fuel to be ran due to safety feature programed in the engine. **SUCCESSFUL**
Performance of Locomotive Engine Fueled with Biodiesel Blend	Performed 1 yearlong study with BNSF engines in Havre, MT rail yard. **SUCCESSFUL**
Engine Exhaust Emissions of Off-spec Biodiesel	Ran three different fuel tests of Biodiesel 100 in an ISL Cummins engine. **SUCCESSFUL**
Out-Reach and Education to Support Developing “Green” Industry in Montana	Due to movement in funding priorities within the project, the scope was scaled back to focus on college classes and general 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. **SUCCESSFUL**
Technical Assistance to Montana and North Central Regional Bio-based companies	The Center successfully assisted three companies with product testing for R&D. **SUCCESSFUL**
Administration	General grant administration.

PROJECT SUMMARY

Task 1.0, Site Development of Bio-Energy Research Center

MSU-Northern renovated the Auto Diagnostics building to install new updated equipment and upgrade the mechanical and electrical systems necessary for the new 750 kW A/C Dynamometer. The building previously held an old eddy current chassis dynamometer that was removed several years past. The renovations brought the building up to code and installed proper ventilation and fire rating for the fuel processing equipment. The building also meets all new Montana State code requirements for energy efficiency.

Task 2: Development of Alternative Biobased Aviation Fuel

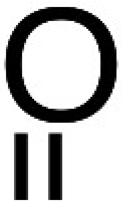
We have planned to make bio-oil (fuel) from lignin by catalytically breaking lignin of lignocellulosic materials. Lignin is an amorphous polymer that, unlike the cellulose fraction of biomass, varies in structure depending on the biomass source. Lignin polymer consists of network of aromatic compounds bonded through very strong carbon oxygen bonds and is hard to break. But upgradation of lignin by breaking the bond can lead to valuable chemicals and aromatic rich fuels.

Methyltrioxorhenium (VII) ($MeReO_3$, MTO) in combination with H_2O_2 creates a potential catalyst for the oxidation of lignin model compounds. When we subjected Kraft lignin to oxidation using H_2O_2 and MTO as catalyst at room temperature there was no oxidative cleavage of lignin detected. Oxidative cleavage reactions using H_2O_2 and MTO in acetic acid at 25°C also led to no oxidative degradation. Similar reactions were carried out on lignin using these MTO catalysts at higher temperatures, 70°C, but no cleavage products were obtained. These results are consistent with the fact that lignins are heavily recalcitrant to oxidative cleavage due to significant amount of C-C and C-O condensed subunits. At even higher temperatures (100ºC), the Kraft lignin was subjected to oxidation with H_2O_2 using MTO catalysts in acetic acid but no lignin degradation was observed, only side chain oxidations of the aliphatic moiety occurred. These results suggest that the system requires a high temperatures, high pressures, and robust catalysts that can tolerate these conditions in order to have complete cleavage of lignin into its component fragment molecules. When we subjected lignin to MTO/H_2O_2 at 300 °C and 5 barr pressure in our high pressure, high temperature batch reactor, lignin degradation was observed by breaking the carbon-oxygen bond as observed by GC-MS.

The fragmented lignin contains phenolic oxygen which was not removed by MTO catalyst. In order to make aromatic hydrocarbon fuel we needed to further deoxygenate the fragmented lignin. Nickel (Ni) based catalyst are known to cleave phenolic oxygen. The research direction changed to include development of a Ni based catalyst that works for removing oxygen from the fragmentated lignin.

Synthesis of deoxygenation catalyst of lignin for bio-based jet fuel and fuel additives

The synthesis of deoxygenated catalyst of lignin requires several step chemical reaction to synthesize the catalyst. The synthetic scheme performed for catalyst synthesis is shown below. Catalysts synthetic process consists of two primary steps, namely (1) functionalizing of solid support (silica) with azide groups (Scheme 1) and (2) N-heterocyclic ligand (NHC) of nickel complex with alkyne group (Scheme 2).



Azide functionalized silica synthesis is shown in **scheme 1**. Alkyne functionalized NHC ligand was synthesized by alkylating bis-imine with TMS protected propargyl group followed by removal of TMS to generate a terminal alkene group on the bis-imine. This alkyne containing bis-amine was reduced to diamine which was cyclized to afford compound **2** (alkyne terminal N-heterocyclic carbene) All the synthesized ligands were characterized by NMR and LC-MS.

(**Scheme 2**).

Finally we anchored NHC ligand with the silica support by azide alkyne click chemistry in presence of Cu (1) catalysts shown in **scheme 3.**

The cleavage reactions was carried out with combination of nickel (0) precursor, $Ni(COD)_2$ and a solid supported NHC ligand (Complex **3**) which formed in-situ catalyst (structure **4**) through deprotonating the corresponding salt (Complex **3**) with a base (NaO^tBu). In an inert atmosphere, $Ni(COD)_2$ was charged at 80 °C with SiO_2-NHC (**3**). The addition of HCl and NaO^tBu in the presence of small amount of an inert solvent, such as THF or xylene, resulted in the SiO_2-NHC-Ni catalysts (**4**). The synthesized SiO_2-NHC-Ni complex carries a strong carbene-nickel and Si-O bonds and was able to tolerate high temperature and pressure to cleave aromatic C-O bonds of lignin.

The catalyst was evaluated for its catalytic activities first on arene ether. Cleavage of the carbon oxygen bond of arene ether, at room temperature and atmospheric pressure, resulted in two aromatic compounds (Eq **1**)

Naturally occurring Kraft lignin with defined structure was subjected to elevated temperatures and pressures (up to 523 K, 5 barr) to cleave lignin's aromatic C-O bonds into non-phenolic aromatic compounds using high boiling green solvents such as GVL, levulinic acid etc. (Eq **2**).

Summary: Naturally occurring lignin was defragmented and deoxygenated with a Ni-NHC catalyst. Fragmentated aromatic products were purified by chromatographic separation and characterized by GC-MS. We did not produce enough sample for fuel properties characterization. This research has opened up the path for further exploration of lignin towards fuels and fuel additives.

Task 3 Development of Camelina Oil-Derived Fuel for Advance Transportation Fuels

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, biofuels continued use appears 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 situation, the development and use of alternative sources of fuels becomes 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 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 oil. Both HEFA and SPK are composed of only hydrocarbons. To mitigate some of the anticipated operational problems associated with the use of renewable fuels, a maximum blend of 50% with conventional jet fuel was employed during these demonstrations.

However, SPK and HEFA present challenges in the production and economic stand point. To date, none of the commercial scale FT facilities are located in the U.S. The four commercially viable technologies based on FT process located in South Africa, the Middle East and Asia are using 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.

Montana State University-Northern Bio-Energy Center had proposed a process 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.

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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. (2009). Aviation and global climate change in the 21st century. Atmospheric Environment, 43(22), 3520-3537.

2 Davis, S.C.; Diegel, S.W. and Boundy, R.G. 2013. Transporation Energy Data Book: Edition 32. U.S. Department of Energy. website: cta.ornl.gov/data (Accessed on 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.

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 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 ethenolyis, had also been reported and demonstrated.[8,9]

This study demonstrated that ethenolysis of camelina biodiesel under mild temperature conditions (20 – 100ºC) using Ruthenium-based catalysts can take place. The products of the camelina biodiesel metathesis consists of a variety of aliphatic and cyclic monoalkenes and dienes. (Table 1) 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% saturated, monounsaturated and polyunsaturated components, respectively. The monounsatured components in camelina biodiesel are primarily oleic (C18:1), and eicosanoic (C20:1) comprising about 24 and 13% of the fatty acid methyl ester content of the 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).

Most of the unsaturated fatty acids however were converted to decenoic acid methyl esters (C10:1), with carbon-carbon double bond at position 9 (terminal alkene) as a result of

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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).

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.

ethenolysis. (Table 1) The 10 -12% saturated components, which are mainly palmitic (C16:0; 7%) and stearic (C18:0; 2%) remained unreacted.

Table 1. 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

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

Legends: [a] – list of the major unsaturated fatty acid methyl esters found in the 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, [e] – 9-octadecene was produced by metathesis of two 1-decene compounds.

Production of Advanced Transportation Fuel from Camelina Oil

One of the challenges of using camelina biodiesel in alkene metathesis is 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. Currently, biodiesel, also known as fatty acid methyl esters, has not been approved by FAA for commercial and military aviation engines. Thus, a fuel containing fatty acid methyl esters could not be accepted as an alternative jet fuel.

In order to solve this issue, the Center investigated the alkene metathesis of camelina oil, instead of biodiesel, for the production of advanced transportation fuels. The hypothesis is that the fatty acids moieties in the triglycerides will remain intact after alkene metathesis and the same hydrocarbons will still be produced. Since oil has 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 Oil-Dri (Perform) bleaching clay and mixing the slurry for 30 minutes. The slurry was then centrifuged and the purified liquid product was collected. For the second step of the process, the purified liquid product from the first step was mixed with 4.0% by wt. of a hydrogenation catalyst (nickel-based catalyst). Hydrogen gas was supplied and maintained at 482 hPa and the slurry was 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.

In a separate experiment, the slurry solution was reacted at atmospheric pressure and in a closed system for one hour at 80°C before undergoing hydrogenation. It is hypothesized that the absence of hydrogen will lead to aromatization of some alkenes.

Table 2. 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.

Notes: The hydrocarbon fraction were 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 undergone ethenolysis and hydrogenation using a nickel-based hydrogenation catalyst. [c] – camelina oil undergone ethenolysis, aromatization (reaction with a nickel-based catalyst in the absence of hydrogen) and then hydrogenation. [d] – not detected by GC/MS.

The gas chromatography-mass spectrometry results of the distillate showed that only the hydrocarbons were collected. (Table 2) 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 (benzene and ethylbenzene).

The presence of 1,4-cyclohexadiene, which is formed via ring closure metathesis of linolenic acid (C18:3) during ethenolysis, presents a potential in producing fuels with aromatics. Results showed that adding an aromatization step during processing produces a distillate with 25.8 ±1.5 % wt. aromatics. (Table 2) The aromatics components in the distillate were composed mainly of benzene and a minimal amount of ethylbenzene.

Table 3. Conversion and selectivity to benzene and alkanes during aromatization and hydrogenation steps.

	REACTION PARAMETERS			
MODEL COMPOUND	Successive aromatization and hydrogenation with 1-dodecene	Successive Starvation and Hydrogenation without 1-dodecene	Aromatization only with 1-dodecene	Hydrogenation only with 1-dodecene
1. 1,4-cyclohexadiene				
Conversion, % wt	>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, % wt	>99.9	----	20.2	>99.9
Hydrogenation				
dodecane	Major	----	Not detected	Major
Isomerization				
4-dodecene	Minor	----	Major	Minor
5-dodecene	Minor	----	Major	Minor

To better understand the formation of aromatics, model compounds where used in various steps of the process. Pure 1,4-cylcohexadiene in the presence and absence of 1-dodecene were used in aromatization and hydrogenation processes using the nickel-based catalyst and heptane as a solvent at 80°C. Successive aromatization and hydrogenation of 1,4-cyclohexadiene in the presence of 1-dodecene afforded benzene and dodecane as major products. Minor amounts of 4-dodecene and 5-dodecene resulted from the isomerization of 1-dodecene. (Table 3) As expected when these reactions were conducted in the absence of 1-dodecene, only the conversion of 1,4-cyclohexadiene into benzene via aromatization was observed. Further experiments proved that the aromatization of 1,4-cyclohexadiene to benzene is only possible during aromatization and not during hydrogenation. When 1,4-cyclohexadiene was subjected to aromatization in the presence of 1-dodecene, cyclohexane was essentially absent in the product resulting almost 100% conversion of 1,4-cyclohexadiene into benzene. Direct hydrogenation of 1,4-cylcohexadiene in the presence of 1-dodecene did not produced benzene; quantitative conversion of 1,4-cyclohexadiene to cyclohexane was observed.

The Center also investigated the fuel performance characteristics of the hydrocarbon distillate (or MSUN BioJet fuel) collected after processing camelina oil. The MSUN BioJet fuel was blended with Jet A, purchased from Havre Airport (Havre, MT), at 50% by volume at room temperature. The MSUN BioJet blend exhibited comparable cloud point, carbon residue and sulfur content with commercial Jet A fuel. (Table 4) On the other hand, there is three times more stable against oxidation compared to commercial Jet A fuel as evidenced by longer petrooxy value. (Table 4) The MSUN BioJet fuel blend also exhibited higher cetane number and cetane index compared to neat Jet A fuel. (Table 5) The lower distillation temperature of the blends at T90, T95 and density compared to neat Jet A fuel suggests the presence of higher amounts of shorter-chain hydrocarbons in the mixture.

Table 4. Some properties of the neat commercial Jet A fuel and MSUN biojet fuel.

Fuel Properties	ASTM Method	Jet A fuel	MSUN BioJet fuel
Cloud point, °C	D2500	Less than −32	Less than −32
Carbon residue, %	D4530	0	0
Sulfur, ppm	D5453	2.05	1.97
Petrooxy, min	D7545	63.8	180.5

Table 5. Some 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% by volume)
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, 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. A stirred tank vessel is the appropriate reactor for this type of reaction system, which is slow reaction and catalyzed by a homogeneous catalyst. 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, can be proposed. In order 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 acres of farm land required is 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 it 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.

Task 4.0 Establishing the Viability of Pure Plant Oils as an Alternative Fuel in Diesel Engines Based on Chemical Properties, Performance and Emission Testing

I. APPROACH--Overview

The Bio-Energy Center investigated the feasibility of using Straight Vegetable Oil (SVO) as a fuel for agricultural production (primarily tractors used during planting and harvesting crops). The Center researched three areas in order to assess the viability of using SVO as a fuel for agricultural producers:

virgin oil processing techniques, ASTM and EIN fuel quality, and heavy duty engine bench testing. To limit the types of oilseed investigated, MSUN focused only on oilseeds that are produced in Montana including:

- Canola
- Linoleic safflower
- High oleic safflower
- Camelina
- Waste Vegetable Oil (WVO)

The Center bought oilseed from local Montana producers and pressed the oilseeds in our pressing facility. This allowed the Center to be in control of the entire process during the evaluation. All fuel processing techniques were developed by the Center. The next step was to evaluate the fuel for fuel qualities in the fuel lab. After successful fuel evaluation, the last step is to test the fuel performance using a 3176 CAT diesel engine on a Taylor engine dynamometer.

II. FEEDSTOCK PREPARATION

When dealing with unconventional feedstock like vegetable oils, it is important to know its qualities and to perform the necessary pretreatment steps before using it to diesel engines. Water (both free and bound) and insolubles (sediments and particulates) are the common contaminants found in both virgin oils as well as waste vegetable oils. Water content and sediments can be removed through physical processes, such as filtration, settling and centrifugation. The oil specifications, listed in Table 1, are the recommended limits to ensure trouble-free engine operation.

Description	Target Value or Specification	Test Method
Water content	≤ 750 ppm	Water Determination by 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

To remove water and insolubles from waste vegetable oils, a multi-step system of filtration and centrifugation can be used. Figure 1 illustrates a possible low-capital setup for this purpose.

Table 1. Proposed Target Specifications.

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

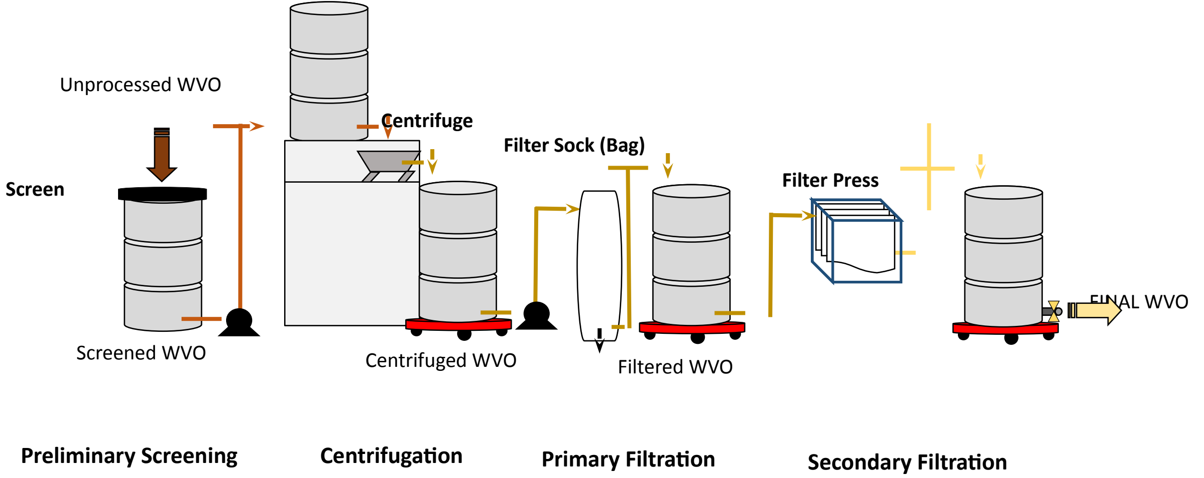


Figure 1. A schematic diagram of a low-capital pretreatment setup for refining WVO.

Preliminary Screening

Waste vegetable oil sometimes 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 2). In order to improve flow and screening capture, it is recommended that the screens are cleaned regularly.

Figure 2. Preliminary screening of waste vegetable oil.

Centrifugation

Centrifugation uses centrifugal force to sediment and 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. This is why 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 3 and 4). Results of the experiment conducted by the Bio-Energy Center showed that there is a significant reduction both in water and sediment content after centrifuging waste vegetable oil (Table 2).

Table 2. Percent removed after centrifugation.

	Percentage amount of contaminant removed after centrifugation	
Contaminant	**Oil was pre-heated to 130°F (55 °C)[a]**	**Oil was 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.

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 still remain. These very fine particles can accumulate and clog fuel

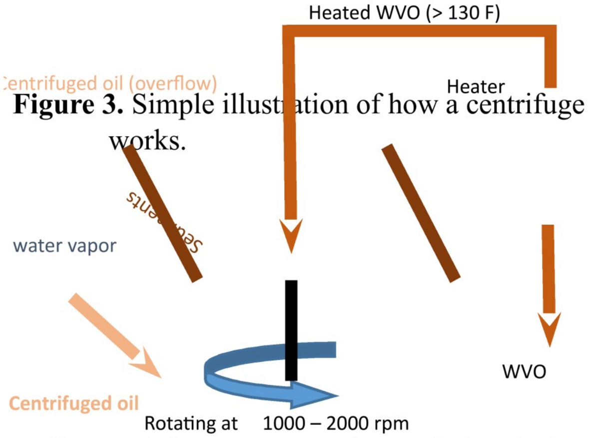


Figure 3. Simple illustration of how a centrifuge works.

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 is used to let the pressure build up inside and push the oil through the filter bag (Figure 5-b). A diaphragm pump is used to push the oil to the filtration unit. One advantage of using this type of filtration housing is 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 6). Filter presses use the fluid's (e.g. oil) 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.

Figure 4. Centrifugation of waste vegetable oil.

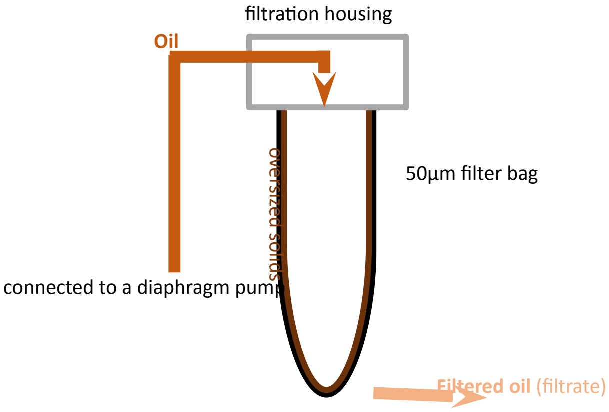


Figure 5. Primary filtration unit. (a) *Left photo:* Bio-Energy Center's primary filtration setup with a 50µm polyester filter bag inside. (b) *Top photo:* Schematic illustration on how solids are removed from an oil during filtration.

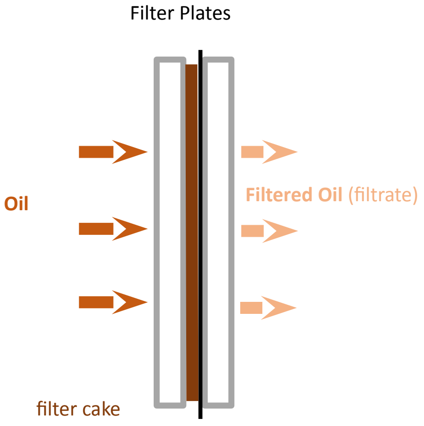
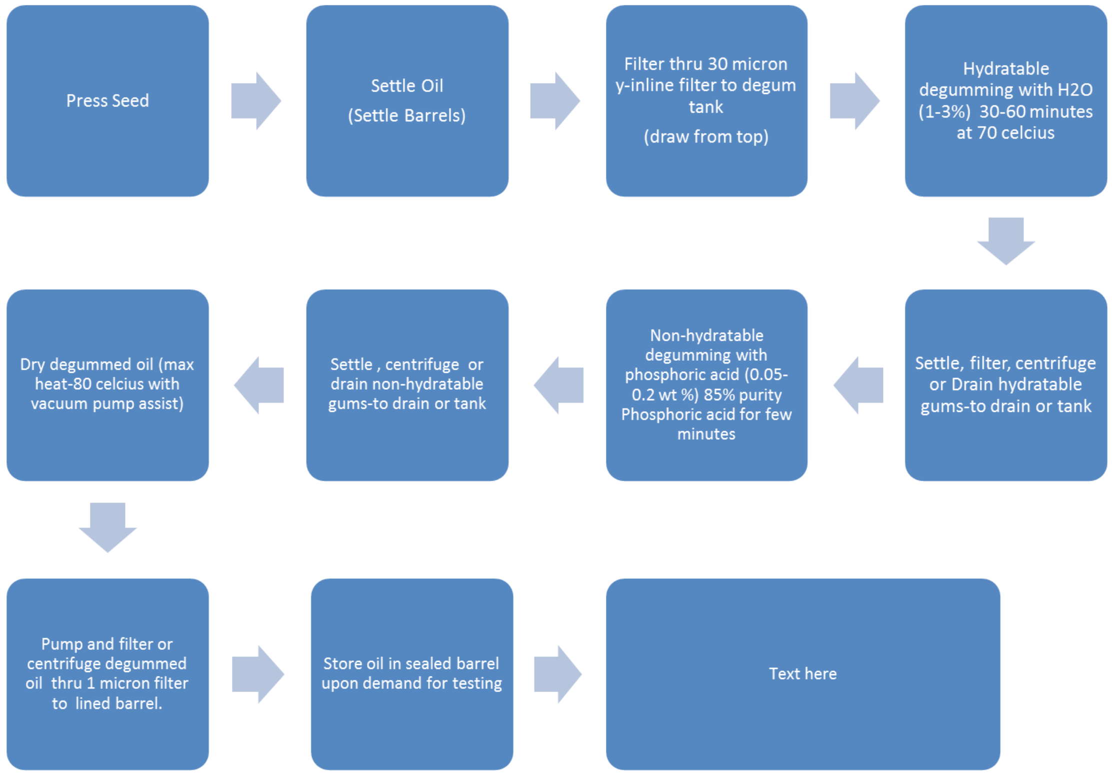


Figure 6. Filter press unit. (a) *Left photo:* Schematic illustration on how solids are removed from an oil in a filter press. (b) *Right photo:* Bio-Energy Center's filter press unit.

The Center also explored different
virgin vegetable oils, that is to say,
pressed from the oilseed. The
remove sediment and phoso-lipids
virgin, cold pressed oils. Three
settling and filter sock filtration,
press filtration. The original plan
performance test with oil from each
early in the research, the Center
filtered via chemical degumming or
not meet fuel quality standards,
fuel. The only purification method
was the filter pressed methold.
altered for the virgin pressed oils to
technique for purification.

techniques for processing
oils that are unpurified after
Center investigated methods to
and gums that are present in
methods were evaluated:
chemical degumming, and filter
was to conduct an engine
purification method. However
discovered that oils that were
filter sock/settling method did
therefore were unusable as a
that produced fuel quality oil
Therefore the research plan was
only use filter pressing

Proposed Chemical Degumming Experimental Design.



II. TEST RESULTS

Tables 3-a and 3-b lists the engine speeds and loads 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. The physical and chemical properties of plant oils used in this projects are summarized in Table 4. Canola and safflower (hi-oleic) oil were found to be suitable plant oil for Montana. It is noted that canola oil has better properties than safflower specially its kinematic viscosity. Camelina oil, due to its high ω-3 fatty acid content, is likely to build up more carbon deposits in the engine, e.g. fuel injectors. This is supported by the high test result of carbon residue of camelina oil (Table 4).

Table 3-a. BEC 3-Mode Test Cycle profile.

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

Table 3-b. BEC 3-Mode Constant Speed Test Cycle profile.

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

Table 4. Fuel properties of plant oils used during the project.

Fuel Property	**OIL TESTED**		
	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}

Notes: ♣ - 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.

The results of the engine performance and exhaust emission analysis using a CAT C15 diesel engine operated over a customized BEC's 3-Mode Constant Speed Test Cycle are summarized in Table 5 and Figures 7-14. The Brake Specific Fuel Consumption (BSFC) are generally higher in SVO than Diesel No 2. The possible reason for this is Diesel No 2 has slightly higher specific energy (amount of energy per unit mass) than the SVO used in this study. Petrodiesel is composed of hydrocarbons which typically has higher energy content (per unit mass) than oxygenated compounds like triglycerides and biodiesel. It is noted that plant oils are composed of mainly triglycerides. Exhaust emission results showed that carbon monoxide, soot and formaldehyde emissions were lower when SVO were used as fuels. Nitrogen oxides (NOx), on the other hand, are generally higher when SVO was used. It is still unclear what causes the increase in NOx emissions when using SVO.

During the project, the Bio-Energy Center moved in to a new research facility that houses a state-of-the-art a steady state engine test cell using an A/C dynamometer. After the test cell was completely commissioned, engine performance and exhaust emission analysis resumed using waste vegetable oil (WVO). A 2007 8.9L ISL Cummins diesel engine was used and operated over AVL's 8-Mode Test Cycle in this experiment. Diesel No 2 was used to establish a baseline. In order to protect the engine from contaminants in the WVO, the Center refined the oil using the setup discussed in Figure 1. During testing, the engine unexpectedly shut down during step 4 when WVO was used. The Center tried several runs to determine what causes the engine to shut down. It was concluded that during steps with high load settings, the computer unit (ECU) of the engine gives incorrect output signals specifically the load. The ECU calculates and sends out signals that the engine is at 100% load even the actual load is just at 60%. It is suspected that the ECU signals the engine to shut down once the calculated percent load reaches beyond 100%. How the computer unit calculates the percent load is still unclear.

Table 5. Engine Performance and Emission Analysis Results using BEC's 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

TEST/STEP		Diesel No. 2	Canola	Safflower♣ (Oleic)	Safflower♣♣ (Linoleic)	Camelina
	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, ppm	1	50.78 ± 4.30	29.32 ± 1.25	28.55 ± 0.88	25.42 ± 0.80	31.54 ± 1.95
	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
H	1	0.69 ± 0.54	0.84 ± 0.21	0.34 ± 0.05	0.49 ± 0.02	0.68 ± 0.19

TEST/STEP		**Diesel No. 2**	**Canola**	**Safflower♣ (Oleic)**	**Safflower♣♣ (Linoleic)**	**Camelina**
CHO , ppm	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.

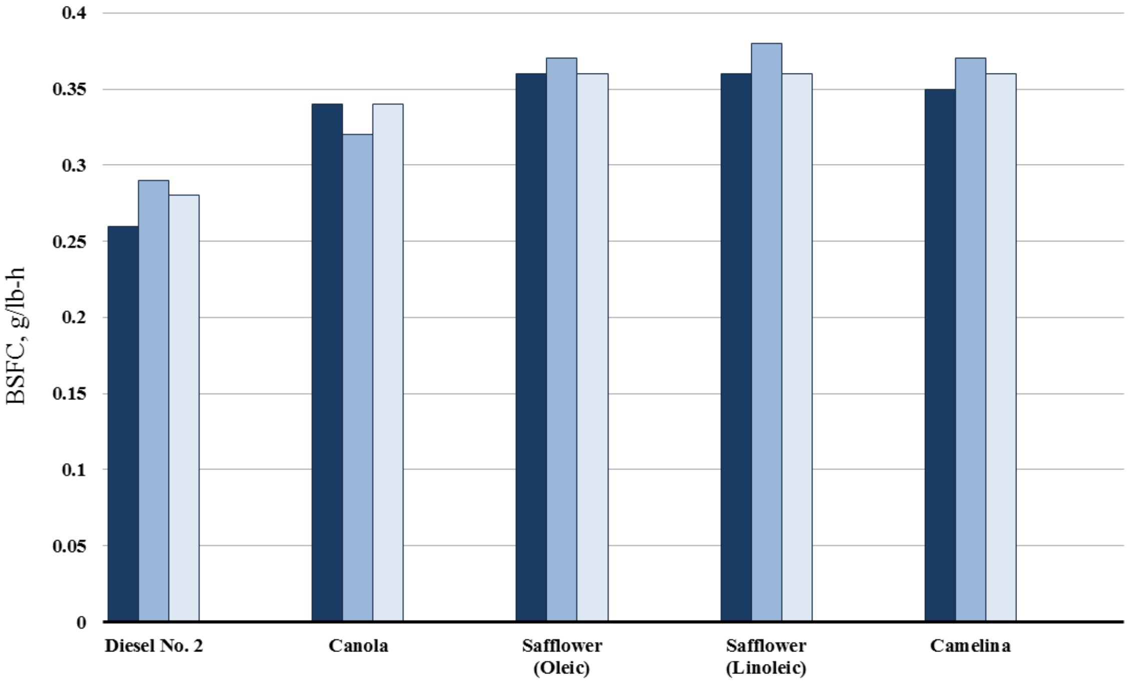


Figure 7. Brake specific fuel consumption of the 400 hP ISL Cummins engine using different fuels. [*Legend:* The bars represents the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

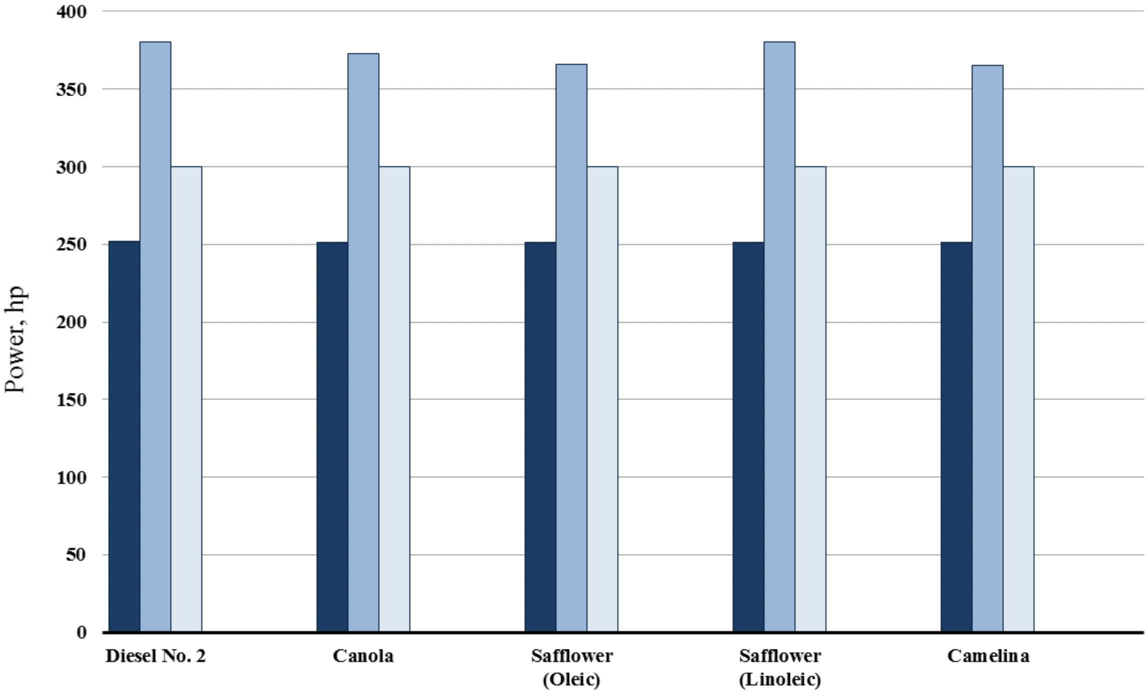


Figure 8. Average engine power of the 400 hP ISL Cummins engine using different fuels. [*Legend:* The bars represents the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

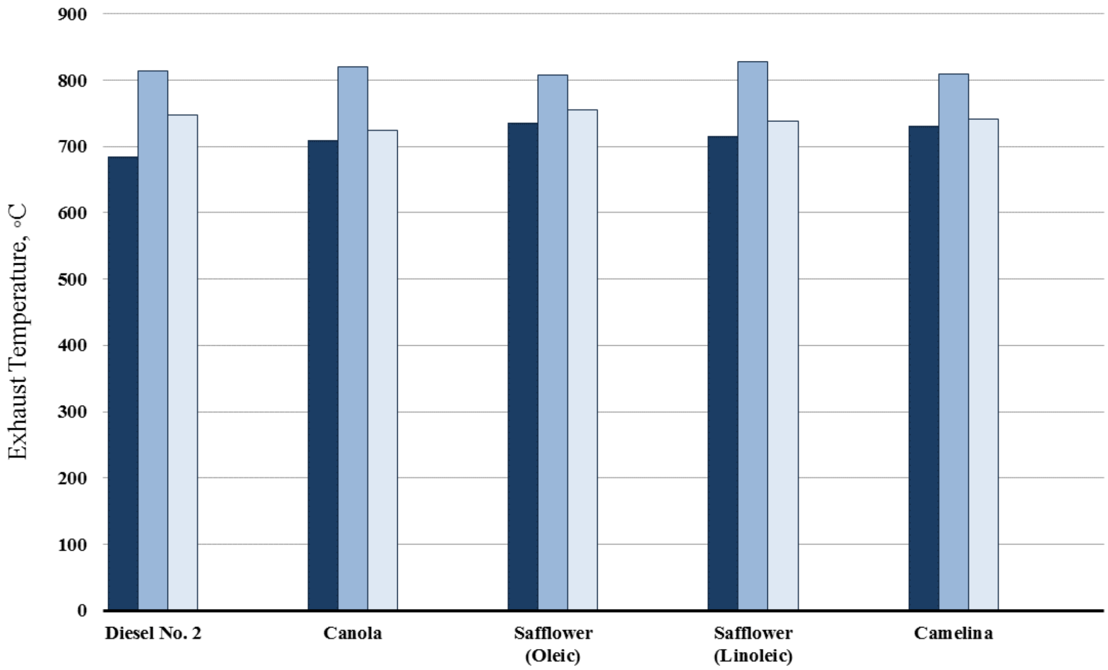


Figure 9. Exhaust temperature of the 400 hP ISL Cummins Engine using different fuels. [*Legend:* The bars represents the following: ■ – Step 1, ▨ – Step 2, □ – Step 3.]

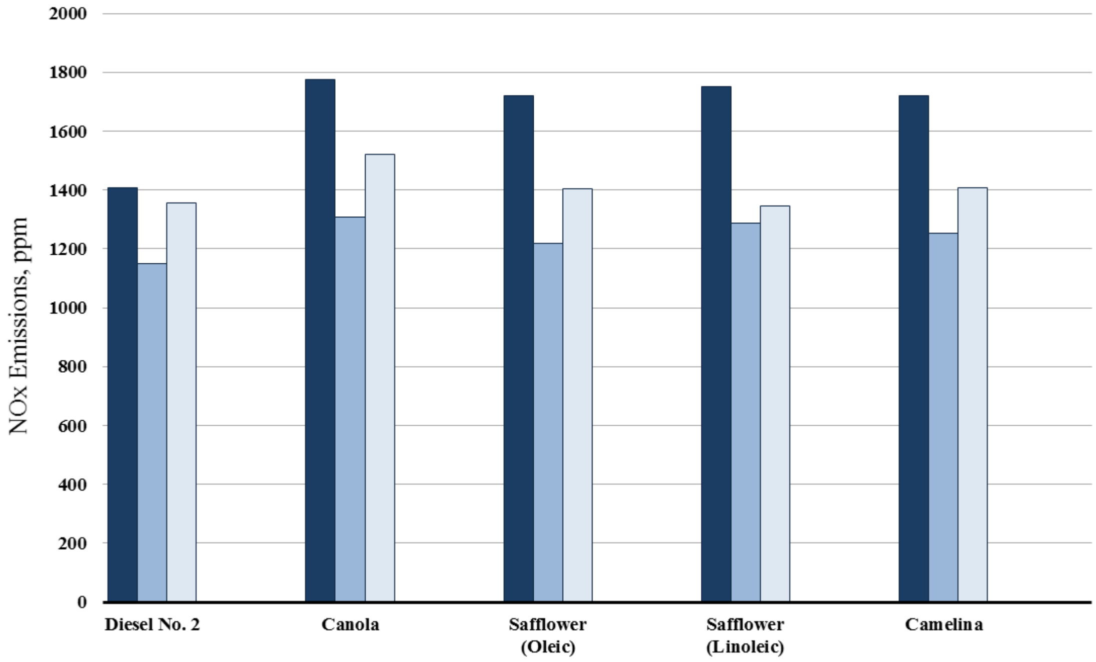


Figure 10. Nitrogen oxides engine exhaust emission concentration using different fuels. [*Legend:* The bars represents the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

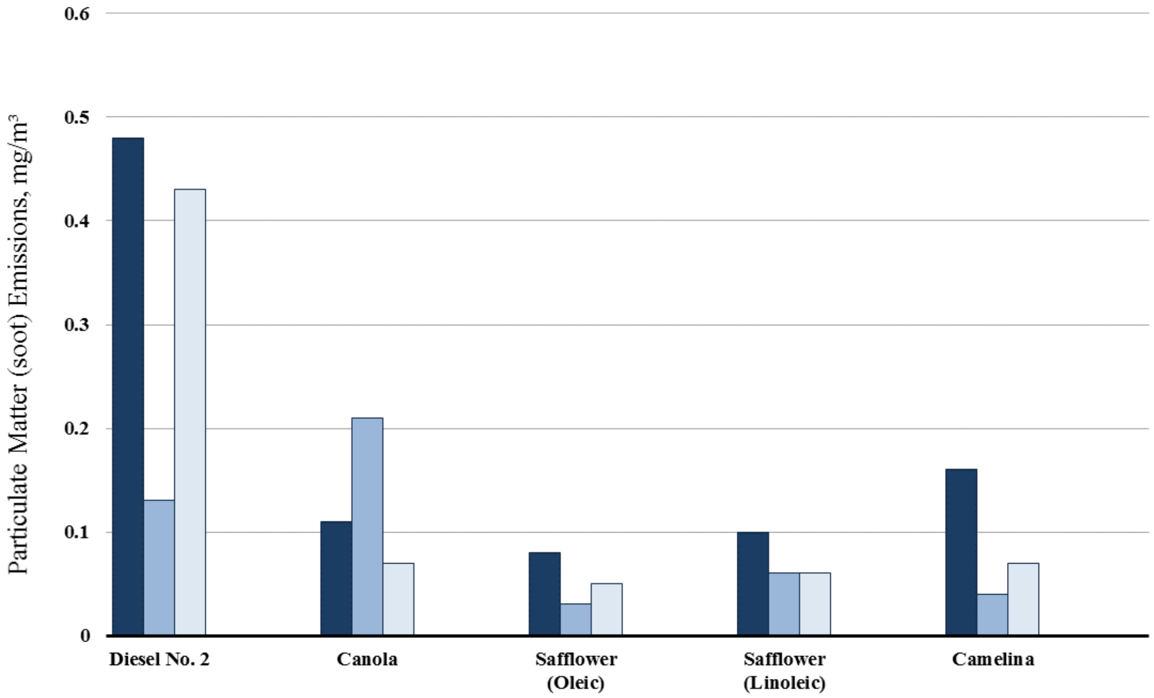


Figure 11. Particulate matter engine exhaust emission concentration using different fuels. [*Legend:* The bars represents the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

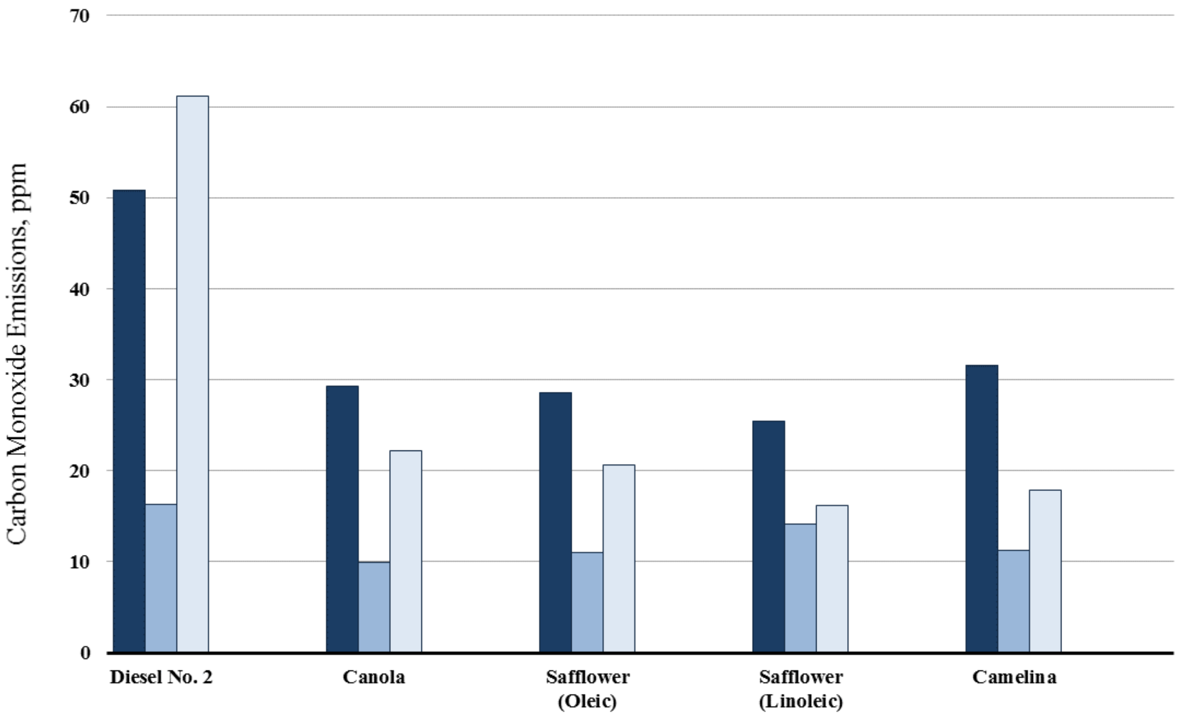


Figure 12. Carbon monoxide engine exhaust emission concentration using different fuels. [*Legend:* The bars represents the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

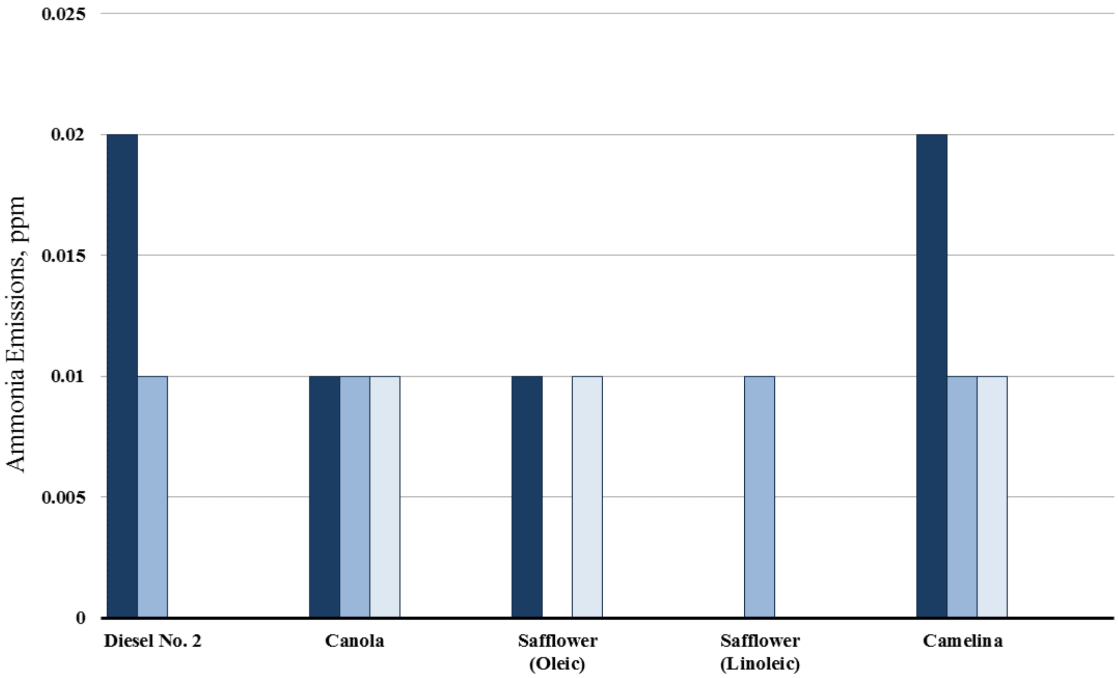


Figure 13. Ammonia engine exhaust emission concentration using different fuels. [*Legend:* The bars represents the following: ■ − Step 1, ▨ − Step 2, □ − Step 3.]

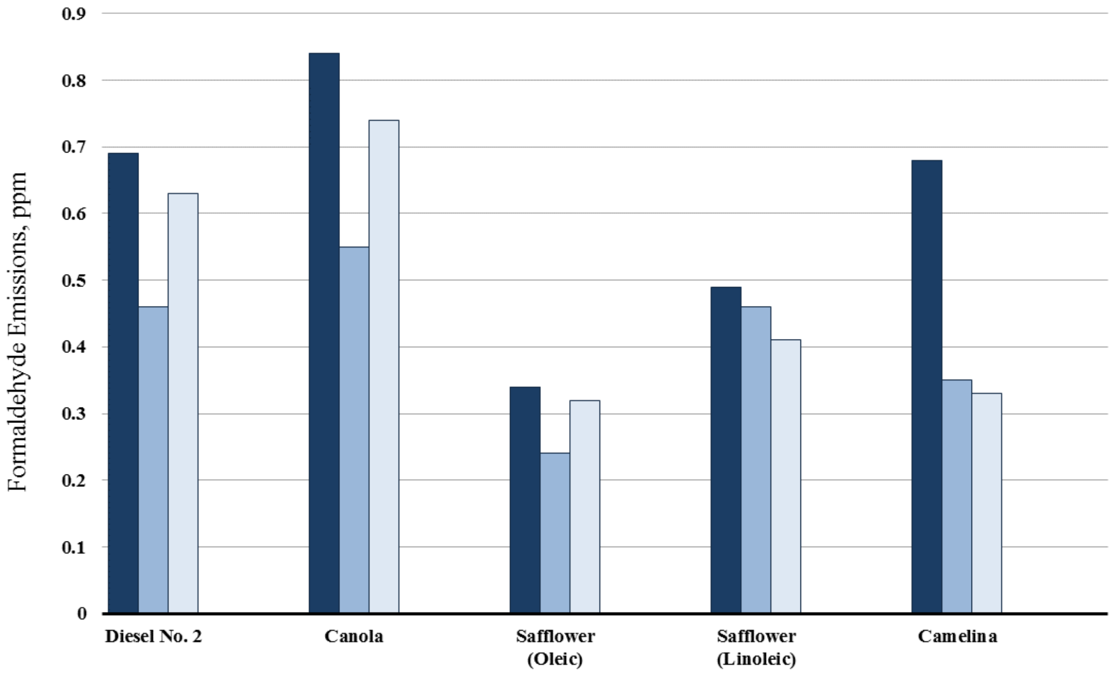


Figure 14. Formaldehyde engine exhaust emission concentration using different fuels. [*Legend:* The bars represents the following: ■ – Step 1, ▨ – Step 2, □ – Step 3.]

Table 6. Engine Performance and Emission Analysis Results using BEC's 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

TEST/STEP		Canola	Safflower♣ (Oleic)	Safflower♣♣ (Linoleic)	Camelina
, %	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, mg/m3	1	0.30 ± 0.22	0.11 ± 0.00	0.73 ± 0.46	0.14 ± 0.02
	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.

Task 5.0 Locomotive Engine Performance and Market Demonstration

Opportunity Link, together with the Bio-Energy Center of the Montana State University Northern and the Havre Diesel Shop of BNSF Railways, worked on developing markets for Montana biodiesel in 2010 to 2012 with funding from the Montana Department of Environmental Quality's *Alternative Energy Development Grant Program*. Project 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 goal of the project was 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, refiners, governments and other stakeholders to anticipate and realize the potential of increased biodiesel production in the region.

Project 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, 1928, was fueled with 20% biodiesel blend while the other used BNSF's bulk diesel fuel to serve as control. Both locomotives were monitored for a one-year period starting July 1st, 2010. Biodiesel used in the project was produced locally from oilseed crops that were grown in Montana. Biodiesel was purchased and produced by the Bio-Energy Center and Earl-Fisher BioFuels respectively. Fuel used in the project was blended at a fuel blending station that was both set-up and financed by BNSF Havre Diesel Shop for project use. During the project period, biodiesel, diesel and fuel blends were tested and analyzed following ASTM specifications by the Bio-Energy Center with a parallel test conducted at the BNSF analysis laboratory in Topeka, KS. Throughout the demonstration period, a wireless monitoring device placed onboard each of the locomotives that recorded real-time engine parameters and fuel consumption. Performance testing followed a standard 92-day maintenance schedule that included injector evaluation, filter evaluation and oil analyses. Two fuel injectors from each locomotive were removed and replaced following maintenance schedule and sent to the manufacturer, Interstate-McBee, for observation and analyses. Locomotive engine emissions were measured after the 12-month demonstration using a Portable Emissions Analyzer Sensor SEMTECH-DS (PEMS), borrowed from the National Renewable Energy Laboratory, that is capable of measuring CO, CO2, O2, NO, NO2, and TH. The project was presented to BNSF executive staff in November 2011 and continually by the Havre Diesel Shop Superintendent.

For a broader biodiesel market, project partners successfully set up a fueling station with Montana biodiesel blend in Havre. Biodiesel was purchased and produced by Earl-Fisher BioFuel and blended and sold by Ezzie's Wholesale in its Havre CENEX station. The 5% biodiesel blend is being sold equivalent to the cost of diesel but where profit from biodiesel is being used for purchasing biodiesel to blend thus ensuring continuity of biodiesel use. Anticipating possible engine issues to be "blamed" on using biodiesel, project partners tapped the National Biodiesel Board and its Diesel Technician Training Program to educate and inform diesel technicians in the state regarding use of biodiesel in automobiles.

Partners continually pursued educating both the public and biodiesel stakeholders (farmers, producers, users, policy-makers) on viability and potential of a community-based oilseed and biodiesel production model in the region. Partners have been successful in presenting project outcomes to a variety of audiences and, more importantly, in obtaining funding and support for continued planning and execution for this development to occur.

4. Project Outcomes & Results

Demonstrated longer-term environmental benefits

1,073 gallons and 14,431 gallons of biodiesel, produced by the Bio-Energy Center and Earl-Fisher BioFuels respectively, were used in the project. This was matched by 77,524 gallons of diesel by BNSF that produced the B20 blend. Regarding biodiesel fuel used, there was a tendency for slight increase in water content during warmer months but aside from this, no fuel properties were found by either the

Bio-Energy Center or BNSF Laboratory in Topeka, KS during the project. One significant project outcome is that Earl-Fisher BioFuels, a Chester, Montana company operated by third-generation farmers Brett Earl and Logan Fisher, became a trusted vendor of the BNSF Fuel Department. Earl-Fisher invoiced BNSF for biodiesel deliveries and was paid directly by BNSF. They are in direct communication with Rocky Elgie, BNSF's fuel department head, and are now in a position to negotiate for future and increased biodiesel supply. The project also demonstrated capacity of BNSF's Havre Diesel Shop to receive bulk biodiesel for blending with bulk diesel and still comply with ASTM D975 diesel fuel specification.

An initial assessment by BNSF for impact of biodiesel use on locomotive performance and maintenance was released as follows:

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

Post-demonstration, "gumming" was observed on fuel injectors taken out during the last quarter of the maintenance schedule. Partners attribute this "gum"-like adhesion to several factors but none that may prove detrimental to continued use of biodiesel blends.

Emissions testing yielded lower NO (2 to 6%), NO_2 (2 to 14%), CO (2 to 16%) and THC (5 to 13%) for the locomotive running on B20 compared to that of the control locomotive. Significant differences were found depending on locomotive modes (from idling and warm up to working up 8 notch levels). Benefits to air quality are indicated by an overall reduction in all of the gasses during warm up. For NO and No_2, greatest environmental benefits are obtained when locomotive are in mid-range power notches; and CO and THC, when locomotives are using less power.

Assessment results above clearly demonstrate environmental benefits of using high quality B20 biodiesel blends for railroad locomotive engines with little to no loss of power. This demonstration is supported by Amtrak's findings from its year-long Heartland Flyer B20 trial in 2011 that *"use of B20 resulted in no more wear than straight ULSD diesel, with no reduction in performance or reliability."*

Demonstrated longer-term economic benefits

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 (via Refrigerated Liquid Methane or 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 listed above, use of biodiesel required no engine modification for BNSF locomotives, demonstrated no issues in its use, and no loss of power. The ease in which the entire fleet can switch to using biodiesel without any engine modification makes it the best option among other alternatives.

In addition, fuel properties of biodiesel such as lubricity, low toxicity and high flash point that makes it safer to handle, combined with environmental benefits of using 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. However, a different set of market conditions – not one conditioned to overseas petroleum supply - will be at play in biodiesel pricing.

Another way that project partners addressed long-term cost efficiency of biodiesel was through the Bio-Energy Center's project on developing a closed-loop, community-based oilseed production model that is funded through the *Western Sustainable Agriculture Research and Education Grant Program*. They are successfully demonstrating how Montana farmers will be able to attain 10% energy independence by allocating a portion of their land to growing oilseeds, having the oil processed into food-grade fuel, and re-using the waste oil into fuel for farming operations. Having to re-use the oil provides value-added product that makes the price of growing oilseed competitive and more advantageous to growing wheat.

Developed markets for Montana biodiesel

In addition to a possible railway industry market for Montana biodiesel, another significant outcome of the project is the successful execution of Montana biodiesel being sold to the public at a local fueling station and therefore opening a new, broader market for Montana biodiesel. Over a hundred community residents, stakeholders, partners and technicians were present when Ezzie's owner, Lary Poulton, opened the 5% Montana biodiesel pump to the public. Area newspapers and television news covered the event, thereby increasing public awareness of both the project and biodiesel availability. The launch was held to coincide with a diesel technician training conducted by the National Biodiesel Board at almost no cost to the project. Over sixty diesel technicians, diesel instructors and diesel tech students in Montana completed the training and are now trained to anticipate answers and solutions to common engine problems usually attributed to biodiesel use. Having the National Biodiesel Board conduct the training provided recognition and credibility to the project's mission of promoting and developing biodiesel markets and is considered one of the major outcomes of the project.

Planning for Oilseed and Biodiesel Development

Project partners had also been successful in furthering the development of oilseed and biodiesel production in Montana. Partners are aware of the breadth and scale of planning and partnerships that are needed to solidify a possible oilseed and biodiesel industry in Montana. Because of this, partners have applied for and have been successfully awarded two regional planning grants that support this objective.

MSU Northern Bio-Energy Center was recently awarded an Economic Development Administration Grant for economic adjustment assistance 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 award will lead to the scale-up of the Bio-Energy research projects and the identification of other valuable co-products. The project will lead to the development of these research outcomes into opportunities for the region's agricultural sector. There will also be support provided for business technical assistance, technology transfer and possible collaboration with public and private sector partners.

Opportunity Link was recently awarded a HUD-EPA-DOT Sustainable Communities Regional on behalf of Northcentral Montana communities. This implies that Northcentral Montana communities will have resources to facilitate planning for sustainable development and t0 develop a 20-year regional, coordinated plan. This planning will include and help address farmer-producer risks and to help develop new market opportunities in the agricultural energy, oil & gas, and biofuel sectors. With BCAP, biodiesel, and sustainable aviation fuel, demand for oilseeds are expected to increase yet with no secure market in sight, our farmer-producers struggle to understand and mitigate oilseed crop risks.

Opportunity Link and the Bio-Energy Center, together with project partners and other stakeholders, will be working together in the implementation of both awards.

Task 6.0 Effects of Contaminants in Canola Biodiesel to Diesel Engine Exhaust Emissions

Abstract

Biodiesel is a biomass-based fuel composed of mono-alkyl esters of long-chain fatty acids. Its potential as an alternative fuel is well recognized in the United States and worldwide. The production and use of biodiesel in the United States have been exponentially growing in the past decade. U.S. Energy Information Administration reported that U.S. produced and consumed about 969 million gallons and 870 million gallons of biodiesel, respectively, in 2012. [USE13] Biodiesel is produced from plant oils and animal fat through a well-established process called transesterification. Aside from the simplicity of making biodiesel, there are several significant benefits of using biodiesel and its blends over petroleum diesel. Biodiesel is undoubtedly a renewable source of energy. A life-cycle analysis of soybean biodiesel conducted by several researchers reported a greater than one net energy ratio, which means energy is gained in producing biodiesel. [Pra08] Among these studies, the highest reported value is 5.54 units of renewable fuel energy output per unit of fossil energy input to produce biodiesel. Although the net energy ratio changes in every study and every year due to continuous changes in industrial practices of producing materials and availability of new information, it is important to point out that all these studies lead to a positive energy gain for biodiesel. Another advantage in using biodiesel is feedstock versatility. It can be made from different plants oils, like canola, safflower, camelina and soybean to animal fats as well as algae oil and waste vegetable oil. It also has been reported in the literature that lubricity of petrodiesel improves when biodiesel is added.[Kno05] The presence of fatty compounds (e.g. fatty acid methyl esters and monoglycerides) in the biodiesel positively affects the lubricity of the fuel. For its environmental benefits, biodiesel and its blends when used in diesel engines produces significantly lower harmful exhaust emissions compared to petroleum diesel. Several studies had observed significant reduction in particulate matter (or soot), carbon monoxide and unburned hydrocarbons in the exhaust emissions when using biodiesel and its blends. [Car02] Unfortunately, biodiesel produces significantly higher NOx emissions compared to petroleum diesel. This is one of the few deficiencies of biodiesel. Biodiesel and its blends have an inferior cold-flow performance and oxidative stability compared to petroleum diesel.[Dun05] The cloud point of biodiesel from different plant oils is above −2°C while ultra-low-sulfur diesel (ULSD), a petroleum diesel, is at or below −18°C.[Mos10] Biodiesel is more susceptible to degradation through oxidation compared to petroleum diesel due to the fact that petroleum diesel consists of a mixture of aliphatic and aromatic hydrocarbons which are more stable than alkyl esters of long chain fatty acids during oxidation.[Mos091] Although, these deficiencies in the fuel properties of biodiesel can be improved through the addition of antioxidants, blending different kinds of

biodiesel (e.g like blending canola, palm, sunflower and soybean biodiesels) and chemical modification (e.g partial hydrogenation). [Mos09]

As mentioned before, biodiesel is an excellent alternative and renewable source of fuel for diesel engines. Although, poor processing and refining practices during production could lead to a fuel with deficient properties and could result to engine problems. For example, the presence of unconverted triacylglycerides (TAG) in the biodiesel affects the cetane number, cloud point, viscosity, and the carbon residue properties[Fer07]. Cetane number, defined as the measurement of the ignition performance of a fuel during compression-ignition, of biodiesel decreases as the amount of unconverted TAG increases. Similarly, the carbon residue increases as more TAG is unconverted to biodiesel. Fernando and his co-workers[Fer07] 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. 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 authors’ 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 fuel does not meet the standard properties in the ASTM, especially for biodiesel, will result to poor engine emissions. This is a major concern for the environment which targets small biodiesel producers who does not sell their product to the market but instead use the biodiesel to run their own operations. Most of the time, small biodiesel producers does not have complex production and refining facilities that can efficiently convert TAG to biodiesel and remove contaminants, best example is methanol, from biodiesel. It is interesting to know if using out-of-specification 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 study is aimed to investigate the emissions of biodiesel contains high TAG, methanol and free fatty acids and compare it with Grade No. 2 ultra-low-sulfur diesel and good quality biodiesel.

1. Methodology

Materials

Canola seeds were purchased from several local farmers in Havre, MT. The oil was extracted from the seed using a Kern Kraft 40 Screw Presses. The methanol (99% purity) and potassium hydroxide (anhydrous) used to produce biodiesel were purchased from Ezzies Wholesale (Havre, MT) and Occidental Chemical Corporation (Dallas, TX), respectively. The biodiesel was produced and refined at the MSUN Bio-Energy Center biodiesel facility using a 55-gallon batch biodiesel processor manufactured by Piedmont Biofuels (Pittsboro, NC). All other chemicals and reagents were purchased from Fisher Scientific Company (Hanover Park, IL) and Sigma-Aldrich, Inc. (St. Louis, MO).

Fuel Properties Testing

The prepared canola biodiesel and the contaminated biodiesel samples 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. The standard methods used in this study are summarized in Table 1. Similarly, the Grade No. 2 ULSD used was characterized using the tests mentioned before except for total and free glycerin, oxidative stability and vacuum distillation. A Rapid Small Scale Oxidation Test or RSSOT (ASTM D7545-14) was used to measure the oxidative stability of both Grade No. 2 ULSD and the prepared canola biodiesel. Please note that D7545-14 test is not required in D6751 and D975. It was used in this study to compare the difference in oxidative stability of Grade No. 2 ULSD and biodiesel.

Table 1. Standard methods used to characterize the ULSD and biodiesel used in this study.

	Grade No. 2 ULSD (S15)		**Neat Biodiesel**	
Property	**Method**	**ASTM D975 limits**	**Method**	**ASTM D 6751 limits**
Acid Number, mg KOH/g	N/A	N/A	D664	0.5 max
Flash Point, °C	D 93	52 min	D93	93 min
Cloud Point, °C	D 2500	Report	D2500	Report
Oxidative Stability , h	N/A	N/A	EN 15751	3 min
Kinematic Viscosity @ 40°C	D 445	1.9 – 4.1	D445	1.9 – 6.0
Sulfur Content, ppm	D 5453	15 ppm	D5453	15 ppm[c]
Carbon Residue[a], % wt.	D 524	0.35 max	D4530	0.05 max
Water and Sediment, % vol.	D 2709	0.05 max	D2709	0.05 max
Total Glycerin, % wt.	N/A	N/A	D6584	0.240 max
Free Glycerin, % wt.	N/A	N/A	D6584	0.020 max
Monoglycerides, % wt.	N/A	N/A	D6584	0.4 max[d]
Methanol Content[b], °C	N/A	N/A	D93	130 min
Distillation, T90 AET, °C	D 86	338	D1160	360 max

Notes: [a] - The carbon residue is run on the 100% biodiesel sample; [b] – if the flash point of biodiesel is below 130°C, the methanol content needs to be determined true EN 14110; [c] – Grade S15 biodiesels; [d] – for Grade No.1-B biodiesels.

Experiment

The prepared canola biodiesel was contaminated with TAG (canola oil) and methanol. Table 3 summarizes the amount of contaminants that was added to the biodiesel. Typically, biodiesel contains around 3 – 5% of methanol after the biodiesel has been separated from glycerin. [Van071] Three percent of methanol by volume of mixture was used in this study. In order to simulate real-life storage and operations, 50 gallons of neat biodiesel was stored in a 55-gallon metal drum for seven months. It is noted that the prepared biodiesel met all the standard properties in ASTM D6751 except for oxidative stability. The oxidative stability index (OSI) of the canola biodiesel, before storage, was at 1.0 h. Due to the low OSI value of the biodiesel and it is stored in a container made of metal, it is expected that the biodiesel will be oxidized after six months.

Table 3. Amount of contaminants that will be added to 50 gallons of canola biodiesel.

Contaminant	Percentage of contaminant in biodiesel (% wt.)	ASTM D6751 limit
Methanol	3.0	N/A
Triglycerides	5.0	0.240[a]

Notes: The densities used in the calculations are the following: canola oil = 0.95 kg/L, methanol = 0.792 kg/L, glycerol = 1.26 kg/L and biodiesel = 0.88 kg/L.
[a] – maximum amount of total glycerin allowed, this is equivalent to 2.3% wt. triglycerides.

Engine Testing and Exhaust Emission Analysis

Grade No. 2 ULSD, canola biodiesel and contaminated canola biodiesel were evaluated using an 8.9 L 2007 model year Cummins ISL compression-ignition engine connected to a 704 hp AVL A/C Dynamometer. The engine was operated over an eight-mode test cycle according to Code of Federal Regulations Title 40 Part 89 Subpart E (Table 2). Three hot-start test were conducted for each type of fuel. Nitrous oxides (NOx), CO, CO_2, H_2O and soot concentrations were measured and collected using AVL SESAM Emission Analyzer and AVL Micro Soot Sensor (AVL North America, Inc, Plymouth, MI). The mass flow of each exhaust emission species were computed according to the equations specified in Title 40 part 89 subpart E of the U.S. Code of Federal Regulations. The brake horsepower, engine speed, air intake mass flow, engine oil temperature and inlet manifold temperature were also recorded during each test cycle. Fuel consumption was determined gravimetrically. Emission and engine data was recorded for every second for at least 5 minutes.

Table 2. Eight-mode test cycle using 8.9 L Cummins ISL engine.

MODE	Engine Speed (rpm)	% Load	Time (min)
1	Rated[A]	100	5.0
2	Rated[A]	75	5.0
3	Rated[A]	50	5.0
4	Rated[A]	10	5.0
5	Intermediate[B]	100	5.0
6	Intermediate[B]	75	5.0
7	Intermediate[B]	50	5.0
8	Low idle	0	5.0

Legend: [A] – engine speed at which the manufacturer specifies the rated engine power.
[B] – engine speed corresponding to the peak engine torque.

2. Results and Discussion

Fuel Properties of Contaminated Canola Biodiesel

As reported in the literature [Dun05], neat biodiesel has an inferior cloud point than petroleum diesel. The cloud point of canola biodiesel was measured at -2.7 ± 0.6°C while the Grade No. 2 ULSD used in this study was below -18°C, lower than the instrument can measure. (Table 3) Similarly using RSSOT, the induction period of neat canola biodiesel was much lower than the ULSD used. This means that the neat biodiesel is more susceptible to oxidation during storage compared to ULSD. The addition of 5% wt. of canola oil to the biodiesel did increased the total glycerin from 0.158 to 0.647, which is no longer on the specification in accordance with ASTM D6751. (Table 4) In addition, the viscosity @ 40°C also increased by 0.4 cSt. Though still within the ASTM D6751 requirements, the increase is due to the high viscosity of canola oil of 35.4 ± 1.0 cSt. Carbon residue remained the same as the control. Fernando et al [Fer07] also observed the same

Table 3. Fuel properties of Grade No. 2 ULSD and neat canola biodiesel.

PROPERTY	FUEL	
	Grade No. 2 ULSD	**Canola B100**
Acid No., mg KOH/g	0.03 ± 0.00	0.24 ± 0.03
Flash Point, °C	54.5 ± 3.5	> 130
Cloud Point, °C	< -18	-2.7 ± 0.6
Viscosity @ 40°C, cSt	2.407 ± 0.012	4.586 ± 0.001
Sulfur Content, ppm	7.8 ± 0.6	1.2 ± 0.6
Carbon residue, %wt.	0.007 ± 0.007	0.025 ± 0.007
Total Glycerin, % wt.	N/A	0.158 ± 0.030
Free Glycerin, % wt.	N/A	0.008 ± 0.001
Monoglycerides, % wt.	N/A	0.214 ± 0.002
Oxidative Stability(RSSOT),min	41.7 ± 0.6	7.9 ± 2.0
Water and Sediment, % vol.	< 0.05	< 0.05
Distillation T90 AET, °C	N/A	358.3 ± 0.1

Table 4. Fuel properties of the contaminated canola biodiesel.

PROPERTY	CONTAMINATED FUEL		
	CBD-TAG	**CBD-MEO**	**CBD-FFA**
Acid No., mg KOH/g	0.27	0.21	0.62
Flash Point, °C	178.5	< 27	170
Cloud Point, °C	-3	-3	-3

Viscosity @ 40°C	4.9893	4.0587	4.8201
Total Glycerin, % wt.	0.647	N.T.	N.T.
Free Glycerin, % wt.	0.005	N.T.	N.T.
Carbon residue, %wt.	0.023	0.046	0.113
Sulfur Content, ppm	1.2	1.2	10.8

NOx and PM exhaust emissions

FUEL	**Emission Species Concentration, g/bhp-h**			
	Nitrogen oxides (NO_x)	**Carbon Monoxide (CO)**	**Carbon Dioxide (CO_2)**	**Particulate Matter (PM)**
Grade No. 2 ULSD	1.96 ± 0.02	0.135 ± 0.001	292.67 ± 0.49	0.0169 ± 0.0008
Canola B100	2.33 ± 0.03	0.086 ± 0.000	299.20 ± 0.69	0.0022 ± 0.0001
CBD-TAG	2.33 ± 0.03	0.091 ± 0.003	308.14 ± 1.96	0.0025 ± 0.0002
CBD-MEO	2.29 ± 0.01	0.100 ± 0.001	293.91 ± 3.09	0.0018 ± 0.0001
CBD-FFA	2.40 ± 0.15	0.085 ± 0.005	301.13 ± 3.94	0.0014 ± 0.0001

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