# Advancing Bio-Based Chemicals and Next-Generation Fuels from Montana's Agricultural Crops *Final Report*

Montana State University Northern Montana State University Billings City College



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#### **Executive Summary**

Industrial oilseeds crops, such as camelina, presents a unique opportunity in addressing Montana's search for alternative energy sources and its steady decline of manufacturing employment. The improvement of Montana's agroecosystem through camelina cultivation can be achieved through the establishment of a biorefinery capable of paying farmers a competitive price resulting in the enhancement of Montana's manufacturing employment and diversification of its energy portfolio. The establishment of a biorefinery will provide sustainable growth in Montana's manufacturing industry and agriculture in two ways: [a] newly developed conversion technologies will open new opportunities to generate numerous Montana jobs through the creation of "green" businesses and [b] oilseed research directly address the federal government's goal of utilizing alternative energy sources to achieve a cleaner environment.

This collaborative project between Montana State University Northern and Montana State University Billings City College has four main objectives: [a] evaluate the environmental life cycle impacts and technoeconomic implications of bio-based chemicals and next-generation fuels from camelina, an industrial oilseeds; [b] formulate and validate a mechanism of producing a blend component to aviation gasoline to eliminate its lead content; [c] develop a novel and robust catalyst that efficiently converts natural oils to bio-based chemicals and next-generation fuels, and; [d] develop an optimum process configuration and perform economic analysis for medium and large-scale pelletizing plants for oilseed meal byproduct stream.

Outcomes of this project include (1) the establishment of life cycle and technoeconomic models for converting camelina into bio-based chemicals and next-generation fuels, (2) the development of an effective method in synthesizing unleaded aviation gasoline from camelina, (3) the creation of a heterogeneous N-heterocyclic carbene that can be widely used in creating unique materials and catalysts, and (4) the successful demonstration of a pilot-scale pelletizing methods of camelina meal for heat production. Both universities have leveraged the research investment provided by the State of Montana through the formation of effective strategies resulting from the establishment of key partners in the region. The connections created by the project with universities outside Montana strengthened the research and education infrastructure (i.e., facilities and curriculum) for both universities.

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#### Advancing Bio-Based Chemicals and Next Generation Fuels from Montana's Agricultural Crops

## 1. Introduction

As Montana's manufacturing employment is steadily declining [1] and the search for an alternative energy source more suitable for the state continues, investment on research and development on processing locally-available biomass to high-value products and renewable energy becomes a necessity. Industrial oilseed crops, such as *Camelina sativa* (camelina) and *Brassica carinata* (carinata), provide Montana the means to address these concerns by creating opportunities to enter the emerging bio-based chemicals market, which includes food supplements, personal care products, fuel additives, and next-generation biofuels. Camelina has been widely researched in Montana with great advancement in agricultural production, seed handling and application, oil processing, feed production, and product development [2][3][4]. Montana has the capacity to produce excellent quality of camelina in large quantities, which can be achieved through crop rotation with winter wheat [5]. The existence of a local biorefinery facility to process the camelina seed or other Montana-grown industrial oilseeds that can pay producers a competitive price fosters the potential for large-scale oilseed production in Montana.

The Montana State University Northern's (MSUN) patented process<sup>1</sup> to synthesize high-value bio-based chemicals (i.e. olefins and oleochemicals) and fuels from industrial oilseeds offers a unique opportunity for Montana to build economic competitiveness, local capacity, and community prosperity in a sustainable chemical industry and energy sector. In addition, MSUN can adapt approved American Society for Testing and Materials (ASTM) processes that converts industrial oilseeds to bio-jet fuels such as Hydroprocessed Esters and Fatty Acids fuels and Synthetic Parrafinic Kerosenes [6]. Both processes were designed on a small scale due to the limited amount of available biomass. Finding a refinery willing to process a small amount of biomass is challenging. However, there is a refinery in Great Falls, Montana (Calumet Montana Refining) that could perform this task. In addition to the economic impact Calumet Montana Refining has to the city and surrounding counties, its size is appropriate for Montana's annual industrial oilseed production.

To improve the biorefinery's sustainability, it is imperative to utilize all byproduct streams, specifically the meal, from seed oil extraction. Montana State University Billings (MSUB) City College has developed a process to produce fuel pellets from underutilized biomass sources such agricultural byproducts and lawn clippings. This technology is applicable to camelina and other oilseed meals that represent a large byproduct stream from seed oil extraction. The development of a value-added disposition to the meal is crucial in improving the economics of the biorefinery.

<sup>&</sup>lt;sup>1</sup> U.S. Patent Application No. 15/301,636

## 2. Project Objectives

The overall goal of the project was to develop the fundamental knowledge base needed to establish and maintain a biorefinery for the production of bio-based chemicals and next-generation fuels. This biorefinery will directly address key issues unique to Montana: [1] steady decline in Montana's manufacturing employment [1], [b] lack of a bio-based chemical industry in Montana, [c] absence of a sustainable large-scale market for Montana's camelina, and [d] limited alternative energy source for Montana.

The project has four primary research objectives: [a] perform "well-to-pump" life cycle analysis (LCA) and technoeconomic assessment (TEA) of the patented process of producing bio-based chemicals and next-generation fuels (Task 1); [b] propose and validate a mechanism of producing camelina-derived alkylated aromatics as a blend component to aviation gas (avgas) (Task 2); [c] develop a robust heterogeneous Grubbs catalyst that achieves efficient conversion of natural oils to bio-based chemicals and next-generation fuels (Task 3), and [d] develop an optimum process configuration and economic analysis for medium and large scale pelletizing plants for oilseed meal byproduct stream (Task 4). Combined, we have the necessary qualifications to develop and advance the science and economics of bio-based chemicals and next-generation fuels. By generating the scientific bases necessary to establish and maintain a biorefinery with high potential for industrial success, the research will provide direct benefit to the agricultural sector which represents a major industry in Montana economy.

## 3. Project Outcomes

## 3.1. Research Results

## <u>3.1.1. Task 1: Life Cycle Analysis (LCA) and Technoeconomic Assessment (TEA) of Bio-based</u> <u>Chemicals and Next-Generation Fuels</u>

The objective of this task is to perform a "wellto-pump" life cycle analysis (LCA) and technoeconomic assessment (TEA) of nextgeneration fuels (renewable aviation gasoline, biojet fuel, and green diesel). This task is achieved through the use of a comprehensive, multi-dimensional approach consisting of (1) geospatial analysis, (2) life cycle assessment, and (3) techno-economic analysis. Results offer an insight on the environmental impact of MSUN's patented process (olefin metathesis and tandem dehydrogenation-alkylation or OMT) relative to hydroprocessed renewable jet



Figure 1. Total energy input, total energy output, and energy returnon investment (EROI). Input energy and output energy are reported 10<sup>10</sup>x and 10<sup>9</sup>x calculated value, respectively.

(HRJ or HEFA) and petroleum-based jet (PTJ). This task revealed that OMT's "well-to-pump" total energy consumption is 10% lower than HRJ, with similar total energy output of all products and co-products for a functional unit of 100,000  $m^3/yr$  fuel (Figure 1). The patented process



(NGR). Both emissions and offset are reported 10<sup>8</sup>x calculated value.

reflected a 14% GHG emissions reduction compared to HRJ (Figure 2). Challenges and opportunities in camelina yield as a function of land availability on a national-level through a county-based approach was utilized through geospatial analysis. The team hypothesized that if camelina is to be used as a rotational crop with winter wheat on a 3-year cycle, the available fallow will provide an estimate of total annual camelina production, using the "best-case scenario" (camelina rotation only). Geospatial analysis suggests that with respect to

the four top wheat-producing states (KS, TX, MT, WA), representing a conservative annual national camelina yield at the "best-case" farming scenario (camelina only, 3-year fallow), <1% total available land will be utilized (Figure 3). Profitability of OMT (biojet fuel case, route 2 only) is 3x higher than HRJ. Relevant technoeconomic cost parameters for the production of 100,000 m<sup>3</sup> fuel/yr functional unit is shown in Table 1. TEA has also highlighted that to be profitable, camelina must have a minimum yield of 1.1 tons/ha-yr (Figure 4).

Table 1. Cost parameters to produce 100,000 m3 fuel/year	Fable 1. Cost	parameters to	produce 100	.000 m3	fuel/year
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Cost Variable	OMT3	HRJ
Capital cost (S)	171.35 M	174.13 M
Materials/Process cost (S/ha)	371.36	301.81
Revenues (S/yr)	127.49 M	91.53 M
Expenses (\$/yr)	80.67 M	72.58 M
Annual net cash flow (\$/yr)	46.82 M	18.95 M
PV expected cash flow (\$)	264.91 M	84.77 M
Profitability index	1.55	0.49

This task attempts to address the research gaps related to camelina cultivation for biofuel production. The deliverable we propose to execute in task 1 have all been implemented. More importantly, we have developed a comprehensive and modular approach to camelina-to-biofuel LCA and TEA that can be applied to other biomass feedstock. Results from this task is to be submitted *to Environmental Science and Technology* journal (impact factor: 5.393) on July 31, 2017. The working title for the paper is "The case of camelina-derived aviation fuel in the United States: multi-dimensional assessment from a geospatial, life cycle, and techno-economic perspective." Results of this task was presented at the 2017 biannual conference of the Association of Environmental Engineering and Science Professors (AEESP) at the University of Michigan in Ann Arbor, Michigan on June 20-22, 2017.



**Figure 3.** Total potential camelina land area, 2015. Average total precipitation reported over the months of April, May, and June, 2015.

#### 3.1.2. Task 2: Production of Camelina-Derived Alkylated Aromatics as a Blend Component to Aviation Gasoline

In this task, we proposed and validated a mechanism for synthesizing alkylated aromatic hydrocarbons derived from camelina. This was accomplished through several activities: (1) identify pertinent mechanism in the synthesis of 1,4-cyclohexadiene (CHD) from camelina, (2) validate such mechanism through experimentation with a model unsaturated fatty acid methyl esters (FAME) and camelina oil, (3) confirm the production of alkylated aromatics with high motor octane number (MON) from CHD through tandem dehydrogenation-alkylation reactions, (4) produce alkylated aromatics from camelina oil through this steps: camelina oil  $\rightarrow$ CHD $\rightarrow$ alkylated aromatics , (4) formulate an unleaded avgas with alkylated aromatics derived from camelina, and (5) determine properties of the newly formulated unleaded avgas in accordance with ASTM.

Plant oils are esters of glycerol and three fatty acids. Camelina oil, in particular, consists of 54% of polyunsaturated fatty acids, fatty acids with two or more double bonds, We hypothesized that olefin metathesis of polyunsaturated fatty acids forms CHD. To validate this hypothesis, we used different unsaturated fatty acid methyl esters (uFAME) with different number of double bonds and converted it to CHD and other products using a metathesis catalyst. Figure 5 plots the CHD yields and conversions after olefin metathesis of these uFAMEs. Results revealed that CHD can only be synthesized from uFAME with two or more double bonds. The graph also shows that the reaction proceeded at low temperatures and better conversions and CHD yields were



**Figure 5.** CHD molar yields and conversions of olefin metathesis of unsaturated fatty acid methyl esters with different number of double bonds.

achieved at 35°C. These results are further substantiated through a subsequent experiment with camelina oil and triolein, an oil consisting of only fatty acids with one double bond. At 35°C, an average CHD yield of  $67.5 \pm 17.2$  % mol were observed for camelina oil while no CHD were produced for triolein. This is yet another evidence that validates our hypothesis. We presented these results at the American Oil Chemists' Society (AOCS) Annual Meeting and Expo, held at Salt Lake City in May 2016.



**Figure 6.** Alkylated aromatics and benzene molar yields of tandem dehydrogenation-alkylation of CHD. *Note:* AB1-p = 1,4-bis (1-methylethyl) benzene; AB1-m = 1,3-bis (1-methylethyl) benzene; AB2 = propyl-cyclohexane. Legend: CatAl – montmorillonite aluminum pillared catalyst; CatK30 – K 30 montmorillonite catalyst. (1:1) – volume ratio of CHD and solvent; (None) – no solvent used.

We then tried to determine if high-octane compounds can be synthesized from CHD through tandem dehydrogenation-alkylation reactions. Our hypothesis was that benzene is synthesized through the dehydrogenation of CHD and an alkylating agent (e.g. olefin) reacts with benzene to form an alkylated aromatic. Propene was selected as the alkylating olefin since it was postulated it will produce cumene, an alkylated aromatic with MON of 102 [7]. Results of the experiment showed that more than half of the CHD were converted to cumene and benzene (Figure 6). The presence of benzene and cumene in the

product confirms that tandem dehydrogenation-alkylation of CHD transpired. Trace amounts of other alkylated aromatics were also detected in product.

We designed an experiment to convert camelina oil, extracted from locally-grown camelina seeds, to cumene. Camelina oil was reacted with propene using similar metathesis catalyst above. The product was then distilled to separate CHD from the oil and other hydrocarbons. The CHD collected was then reacted with propene using the montmorillonite catalyst. Product analysis showed that the final product contains cumene and benzene (Figure 7). Benzene, while not the desired product, could be separated from cumene through distillation and alkylated to synthesize more alkylated aromatics. The results of the three experiments provides substantial evidence that renewable alkylated aromatics can be produced from camelina oil.



**Figure 7.** Alkylated aromatics (cumene) and benzene molar yields of tandem dehydrogenation and alkylation of CHD. *Note:* AB1-p = 1,4-bis (1-methylethyl) benzene; AB1-m = 1,3-bis (1-methylethyl) benzene; AB2 = propyl-cyclohexane. Legend: CatK30 - K 30 montmorillonite catalyst. (1:1) – volume ratio of CHD and solvent; (None) – no solvent used.

We used a composition-based octane model developed by Gosh et al [8] to identify the molecular composition of an unleaded avgas with alkylated aromatics derived from camelina. A Visual Basic program was written to quickly calculate MON of numerous combination of blends of hydrocarbons. Over 70 hydrocarbons were considered in the search of unleaded aviation gasoline with high MON. After formulating an unleaded avgas with alkylated aromatics, we validated its



Figure 8. MON and vapor pressure at 38.4°C of the newly formulated unleaded avgas.

MON through experiments. We prepared the newly prepared unleaded avgas by mixing cumene and other hydrocarbons (e.g., alkylated aromatics, linear alkanes, and branched alkanes). The prepared samples were sent to Intertek Laboratories and Calumet Montana Refinery (Great Falls, MT) for characterization. Results showed that cumene can be used to make unleaded avgas (Figure 8). Similarly, densities of the fuels were also within the limits set by ASTM D7719 [9]. Sample UA4 have a vapor pressure of 47.0 at 37.8°C which is within the ASTM D7719

limit. We presented these results at the American Oil Chemists' Society (AOCS) Annual Meeting and Expo, held at Orlando, Florida in May 2017.

The findings for this task will be submitted to *Energy and Fuels* (impact factor: 3.091) with a working title of "Synthesis of Renewable Alkylated Aromatic Hydrocarbons from *Camelina sativa*" at the end of July 2017.

#### 3.1.3. Task 3: Development of Heterogeneous Grubbs Catalyst for Biomass Conversion

In this task, we proposed to develop two kinds of heterogeneous catalysts: (1) silica-supported Grubbs catalyst and (2) silica-supported polymeric Grubbs catalyst. We have recognized the importance of developing a robust heterogeneous Grubbs catalyst for olefin metathesis of plant oils, which is vital in achieving significant reduction in processing costs. Silica was chosen as the support for both catalysts because of its wide availability and large pore size that allow reagents greater access to active sites. A number of research on coordination of metals to silica via metal oxide bonding has been previously explored, hinting of the possibility that it could be done.

Heterogeneity of an NHC was achieved through a 1,3-dipolar cycloaddition of an alkyne to an azide or an azide-alkyne effectively forming a covalent bridge. The reaction is achieved through "click" chemistry, a term coined by Barry Sharpless to describe the highly-efficient, regioselective nature of the reaction [10]. The triazole formed is chemically inert due to the large activation barrier necessary to break the cyclic structure apart, making it a strong linker [11]. Because of the ease with which an azide can be transferred with an aliphatic amine and the necessity of having a primary azide with a flexible alkyl chain, readily available aminopropyl-functionalized silica proved to be a cost effective solid support. Additionally, more concentrated silica polyamine composites (SPCs) can be synthesized from silicon dioxide as described by Rosenberg et al [12].

During the study, we characterized and monitored the concentrations of products and reagents in the sequential steps of synthesizing the heterogeneous NHC. We had discovered reactions that were either inefficient (i.e., low yields) or reactions did not proceed and we had to find other ways to synthesize the heterogeneous NHC. After several modifications, we had developed a new route which has fewer reaction steps and needs less solvents than originally planned. Results revealed a successful synthesized heterogeneous NHC. Figure 9 shows the physical changes in the color

of the silica as the synthesis progress. It is also seen in the SS <sup>13</sup>C-NMR as the aromatic region of the spectra becomes more crowded and, finally, in the XPS spectra by the increase in the ratio of C:N on the surface of the silica.

A silica-supported Grubbs catalyst was synthesized using the heterogeneous NHC. Experiments on model compounds revealed the catalyst's activity but a comprehensive characterization of the heterogeneous Grubbs catalyst has not been conducted. We were not able to create the silica-supported polymeric



**Figure 9.** (a) XPS data of the heterogeneous NHC; (b) From left to right: amine-functionalized silica, azide-functionalized silica, clicked silica, diamine silica, and cyclized ligand silica; (c) SS<sup>13</sup>C-NMR of heterogeneous NHC.

Grubbs catalysts because we had significantly modified the heterogeneous NHC, the building block for both catalysts. As a contingency, we are continuing this research under our research contract with Elevance Renewable Sciences to evaluate the catalyst's recyclability and efficiency in olefin metathesis of camelina oil. In conclusion, the simple synthesis, discovered under this task, promises a wide application both on olefin metathesis and other reactions.

#### <u>3.1.4. Task 4: Design Study Documenting an Optimum Process Configuration and Economic</u> Analysis for Medium- and Large-Scale Pelletizing Plants for Camelina Meal

There are five outcomes from this task, namely: (1) development of an optimized process for fuel pellet production from camelina meal, (2) manufacture of a range of pellet compositions to verify producibility, (3) testing of products in a range of commercially-available multi-fuel pellet stoves, (4) determination of potential markets tested and product price including a fish food for export, and (5) preparation of study design for 40,000 to 500,000 ton per year pelletizing plants with economic analysis.

A pellet production process has been successfully designed and commissioned at MSUB City College. A patent application has been developed covering the process and has progressed through first review with senior MSUB administration and our patent Legal counsel advises that attorney. incorporating an apparatus would enhance Our work is focused on patentability. applying existing technology to develop new processes and industry. Patent application development was valuable to check patentability, and helps verify our free rights to practice the technology.

Table 2. Different feedstocks used to make pel	lets.
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Feedstock	Pellet Characteristics
100% camelina meal	Pelletizes well with moisture
	added. Product sticky.
100% lawn clippings	Pelletizing easily into a durable and long lasting pellet.
100% straw	Difficult to pelletize. Camelina
	oil was an effective pelletizing aid.
99% straw / 1% kaolin	Kaolin improved combustion
	performance for straw.
98% straw / 2% CaCO3	Calcium Carbonate improved
	combustion performance for
	straw.
50/50 grass/camelina meal	Good performance.
50/50 straw/camelina meal	Good performance.
75/25 grass/camelina seed	Pellet durability low.



Clockwise from bottom left are straw pellets with 1% kaolin, grass with 25% camelina seed, 100% grass, 50/50 grass/camelina meal in the white pale, 100% straw in the large barrel, and 100% grass in the burlap

100% camelina pellets in the blue barrel, grass with 25% camelina seed in the gray barrel, straw in the large white pale, and 50/50 straw/camelina meal in the red bucket.



Burn pot of the Model 6041 US Stove Multi-Fuel Heater after burning 9.8 lbs of straw pellets. The stove stayed lit, but it would likely have gone out soon either to an overfull burn pot or a stalled agitator.

Burn pot of the Model 6041 US Stove Multi-Fuel Heater after 17.06 lbs of straw pellets with 2% CaCO3. Still a lot of ash, but the grains are smaller and the agitator was not grinding on them.



Burn pot of the Enviro M55 Steel Freestanding Multi-Fuel Pellet Stove after 27.17 lbs of straw pellets. Pot is only lightly fouled with clinkers from this challenging fuel. This stove could burn overnight on 100% straw.

Figure 10. Various pellets used in the study.

We successfully demonstrated a pellet production process with a capacity of 2,400 lb/day. Students involved in the project configured several pieces of major equipment into an automated processing plant. The effort took two required summers and extensive modification of equipment to yield results that could be commercialized. Photos of students working on the equipment can be found in the Supporting Information section of the report. A wide range of pellet compositions have been produced at MSUB City College including the following blends (Table 2).

Pellet compositions were tested in an Enviro M55 Steel Freestanding Multi-Fuel Pellet Stove and a Model 6041 US Stove Multi-Fuel Heater. All the advanced fuel pellets tested were more challenging to burn than conventional wood pellets. High ash content resulted in clinker formation

that rapidly clogs burners in conventional wood stoves causing flameout. Reliable short-term operations on all fuels were achieved, but extended operations require more routine maintenance than with wood

pellets. 100% straw pellets proved to be the most challenging fuel with the highest clinker formation rates even in multi-fuel stoves. The addition of kaolin clay or Calcium Carbonate to the straw pellets significantly improved straw pellet combustion performance [13][14]. Figure 10 shows a snapshot of some furnace testing results.

Pricing and markets for advanced fuel pellets were evaluated including as an alternative to wood pellets for fuel and as animal feed for camelina meal. Price for the advanced fuel pellets produced will be discounted relative to wood pellets due to greater routine cleaning needs and fewer consumers with multi-fuel stoves capable of burning these pellets. A summary of our price assessment is shown in Table **3**.

Table	3.	Determined	retail	price	of	wood	and
	lvanced fuel p						

Туре	Unit	Wholesale	Retail Price
Wood Pellets	\$/Short Ton	165	\$247
Advanced Fuel Pellets	\$/Short Ton	115	\$170

Camelina meal is a better input to animal feed manufacture than fuel because feeds are priced significantly higher. Camelina meal competes with canola meal [15] which is valued at 13-18 cents per pound over the last seven years [16]. This equates to 260-360 \$/st which is greater than the price of camelina fuel pellets even before pelletizing costs are added.

While alternative fuel economics are challenging in an environment of low oil prices, a highlight of our research is a potentially feasible 40,000 ton/year case processing wheat straw residue. Low capacity cases were not economic due to high investment costs per ton and high labor costs. Yard clipping cases were not economic due to high transportation and handling costs. Hay cases were not economic because hay has a higher value as an animal feed. Wheat straw is a lower cost raw material with good availability. Product outlets for straw pellets would have to be developed including increased use of residential multi-fuel heaters and commercial outlets, but this is feasible because the lower cost straw pellets offer a savings relative to wood pellets.

We are planning to publish a book titled "Design Study for Fuel Pellet Production from Underutilized Biomass" which includes detailed methods used in and results from this task. The book will be available on the MSUB website and Google Books and will be a good resource for people interested in starting a pellet milling operation including farmers, farm cooperatives, landfill operators, engineers, designers, and financial institutions.

## 3.2. Patents Filed and Partnerships Established

We successfully established several partnerships, both in academic, non-profit organizations, and private sector, with this project. These connections enabled MSUN and MSUB City College to pursue additional projects with the goal of creating a camelina-derived biorefinery in Montana. We had also successfully filed a provisional patent to protect the discovered heterogeneous NHC which has the potential to be applied to wide range of catalysts and heterogeneous materials.

Connections Made:

- Calumet Refining Great Falls
- Elevance Renewable Sciences, Inc. Illinois
- Old Dominion University Virginia
- Omega Grains, LLC Bigfork
- Opportunity Link Havre
- Story Mills Oils Laurel
- Texas A&M University Texas
- University of Idaho Idaho
- Wayne State University Michigan

Patents Filed:

Title: Silica-Supported N-Heterocyclic Carbene Inventors: Randy Maglinao and Alexandra Jones Filing Date: March 22, 2017

#### 3.3. Other Projects Enabled by the Research

We are pleased to report that as of today, the following are the grant proposals that <u>have been</u> <u>submitted</u> and <u>pending to be funded</u>. In all cases, MSUN is either the lead institution or collaborator institution. This is particularly important to PI Resurreccion as he develops his own research team and prepares for his <u>NSF-CAREER</u> grant.

Investigators	Supporting agency and agency active award/pending proposal number	Total \$ amount	MSUN \$ amount share	Effective and expiration dates	Title of the project
Kumar, S. Gupta, R. Hatcher, P. <b>Resurreccion, E.</b> Shende, R. Stuart, B. Boss, D. <b>Maglinao, R.</b> Wang, X.	NSF/Innovations at the Nexus of Food- Water-Energy Systems (INFEWS)	2,000,000	803,177	10/01/2017 to 09/30/2020	Sustainable production of biofuels, biochemicals, and biocarbon from camelina
Lee, J. Spokas, K. Lentz, R. Hatcher, P. Donat, J. Kumar, S. Zhang, H. Wang, X. <b>Resurreccion, E.</b> Heemstra, J. Day, D.	NSF/Innovations at the Nexus of Food- Water-Energy Systems (INFEWS)	2,000,000	70,212	10/01/2017 to 09/30/2020	Advanced clean hydrophilic biochar for agriculture, energy, and water sustainability
Kumar, S. Resurreccion, E. Wang, X. Stuart, S. Maglinao, R. Shende, R. Gupta, R	USDA- NIFA/Foundational/ Bioenergy, natural resources, and environment (BNRE)	500,000	145,393	12/01/2017 to 11/30/2020	Camelina as a rotation crop and its impact on land use change under multi-products scenarios
Maglinao, R. Resurreccion, E. Kumar, S.	USDA- NIFA/Sustainable bioenergy and biproducts (SBB)	500,000	148,061	12/01/2017 to 11/30/2020	Sustainable high- value biolubricants from wet unhydrolyzed solids (UHS)
Wang, X. Kumar, S. <b>Resurreccion, E.</b>	USDA- NIFA/Resilient agroecosystems in a changing climate	877,349	150,000	12/01/2017 to 11/30/2020	Interactive impacts of climate variability and biofuel-related agricultural land use change on water quantity and quality
Lee, J. Wang, X. <b>Resurreccion, E.</b> Kumar, S. Heemstra, J. Zhang, H.	USDA- NIFA/Resilient agroecosystems in a changing climate	500,000	28,506	12/01/2017 to 11/30/2020	Surface- oxygenated biochar for resilient agroecosystems

Name (List)	Supporting agency and agency active award/pending proposal number	Total \$ amount	MSUN \$ amount share	Effective and expiration dates	Title of the project
Resurreccion, E. Kumar, S. Maglinao, R. Capareda, C.	USDA- DOE/Biomass Research and Development	2,000,000	1,000,000	10/01/2017 to 09/30/2020	Sustainable production of biofuels, biochemicals, and biocarbon from camelina
Resurreccion, E. Zhang, Y. Kumar, S. Wang, X. Yang, K. Carcone, A.	USDA- DOE/Biomass Research and Development	2,000,000	800,000	10/01/2017 to 09/30/2020	Advanced clean hydrophilic biochar for agriculture, energy, and water sustainability

In addition, these 2 proposals are being prepared and are both due 09/22/2017:

With these pending grant proposals and with all our commitment to our collaborators (Omega Grains, Calumet Great Falls, Old Dominion University, South Dakota State University, Virginia Commonwealth University, Wayne State University, Texas A&M University, University of Idaho, University of Minnesota, Montana State University, Montana State University Billings, USDA), we are expected to fulfill preliminary data gathering. More importantly, our agreement with Omega Grains in establishing a camelina biorefinery as quickly as possible, highlights the tremendous impact this project has on the agroeconomy within Montana.

## 3.4. Jobs Created

This project supported 26 jobs at MSUN and MSUB City College with over 21,000 work hours. Moreover, we are anticipating the hiring of more than four additional scientists and over ten undergraduate researchers resulting from the several project proposals submitted to various funding agencies. The connections made by MSUN and MSUB to Omega Grains, Calumet Refinery, and Story Mills will help establish the local, camelina-based biorefinery which will create sustainable careers for Montanans.

Jobs Created: Research Scientists/Investigators: 4 Professional Staff: 2 Research Associate and Assistants: 1 Undergraduate and Graduate Students: 20

## 4. Project Impacts

This project had helped MSUN and MSUB City College to expand both universities' research capabilities and facilities. It has provided MSUN and MSUB City College faculty members, who have full-time teaching responsibilities, the opportunity to engage in research work and grant preparation. These activities are helping faculty members to integrate research and education.

In MSUN, the discoveries made from understanding the mechanisms involved in producing alkylated aromatics and heterogeneous NHC had led to new ideas and more value-added products from biomass. Currently, MSUN's ambitious efforts to expand its reach beyond the state and be nationally-recognized as a research center is coming into fruition because of this project and will continue as MSUN direct its focus on hiring a research director who will carry on this mission. Collaborations with several universities located in the eastern, southern, and western part of U.S. is an indication of our efforts becoming successful.

One of the direct, tangible impacts of this project to MSUB City College is achieved through it's work on camelina meal. Screening various pellet production facility configurations has indicated that a mid-size plant producing straw pellets at a rate of 40,000 tons per year may be economically viable. This has a significant long-term potential to Montana's agricultural and industrial base. Benefits include upgrading an agricultural byproduct, enhancing agricultural output and revenue, increasing industrial output and employment, increasing the use of a renewable fuel, providing consumers with a low-cost option for space heating applications, and increasing markets for multifuel stoves enticed by increasing availability of low cost fuel.

The project provided \$43,982 in equipment and supplies to MSUB City College. These supplies will continue to be used to benefit education and students in years to come. Independent research is an example that has been enabled in large part by this grant. Nine 1st and 2nd year students developed research projects and present their work at the MSUB Research and Creativity Conference in the spring of 2017 alone including:

- 1. Oil press alarm and shutdown system for unattended operation.
- 2. Soap making as a value-added product from Montana oil seed production and from byproduct glycerin from biodiesel production.
- 3. Pellet furnace efficiency improvements for lower CO2 emissions and improved economics.
- 4. Fuel and feed pellet production optimization from Montana's Agricultural Crops.

Another way that the grant is yielding long-term benefit is by providing authentic learning activities consistent with problems from industry. These activities help prepare our students for challenges like what they are likely to encounter in industry, and helps develop the strongest workforce possible. Skills learned include some of the most valuable in industry such as parameter optimization, economic analysis, troubleshooting, and maintaining safe and reliable operations on large-scale equipment. Example learning activities include:

- 1. Oil press labs that involve students in authentic troubleshooting and optimization activities important for their future success and to our industrial partners.
- 2. Furnace efficiency labs built on the multi-fuel furnaces provided and instrumented by the grant.

Our industrial partners are focused on efficiency and have specialist in operations and engineering tasked with maintaining furnace efficiency and minimizing  $CO_2$  emissions. We can now develop students into efficiency experts by optimizing furnaces themselves.

Work on the grant has developed an entrepreneurial spirit in student researchers. At least two student researchers have demonstrated interest in further pursuing business development

opportunities based on interests developed from the grant. One student has pursued control system job opportunities at a wood processing plant based on their interest in the control systems they build in the project. That student has also expressed interest in building systems to enhance the safety and effectiveness of small-scale biodiesel facilities based on related work making biodiesel from camelina oil. Another student has expressed interest in running a pellet plant if we are able to develop a viable process.

#### 5. Conclusions

This project has successfully generated substantial information which could help establish a local, camelina-based biorefinery facility and increase Montana's manufacturing and agricultural industry. It has been determined that a biorefinery processing camelina can be profitable and competitive against other processes (e.g. HJT). Experimental results have proven that unleaded avgas can be made from camelina using our patented conversion technology. We also concluded that the meal, a by-product of camelina oil extraction, would be more economical to be used as an animal feed instead as a fuel. The project was an overall success and its outcomes, including the connections established and pending projects, will greatly help Montana.

## 6. References

- Polzin, P. 2014. *The state of Montana manufacturing: 2014 Edition*. Montana Manufacturing Extension Center. http://www.mtmanufacturingcenter.com/PDFs/State\_MT\_Mfg\_14.pdf. (Accessed on May 14, 2015).
- Jackson, G. and J. Miller. *Effect of nitrogen, phosphorus and sulfur on yield, oil content, and oil quality of camelina*. 2005. http://ag.montana.edu/wtarc/Web2005/Soils/Camalina/2005CamelinaNPS.pdf. (Accessed on May 14, 2015).
- 3. Maglinao, Randy L. and Md. J. Abedin. 2014. *Developing a conversion process technology to produce next generation fuels and chemicals from natural oils*. Montana Professor: A Journal of Education, Politics, and Culture. 24(1), 12-15.
- McVay K.A. and P.F. Lamb. 2008. Camelina production in Montana. Montana State University Extension. March, 2008. http://store.msuextension.org/publications/AgandNaturalResources/MT200701AG.pdf. (Accessed on May 3, 2013).
- 5. Moser, B.R. 2010. *Camelina* (<u>Camelina sativa</u> *L.*) *oil as a biofuels feedstock: Golden opportunity or false hope?* Lipid Technology. 22(12), 270-273.
- 6. ASTM D7566-14c, *Standard specification for aviation turbine fuel containing synthesized hydrocarbons*, ASTM International, West Conshohocken, PA, 2014. www.astm.org.
- 7. Do, P. T. M.; Crossley, S.; Santikunaporn, M.; Resasco, D.E. Catalytic strategies for improving specific fuel properties. *The Royal Society of Chemistry: Catalysis.* **2007**, 20, 33-64.
- 8. Ghosh, P.; Hickey, K.; Jaffe, S. B. Development of a detailed gasoline composition-based octane model. *Industrial Enngineering Chemical Research.* **2006**, 45, 337-345.
- 9. ASTM D7719-16a, Standard Specification for High Aromatic Content Unleaded Hydrocarbon Aviation Gasoline, ASTM International, West Conshohocken, PA, 2016, <u>www.astm.org</u>.
- 10. Espeel, P.; Du Prez, F. "Click"-inspired chemistry in macromolecular science: Matching recent progress and user expectations. *Macromolecules*. **2015**, 48, 2–14.
- 11. Meldal, M.; Tornøe, C. Cu-catalyzed azide- alkyne cycloaddition. *Chem. Rev.* **2008**, *108*, 2952–3015.
- Abbot, G.; Brooks, R.; Rosenberg, E.; Terwilliger, J.B.; Ross, A.; Ichire, O. Surface-bound ruthenium diamine organometallic complexes: Excited-state properties. *Organometallics*. 2014, 33, 2467–2478.
- 13. Scott C. Clinkers from burning grass pellets and others. )October 7, 2015) Accessed on April 2017. http://www.pelheat.com/clinkers.html.
- 14. United States Stove Company. (n.d.). Installation/Operator's Manual Model(s) 6041, 6041TP, 6041HF, 6041I. South Pittsburg, TN, USA: United States Stove Company.
- 15. Irwin B. A Feed Stock Evaluation; Camelina. Richmond CA: A Whole Energy Fuels Corp. Accessed on April 2017. http://whole-energy.com/wpcontent/uploads/2015/04/Camelina-White-Paper.pdf.
- 16. Ash, M. (2017). *Oil Crops Outlook*. United States Department of Agriculture. Accessed on April 2017. http://usda.mannlib.cornell.edu/usda/current/OCS/OCS-05-12-2017.pdf.

## 7. Supporting Information

The following are the oral and poster presentations we have produced during the duration of the projects. This was important to expose the scientific community, investors, and academic institutions our research findings to contribute new knowledge to biofuels and oilseed industries and receive feedback from colleagues to validate our research.

Authors	Presentation Title	Conference
Randy Maglinao	Synthesis of Renewable 1,4-	2016 Annual American Oil
Chazley Hulett	Cylohexadiene from Camelina	Chemists' Society (AOCS) Meeting
Eleazer Resurreccion	sativa through Olefin Metathesis	and Expo, Salt Lake, UT
Randy Maglinao	Process development of a	2017 Annual American Oil
Chazley Hulett	sustainable aromatic hydrocarbons	Chemists' Society (AOCS) Meeting
Eleazer Resurreccion	derived from Camelina sativa	and Expo, Orlando, FL
Alexandra Jones		
Randy Maglinao	Evaluation of Octane Number	2017 Annual American Oil
Chazley Hulett	Property of Renewable	Chemists' Society (AOCS) Meeting
Eleazer Resurreccion	Hydrocarbons Synthesized from	and Expo, Orlando, FL
Alexandra Jones	Camelina sativa	
Alexandra Jones	Development of robust covalently-	253 <sup>rd</sup> American Chemists' Society
William Cochran	linked N-heterocyclic carbenes and	(ACS) National Meeting and
Eleazer Resurreccion	silica	Exposition, San Francisco, CA
Randy Maglinao		
Eleazer Resurreccion	Advanced Fuel Production from	2017 Biannual Conference of the
Mason Martin	Camelina Oil	Association of Environmental
Paul Jeffrey		Engineering and Science Professors
Randy Maglinao		(AEESP), Ann Arbor, MI
Benjamin Rice		
Javad Roostaei		
Yongli Zhang		

Below are photos of MSUN and MSUB City College students working on the project and participating on international technical conferences. More pictures are available at the Advanced Fuels Center website (<u>https://msunafc.com</u>), PI Resurreccion's website (<u>https://techsci.msun.edu/epresurreccion</u>), PI Sullivan's website (<u>www.msubillings.edu/cotfaculty/sullivan</u>/), and the Montana Research and Economic Development Initiative website (<u>https://mus.edu/research/Funded/Bio-BasedFuels.asp</u>).



Top Left: Alex (left) and William (left), a Biology student, presenting the results of Task 3 at the 253<sup>rd</sup> American Chemists' Society National Meeting and Exposition at San Francisco, CA

Bottom Left: Chazley, a Biology student, winning a student poster award at the 2017 American Oil Chemists Society Meeting and Expo at Orlando, FL



Top Right: Lane, a Civil Engineering Technology student, using the Acid Number Test Unit.



Tyler, Anthony, and Jade at the pellet mill and screener.



Greg, Alex, Adam, and Jason conditioning camelina seed for oil extraction.



Paul and Cody designing and building the pellet plant control system.



Tyler, Sam, Jade, and Casey operating the hammer mill grinding straw.

