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Canola Oil Fuel Cell Demonstration

Volume II—Market Availability of Agricultural Crops for Fuel Cell Applications

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Joel Lindstrom, Michael J. Binder, Franklin H. Holcomb, and
Scott M. Lux

June 2006



A Resource Conservationist at Flathead Indian Reservation Tribal Complex, Pablo, MT checks a field of canola in bloom.

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Abstract: Fuel cells are electrochemical devices that convert chemical energy to electrical energy with very high efficiency, and with very low levels of environmental emissions. The reformation of vegetable oil crops for fuel cell uses is not well known; yet vegetable oils such as canola oil represent a viable alternative and complement to traditional fuel cell feedstocks. This report summarizes a study conducted to identify various Montana oil crops available for reforming as a feedstock fuel in fuel cell applications. The use of vegetable oils, or bio-fuels, in Montana alone could potentially sustain more than 6000 fuel cell units, 5.0 kW in size. Many vegetable oils were found to be viable options for production and use in fuel cells in Montana. This project was undertaken to demonstrate a year-long operation of a fuel cell in Yellowstone National Park using canola oil feedstock. This study performed a literature search to: (1) determine the market availability of agricultural crops that produce vegetable oil, and (2) determine the amount of vegetable oil that could be extracted to serve as a feedstock in fuel cell applications.

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Preface

This study was conducted under Work Unit CFE-B033, "Canola Oil Fuel Cells." The technical monitor was Mr. Bob Boyd, Office of the Director, Defense, Research, and Engineering (ODDR&E).

The work was performed by the Energy Branch (CF-E), of the Facilities Division (CF), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigators were Michael J. Binder and Franklin H. Holcomb. Part of this work was done by SoBran, Inc., Leonardo Technologies, Inc., and Montana State University under GSA Task Order Number 5TS5703C271. John W. Adams and Craig Cassarino are associated with Leonardo Technologies, Inc. (LTI), Bannock, OH. Dr. Lee Spangler, Dr. Duane Johnson, and Joel Lindstrom are affiliated with Montana State University (MSU), Bozeman, MT. Dr. Thomas Hartranft is Chief, CEERD-CF-E, and L. Michael Golish is Chief, CEERD-CF. The associated Technical Director was Gary W. Schanche, CEERD-CVT. The Director of CERL is Dr. Ilker R. Adiguzel.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL James R. Rowan, and the Director of ERDC is Dr. James R. Houston.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
cubic inches	0.00001638706	cubic meters
degrees (angle)	0.01745329	radians
degrees Fahrenheit	$(5/9) \times (^\circ\text{F} - 32)$	degrees Celsius
degrees Fahrenheit	$(5/9) \times (^\circ\text{F} - 32) + 273.15$	kelvins
feet	0.3048	meters
gallons (U.S. liquid)	0.003785412	cubic meters
horsepower (550 ft-lb force per second)	745.6999	watts
inches	0.0254	meters
kip per square foot	47.88026	kilopascals
kip per square inch	6.894757	megapascals
miles (U.S. statute)	1.609347	kilometers
pounds (force)	4.448222	newtons
pounds (force) per square inch	0.006894757	megapascals
pounds (mass)	0.4535924	kilograms
square feet	0.09290304	square meters
square miles	2,589,998	square meters
tons (force)	8,896.443	newtons
tons (2,000 pounds, mass)	907.1847	kilograms
yards	0.9144	meters

1 Introduction

Background

Fuel cells are electrochemical devices that convert chemical energy to electrical energy with very high efficiency. Since fuel cells produce electricity by electrochemical conversion, they generally exhibit “good neighbor characteristics”; i.e., they are quiet and produce very low levels of environmental emissions. Fuel cell technology is also sufficiently developed to meet the electrical demand at some sites in Yellowstone National Park. These attributes make fuel cell technology very desirable for electricity generation, and perhaps cogeneration, in environmentally sensitive locations like Yellowstone.

Hydrogen is necessary for fuel cells, but it is not widely available in its elemental state. Traditional feedstocks for fuel cells include hydrocarbons such as natural gas and propane that must be reformed into a hydrogen-rich gas. The reformation of vegetable oil crops for fuel cell use is not well known, yet vegetable oils do represent a viable alternative and complement to traditional fuel cell feedstocks. Canola oil is one of several valuable renewable vegetable oil crops produced in Montana and other locations near Yellowstone National Park. In fact, canola biodiesel has already been used by Yellowstone National Park in its “Truck in the Park” project (Haines and Evanoff 1998), but the Park eventually migrated to soy biodiesel because it was more readily available and affordable.

This project was undertaken to demonstrate a year-long operation of a fuel cell in Yellowstone National Park using canola oil feedstock. Preliminary to the demonstration, a literature study was done to:

- identify reformer technology development and applications
- establish the state-of-the-market for reformer technology with an emphasis on agricultural biomass.
- identify and quantify the potential for Montana agricultural crops to yield oils to be used as a feedstock for fuel cell applications.

Objectives

The overall objective of this project is to perform a 1-year demonstration of a fuel cell operating on canola oil at Yellowstone National Park. The specific objective of this preliminary work was to conduct a literature study to

determine the availability of vegetable oil producing agricultural crops in Montana, and to determine the amount of hydrogen that could be generated from the oils harvested for use in a fuel cell system.

Approach

The overall project is to be conducted in three phases:

1. *Assess biofuel reformation technology.* This work was previously completed and documented (Adams, et. al 2004).
2. *Assess biofuel crop production.* This report describes Phase 2 in which six species of crops in Montana were identified to produce vegetable oil. A model was developed that calculated the amount of hydrogen that could theoretically be produced from these agricultural crops. An investigation of the production of biodiesel was also undertaken.
3. *Complete a 1-year canola oil fuel cell demonstration at Yellowstone National Park.* Phase 3 should begin in the Fall of 2006.

Scope

Investigation of the costs to plant, harvest, and reform the vegetable oils considered in this study was beyond the scope of this research.

Mode of Technology Transfer

This study forms the basis for continuing research into the technical and operational issues associated with the operation of a fuel cell on vegetable oil. This report will be made accessible through the World Wide Web (WWW) at URL:

<http://www.cecer.army.mil>

2 Biodiesel Fuel – How It Is Derived

Vegetable Oil Crop Yield Model

Tables 1 and 2 list expected yields of Montana grown vegetable oils and the hydrogen they could generate. Included crops are canola, crambe, mustard, rapeseed, safflower, and sunflower. These six species were selected for evaluation based on the production requirements for each crop. By comparison, other less-known crops such as camelina are poorly defined in terms of production. Crops such as safflower and sunflower are also as well known as canola. Consequently, more variables are used to define canola, flax, safflower, and sunflower. Crops with relatively little production information (e.g., crambe and mustard) used fewer variables. Therefore, areas defined for crambe and mustard may be over-estimated since fewer variables constrain the defined production areas. Preliminary trials of both these species, however, indicate they are highly adaptable to many Montana environments.

For the purpose of this study, it was assumed that 100 percent of the hydrogen could be extracted from the vegetable oil. In most applications, however, a 70 to 80 percent assumed conversion efficiency would be more accurate. Data for potential production of oilseeds was derived by entering variables into an ARC/Info crop mapping system using Global Positioning Satellite (GPS) technology developed by Montana State University. This crop mapping system uses as many as 150 variables, and each can be evaluated at a multitude of levels. For example, one such variable would be “days of frost-free production,” which, for canola, was set at 110 to 115 days. Each variable can be layered on top of the prior variable to create a crop map of all conditions defined.

Figure 1 shows such a crop map for a canola oil crop, which indicated a defined area of high productivity for the specified crop. The grid units are defined as 2 by 3 miles in size with at least 50 percent of that area being highly adapted to canola production. Other variables include soil type, rainfall patterns, soil types, first and last frost, etc.

Table 1. Oil/hydrogen production using Class I land (optimum production environment) in Montana.

Crop	Acres Planted	Seed Yield (lbs/acre)	Seed Production (lbs)	% Oil Yield*	Oil Recovered (lbs)	% H ₂ Yield**	Total H ₂ Production (lbs)
Canola	55,000	1,200	66,000,000	39%	25,740,000	11%	2,831,400
Crambe	68,000	1,000	68,000,000	32%	21,760,000	14%	3,046,400
Mustard	85,000	1,000	85,000,000	32%	27,200,000	10%	2,720,000
Rapeseed	35,000	1,100	38,500,000	39%	15,015,000	14%	2,102,100
Safflower	65,000	1,200	78,000,000	34%	26,520,000	12%	3,182,400
Sunflower	25,000	900	22,500,000	42%	9,450,000	10%	945,000
Total per annum			358,000,000		125,685,000		14,827,300
*% pounds of oil yield per pounds of seeds							
** % pounds of H ₂ yield per pounds of oil							

Table 2. Oil/hydrogen production using Class I and Class II land (optimum and economically feasible production environments) in Montana.

Crop	Acres Planted	Seed Yield (lbs/acre)	Seed Production (lbs)	% Oil Yield*	Oil Recovered (lbs)	% H ₂ Yield**	Total H ₂ Production (lbs)
Canola	110,000	1,200	132,000,000	39%	51,480,000	11%	5,662,800
Crambe	80,000	1,000	80,000,000	32%	25,600,000	14%	3,584,000
Mustard	400,000	1,000	400,000,000	32%	128,000,000	10%	12,800,000
Rapeseed	65,000	1,100	71,500,000	39%	27,885,000	14%	3,903,900
Safflower	100,000	1,200	120,000,000	34%	40,800,000	12%	4,896,000
Sunflower	65,000	900	58,500,000	42%	24,570,000	10%	2,457,000
Total per annum			862,000,000		298,335,000		33,303,700
*% pounds of oil yield per pounds of seeds							
** % pounds of H ₂ yield per pounds of oil							

In many areas, crops such as canola, crambe, mustard, and rapeseed overlap in production requirements. Since no more than one fourth of the suitable land can be used annually for any one crop, crop rotation was considered essential. For example, in the first year of production, an acre of land could be planted to canola. The following year, the same acre could be planted with sunflower, followed by crambe and safflower. In the fifth year, the land would return to canola. This would achieve maximum land use for fuel production.

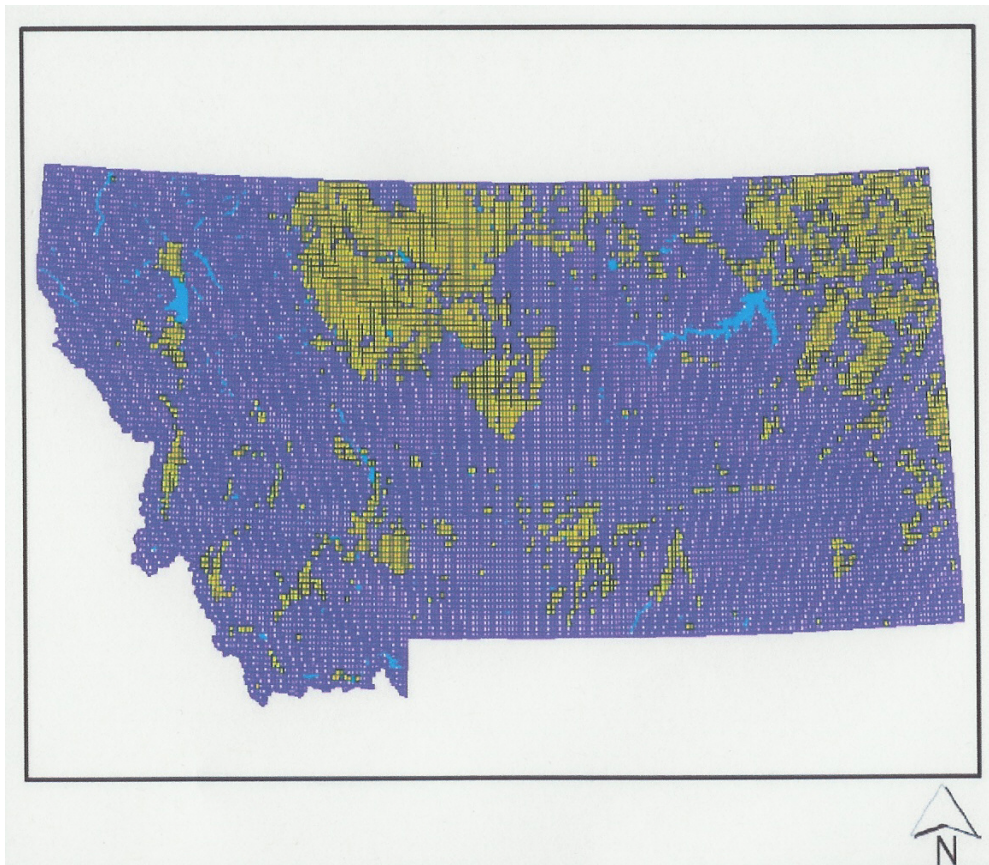


Figure 1. Class I land available (shown as light areas) to plant canola crop on an annual basis in Montana.

Land types used in this analysis were Class I and Class II farmlands. These lands represent the typical farmlands being used in agriculture. In the selection process, the availability of farm equipment and producers was as equally important as the adaptation of the land itself. Other conditions (e.g., rainfall, soil pH, salinity, and frost-free period) were variable. For example, rainfall for dry land production was established as 12 in. for canola and sunflower, but 14 in. for safflower. For mustard, a minimum rainfall of 10 in. was used.

Selection of a Vegetable Oil Hydrogen Source

Feedstocks used for the generation of hydrogen are typically introduced into a reformer system as a fluid, for ease of operation. The most obvious choice of a fluid would be in the form of water, alcohol, or oil. A catalytic system should be capable of isolating hydrogen from any of these media. However, the yield of hydrogen from water is relatively low due to the low molecular weight of water (MW=18) and low yield of hydrogen (11 percent by weight, assuming 100 percent efficiency). Water generates no byprod-

ucts and therefore has little economic advantage beyond fuel generation and must be decontaminated before use. Alcohols improve efficiency (20 percent hydrogen yield), but are relatively expensive to generate from natural sources. They do, however, generate byproducts with economic value. The best combination of yield and molecular weight for the generation of hydrogen appears to be in vegetable oil or animal fats. Since animal fats are not fluid at normal operating temperatures and their availability is limited, they were not considered further in this study.

Vegetable oils can be crafted from a multitude of sources suitable for production in Montana. These vegetable oils and others, e.g., soy, may also be suitable for production in other states. Montana vegetable oils typically are derived from:

- canola (*Brassica napus* or *B. rapa*)
- crambe (*Crambe abyssinica*)
- mustard (*Brassica juncea*)
- rapeseed (*Brassica napus*)
- safflower (*Carthamus tinctorus*)
- sunflower (*Heliothus annus*).

The oils are easily derived by crushing the seed and extracting the oils via solvent systems. These solvents are typically recycled hexane, alcohol, or carbon dioxide. The extracted vegetable oils remain fluid at relatively low temperatures (-10 to -20 °C) and are relatively efficient as sources of hydrogen (10 to 14 percent by weight). In their native state, vegetable oils exist primarily as triglycerides (three fatty acids, R_1 , R_2 and R_3 in Figure 2, bonded to a molecule of glycerin). This study assumed all vegetable oils to be produced as triglycerides.

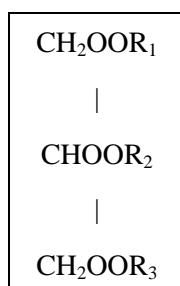


Figure 2. A triglyceride (vegetable oil) molecule.

Conversion of Vegetable Oil to Biodiesel

Biodiesels typically have shorter molecular chains compared to their originating oils (Table 3). Shorter molecular chain materials are, in general,

easier to reform to high quality syngas for fuel cell applications. “Fuel reformation,” also known as “fuel processing,” is used to convert hydrocarbons such as canola and other vegetable oils into hydrogen (H₂) rich gas streams. The remaining components in reformed fuel streams are designed to be either carbon monoxide (CO) or carbon dioxide (CO₂), depending on the fuel cell type used subsequent to the reformer. Some fuel cells may be poisoned by CO, CO₂, and other impurities while other fuel cells, such as high temperature fuel cells, may use CO as a fuel. Fuel reformation can occur independently at temperatures around 1400 °C. Often, a catalyst is used to lower this reaction temperature to 500 to 800 °C to reduce the size of the reformer and to achieve better control of reaction kinetics.

Table 3. Selected fuel formulas.

Fuel	Average Empirical Formula
Gasoline	C _{7.3} H _{14.8} O _{0.1}
Dodecane (Diesel)	C ₁₂ H ₂₆
Jet Fuel A	C _{12.5} H _{24.4}
Canola Oil	C ₅₉ H ₉₄ O ₅
100% Canola Biodiesel (CME)	C ₁₉ H ₃₅ O ₂
100% Canola Biodiesel (CEE)	C ₂₀ H ₃₇ O ₂
100% Rapeseed Biodiesel (RME)	C ₄₁ H ₂₈ O ₂
100% Rapeseed Biodiesel (REE)	C ₂₂ H ₄₃ O ₂
100% Soy Biodiesel	C _{18.8} H _{34.6} O ₂

Blending the vegetable oil with a metallic salt and water causes gums and other contaminants in the oil to flocculate, or become solid. These solids can be removed from the oil. This solid contaminant is typically called “soap stock” and can be used in cosmetics or other industrial applications. The clarified oil is then remixed with a metallic salt (e.g., sodium or potassium hydroxide) and an alcohol (e.g., methanol or ethanol). This blend is placed under heat and pressure producing three new products:

- an ester of the alcohol, e.g., biodiesel
- fatty acids
- glycerin.

The type of ester produced is determined by the alcohol used in its manufacture. Methanol is typically derived from petroleum processing and is more toxic and hazardous to handle compared to ethanol. Ethanol can be produced from a variety of agricultural products, but is more expensive

than methanol. By combining alcohols and vegetable oils under heat, pressure, and a catalyst, two products can be generated:

1. Methyl or ethyl esters- long chain polymers of fatty acids and alcohols (designated as R_x in Figure 3)
2. Glycerin (or glycerol).

By producing esters, the triglycerides become simple long chain molecules, known as biodiesels (Figure 3). Typically the alcohol used for the conversion of vegetable oils to biodiesels is either methanol or ethanol. When ethanol is used, the biodiesel would be a completely renewable natural product.

Preliminary work done to characterize and evaluate reforming technologies (Adams et al., August 2004) indicates that catalytic partial oxidation (POX) reforming appears to be the most applicable technology for canola (rapeseed) oil or canola (rapeseed) biodiesel reforming. Catalytic partial oxidation reformers had the most related experience and therefore the most potential to meet the expectations for canola (rapeseed) reformer / fuel cell application.

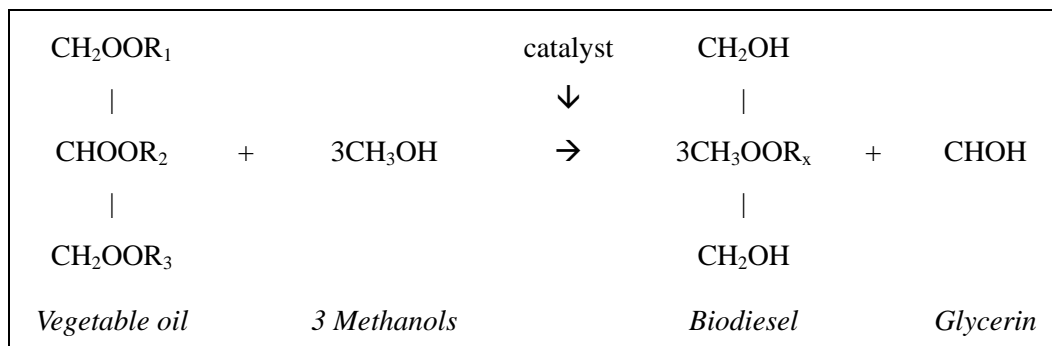


Figure 3. Biodiesel production.

3 Results of Analysis

Assuming a maximum production system with optimum production conditions, the theoretical hydrogen production annually would equal approximately 14.82 million pounds from oilseeds in Montana (Table 2). If the variables are relaxed to allow lands with some limitations to enter production, potential oil production could be increases to more than 298 million pounds, resulting in a theoretical hydrogen production of 33 million pounds (Table 3). Maximum production represents maximum input including Class I soils, high rainfall or irrigation, and optimum frost-free period. Class II lands involve production on lands of low productivity (lower fertility, salt, or low rainfall). Oilseed crops will be competing for class I lands with other crops. Class II lands are less competitive and more likely to be used for oilseed production.

As oils become more unsaturated (lacking hydrogen), yields of hydrogen will decrease. Polyunsaturated oils include flax, safflower, soybean, and sunflower. Higher oleic oils such as canola, crambe, and mustard have more saturated oils and will yield more hydrogen. However, high oleic versions of safflower, sunflower (and soon soybean) oils will be available as well. The yield of pounds of hydrogen per pound of oil (% H₂ yield) between the six crops in this study averages approximately 0.12 lb of hydrogen per pound of oil.

These results show seeds, oil, and hydrogen yields to be nearly the same for the six selected oil crops (Table 4). Differences are due to saturation of the oil derived from each crop planted. Other changes could result from efficiencies that would affect the yields at each stage of production.

Table 4. Oil/hydrogen production per acre.

Crop	Oil Recovered (lbs/acre)	Total H2 Production (lbs/acre)	H2 Yield (lbs H ₂ /lbs Oil)
Canola	468	51.5	0.11
Crambe	320	44.8	0.14
Mustard	320	32.0	0.10
Rapeseed	429	60.1	0.14
Safflower	408	49.0	0.12
Sunflower	378	37.8	0.10

For this DOD/CERL project, “Field Demonstration of Advanced, Pre-commercial Technology for the Conversion of Canola Oil for use as an Acceptable Fuel in Fuel Cell Applications,” CERL and its Fuel Cell Test and Evaluation Center have projected consumption rate of 100 gal of canola biodiesel per week (with 24/7 operation) for a 5.0 kW fuel cell. Assuming a projected consumption rate, and using a volume factor of 5.5 : 5.0 for the conversion of a vegetable oil to its biodiesel corollary, the estimated annual production (theoretical maximum) of the six identified Montana oil crops for fuel cell applications could (theoretically) sustain more than 6,000 fuel cell units, 5.0 kW in size, on an annual basis. Table 5 lists the data inputs and shows the calculation in more detail.

Table 5. Calculation of number of fuel cells capable to be supported (theoretically) from biodiesel derived from Montana seed crop grown on Class I and II lands.

Data Source			
A	Oil Yield	298,000,000	pounds of vegetable oil
B	Density	8	pounds per gallon
C	Oil Yield	37,250,000	gallons of vegetable oil
D	Biodiesel Conversion Factor	1.1	oil to biodiesel
E	Biodiesel Yield	33,863,636	gallons of biodiesel
F	5 kW Fuel Cell Consumption	100	gallons of biodiesel per week*
G	Annual 5 kW Fuel Cell Consumption	5,200	gallons of biodiesel per year*
H	Number of 5 kW Fuel Cells Supported	6,512	number of 5 kW fuel cell units
*assuming 24/7 operation.			
Formula:			
$\text{Number of Fuel Cell Units} = \frac{A}{B \times D \times G} = \frac{298,000,000}{8 \times 1.1 \times 5,200} = 6,512$			
This number represents the number of 5kW fuel cells (similar to one specified for the Yellowstone National Park demonstration) that can be operated for 1 year on the vegetable oil produced on Class I and II land in the State of Montana.			

4 Conclusion

This study concludes that vegetable oils represent a viable alternative and complement to traditional fuel cell feedstocks. This study identified and quantified the potential for six different Montana vegetable oil crops as a fuel feedstock for fuel cell applications. Using a combination of Class I and Class II lands, a total oil recovery of more than 298 million lb (37.25 million gal) is estimated from all six crops. This level of annual production is estimated to be sufficient to sustain more than 6,000 fuel cell units, 5.0 kW in size.

The current project to demonstrate a 5.0 kW fuel cell in Yellowstone National Park using a canola biodiesel will confirm various fuel cell system operating parameters, including biodiesel consumption. Future projects could be designed to assess the feedstocks derived from oil crops other than canola.

Abbreviations

<u>Term</u>	<u>Spellout</u>
CERL	Engineer Research and Development Center, Construction Engineering Research Laboratory
C	carbon
CO	carbon monoxide
CO ₂	carbon dioxide
DOD	U. S. Department of Defense
H ₂	hydrogen
kW	kilowatt
lbs	pounds
LTI	Leonardo Technologies, Inc.
MSU	Montana State University
MW	molecular weight
O	oxygen
R	designation of various chemical elements
YNP	Yellowstone National Park

References

Haines, H., and J. Evanoff, "Environmental and Regulatory Benefits Derived From the Truck in the Park Biodiesel Emissions Testing and Demonstration in Yellowstone National Park," *BioEnergy '98: Expanding BioEnergy Partnerships* (1998), pp 934-943.

Adams, John W., Craig Cassarino, Joel Lindstrom, Lee Spangler, Michael J. Binder, and Franklin H. Holcomb, *Canola Oil Fuel Cell Demonstration: Volume I – Literature Review of Current Reformer Technologies*, ERDC/CERL Special Report (SR)-04-24 (Engineer Research and Development Center, Construction Engineering Research Laboratory [ERDC-CERL], Champaign, IL, August 2004).

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