ERDC/CERL SR-04-24

Construction Engineering Research Laboratory

US Army Corps of Engineers®
Engineer Research and Development Center

Canola Oil Fuel Cell Demonstration

Volume I – Literature Review of Current Reformer Technologies

John W. Adams, Craig Cassarino, Joel Lindstrom, Lee Spangler, Michael J. Binder, and Franklin H. Holcomb

August 2004

Canola at post-bloom stage.

Approved for public release; distribution is unlimited.

ERDC/CERL SR-04-24
August 2004

Canola Oil Fuel Cell Demonstration: Volume I – Literature Review of Current Reformer Technologies

Michael J. Binder and Franklin H. Holcomb

Construction Engineering Research Laboratory
PO Box 9005
Champaign, IL 61826-9005

John W. Adams (LTI), Craig Cassarino (LTI)

Leonardo Technologies, Inc. (LTI)

3606 Collins Ferry Road, Suite 103
Morgantown, WV 26505

Joel Lindstrom (MSU), Dr. Lee Spangler

Montana State University (MSU)
Billings, MT 59101

Final Report

Approved for public release; distribution is unlimited.

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000

Under Work Unit # CFE-B033, “Canola Oil Fuel Cells.”

ABSTRACT: This literature review identifies fuel reformer technologies that may be pertinent for reforming canola / rapeseed oil and other agricultural biomass including biodiesel. A description of candidate reformers is presented, noting characteristics generally inherent to each configuration. A comparison of the identified reformers is accomplished by rating each reformer against a set of specific criteria, essential for attaining operating characteristics desired for canola / rapeseed oil given applications.

DISCLAIMER: The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. All product names and trademarks cited are the property of their respective owners. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.
DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

Contents

List of Figures and Tables ..... **v**

Conversion Factors ..... **vi**

Preface ..... **vii**

1 Introduction **1**

Background 1
Objectives 2
Approach 2
Mode of Technology Transfer 2

2 Fuel Reformation **3**

Steam Reforming 4
Partial Oxidation Reforming 5
Auto thermal Reforming 6
Thermal Decomposition 7
Market Summary 7

3 Application Considerations **9**

Fuel Properties 9
Reformer Degradation 10
Reformer Dynamics 12
Reformer Cost 12

4 Reformer Evaluation **14**

5 Telephone Interviews – Industry and Academic **17**

List of Organizations Contacted 17
Findings of Interviews 18

6 Conclusion **19**

References **20**

Report Documentation Page **22**

List of Figures and Tables

Figures

1 SOFC vs. PEM reformation (Zizelman et al. 2000) 3
2 Steam reformation 5
3 Partial oxidation reformation (Ahmed and Krumpelt 2001) 6
4 Autothermal reformation (Ahmed and Krumpelt 2001) 7

Tables

1 Fuel properties 9
2 Reformer evaluation 15
3 Contact list 17

Conversion Factors

Non-SI* units of measurement used in this report can be converted to SI units as follows:

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) x (°F – 32)	degrees Celsius
degrees Fahrenheit	(5/9) x (°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
kips per square foot	47.88026	kilopascals
kips 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

*_Système International d'Unités_ ("International System of Measurement"), commonly known as the "metric system."

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. 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 technical editor was William J. Wolfe, Information Technology Laboratory.

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 John Morris III, EN and the Director of ERDC is Dr. James R. Houston.

1 Introduction

Background

Fuel cells are electrochemical devices that convert chemical energy to electrical energy with very high efficiency. Due to their electrochemical conversion, fuel cell systems operate with very low environmental emission levels and exhibit "good neighbor characteristics." Thus, fuel cell technology has very desirable attributes for electricity generation, and perhaps cogeneration, in Yellowstone National Park.

Canola oil is a valuable renewable crop that is produced in Montana and other locations near Yellowstone National Park. The biodiesel corollary is also considered in this report since an infrastructure has already been established for the use of soy biodiesel through Yellowstone National Park's "Truck in the Park" project (Haines and Evanoff 1998). In addition, biodiesels typically have shorter molecular chains compared to their originating oil, such as canola oil. Shorter molecular chain materials are, in general, easier to reform to high quality syngas.

Fuel cell technology has a sufficient development status to meet this demand, however, the reformation of canola oil and other liquid forms of biomass for fuel cell use is not well known. This project is evaluating the technical and operational issues associated with the conversion of harvested biomass—specifically canola (also referred to as rapeseed) oil—into a gas stream of sufficient quality so as to serve as an adequate and sustainable fuel source for fuel cell applications. The project will demonstrate the use of a canola oil feedstock during a year-long operation of a fuel cell in Yellowstone National Park. The initial step in this work was to conduct a literature study to identify reformer technology development and application work and to establish the state-of-the-market for reformer technology. Particular emphasis was placed on reformer applications associated with canola oil and other agricultural biomass.

Objectives

The overall objective of this project is to evaluate the technical and operational issues associated with the conversion of harvested biomass—specifically canola (also referred to as rapeseed) oil—into a gas stream of sufficient quality so as to serve as an adequate and sustainable fuel source for fuel cell applications. The specific objective of this preliminary work was to conduct a literature study to identify reformer technology development and application work, and to establish the state-of-the-market for reformer technology, placing particular emphasis on reformer applications associated with canola oil (and other agricultural biomass).

Approach

A literature study was conducted to identify reformer technology development and application work, and to establish the state-of-the-market for reformer technology. A telephone interview was done to contact 26 companies, individuals, universities or institutions involved in manufacturing, development or research, to explore their activities in or perspective of reformer technology applications for canola (rapeseed) oil for use in fuel cell systems. The findings of the literature study and interviews were compiled and are documented in this report.

Mode of Technology Transfer

This literature review forms the basis for continuing research into the technical and operational issues associated with the conversion of canola oil into a gas stream to serve as fuel source for fuel cell applications. This report will be made accessible through the World Wide Web (WWW) at URL:

http://www.cecer.army.mil

http://www.dodfuelcell.com

2 Fuel Reformation

Fuel reformation, also known as fuel processing, is used to convert hydrocarbons into hydrogen (H_2) rich gas streams. The remaining components in reformed fuel streams are designed to be either carbon monoxide (CO) or carbon dioxide (CO_2), depending on the fuel cell type subsequent to the reformer. It should be noted that low temperature fuel cells may be poisoned by CO, whereas high temperature fuel cells use CO as fuel. Due to this strict fuel requirement for low temperature fuel cells, high and low temperature shift reactors are often deployed, as well as a carbon monoxide scrubber, as shown in Figure 1.

This report addresses only the primary reformation step, and not the subsequent cleanup steps required for the low temperature fuel cell systems. Therefore, it should be kept in mind that reformate mixtures preferred from the primary reformer for phosphoric acid and polymer electrolyte membrane (PEM) fuel cells consist of H_2 and CO_2, and reformate mixtures preferred for carbonate and solid oxide fuel cells consist of H_2 and CO (also known as syngas or synthesis gas).

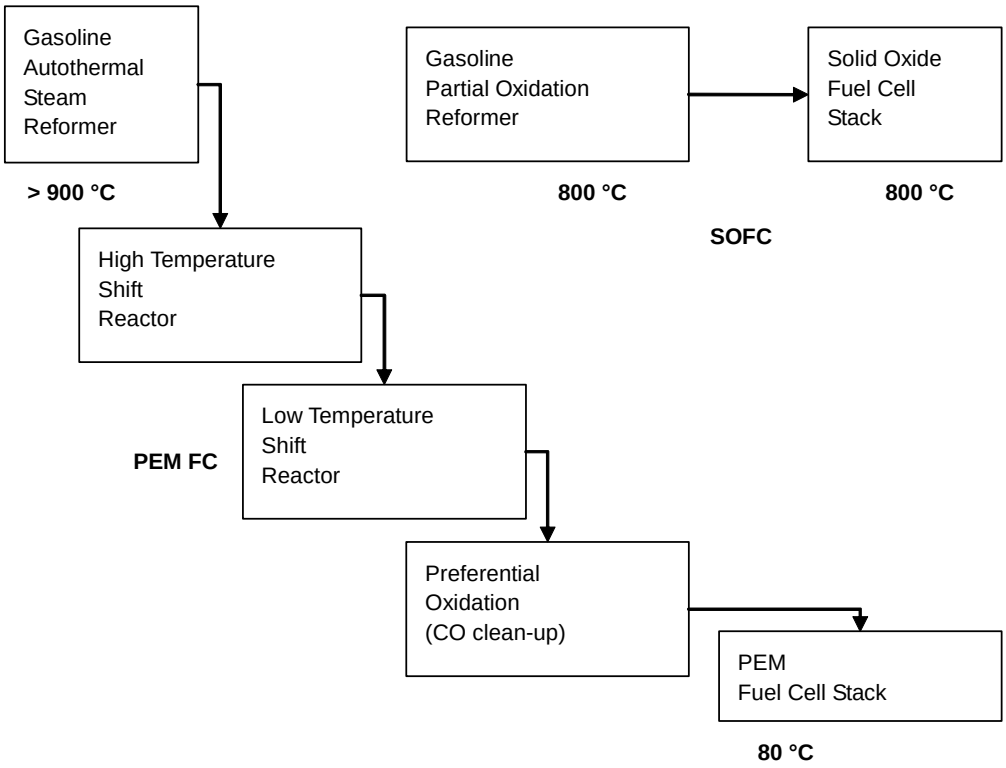

Figure 1. SOFC vs. PEM reformation (Zizelman et al. 2000).

Fuel cell system reformers typically consist of a tubular or planar vessel that houses a refractory catalyst support structure. Reformer characteristics such as compactness and chemical activity are balanced by such offsetting attributes as fouling propensity, pressure drop, and flow maldistribution. Reformer designers want the reactor to be compact to minimize footprint, but also to aid in maintaining a high level of mix and therefore chemical conversion by having a small hydraulic diameter. Pressure drop is an important consideration in the reformer since air compressors versus lower power consuming air blowers may be needed.

Fuel reformation can generally occur independently at temperatures around 1400 °C, where a catalyst is often used to lower the reaction temperature to 500-800 °C. This is not only used to reduce operating temperature, but also to reduce the size of the reformer and to achieve better control of reaction kinetics.

Reformer efficiency can be defined as the lower heating value of anode fuel(s) produced divided by the lower heating value of fuel used. Quality of reformate (primarily syngas) is another indication of reformer performance, since higher hydrogen content of the syngas is better for fuel cell applications. Reformer product or reformate composition is dependant upon the composition of reactants, length of reaction, and approach to thermodynamic equilibrium. Reformation techniques can generally be characterized by the chemical process or processes deployed (described in the following sections).

Steam Reforming

Steam reformation (SR) technology has a long history of deployment in the chemical processing industry. This technique is considered to be the most cost effective for large-scale hydrogen production because of its ability to obtain unrivaled levels of efficiency. Steam reformation is an endothermic reaction whereby steam and heat is applied to the fuel to form a hydrogen rich fuel stream. A generic equation for steam reformation of oxygenated fuel is:

$$C_nH_mO_p + (2n - p)H_2O \rightarrow nCO_2 + (2n - p + \tfrac{m}{2})H_2$$

Often this reaction is used to reform methane (CH_4), where the stoichiometric reaction product favors CO versus CO_2, which is in contrast to the reformation of oxygenated fuels. Also, the steam reformation reaction is accompanied by the water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Steam reforming effluent generally contains a mixture of at least H_2, CO, and CO_2. The steam reformation reaction is strongly endothermic and requires heat input, where generally a combustion vessel is placed adjacent to the reformation vessel. A generic formula for the combustion of oxygenated fuels is:

$$C_nH_mO_p + \left(n + m/4\right)$$

Radiation from high temperature fuel cells such as the planar solid oxide type can also be used as a heat source for the reformer, further increasing its efficiency. Figure 2 shows a general schematic of steam reformation.

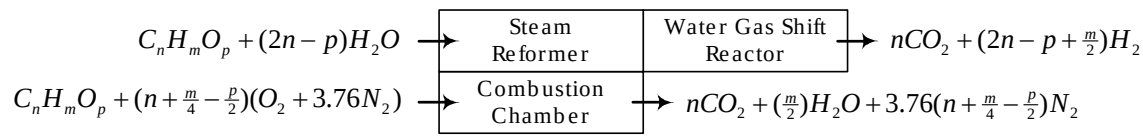

Figure 2. Steam reformation.

Steam reforming equilibrium is favorable at low pressure, high temperature, and high steam ratio. The steam reforming process is highly dependant on the reactor's internal temperature profile where a reactor will operate at peak efficiency when the temperature profile is uniform and at the desired temperature. This design constraint limits passage cross section area, where pressure drop and wall temperature profiles determine the length requirement. Reactor tubes are often bundled in parallel to abide by all of these constraints. A large disadvantage of conventional steam reformers is that heat transfer limits them so that they are bulky in size, have a slow startup time, and have less ability to react to transient operation. Furthermore, the loss of steam to a steam reformer is a certain mode of failure.

Partial Oxidation Reforming

Partial oxidation (POX) is a technique that partially combusts a fuel stream with a sub-stoichiometric amount of air. Fuel flexibility is an advantage for the POX approach, for it is easier to convert heavy hydrocarbon fuels (Pastula et al. 2001). POX is known for having short start up time, for being simple and reliable, and for having good load following characteristics. A disadvantage of the POX reaction is that it is more selective to CO than is the steam reforming reaction. A general equation for partial oxidation of oxygenated fuels is:

$$C_nH_mO_p + x(O_2 + 3.76N_2) + (2n-2x-p)H_2O \rightarrow nCO_2 + (2n-2x-p+\tfrac{m}{2})H_2 + 3.76(x)N_2$$

Figure 3 shows a general schematic of partial oxidation.

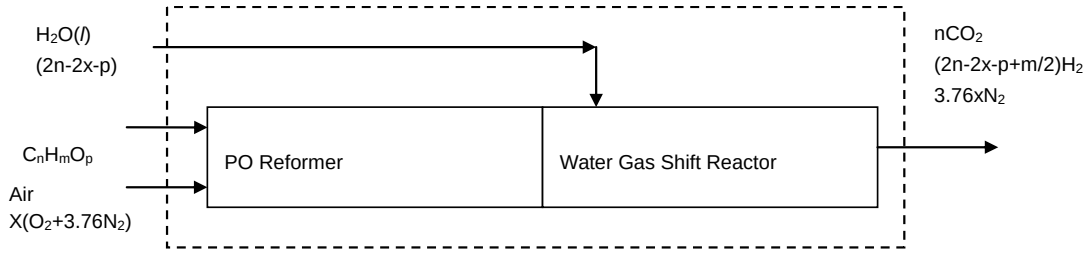

Figure 3. Partial oxidation reformation (Ahmed and Krumpelt 2001).

Although it is shown in Figure 3 as well as in the POX equation, the reaction does not require input of water. Partial oxidation reformers can use more than one reaction pathway, commonly referred to as direct or indirect pathways. In one form of the direct pathway, the entire fuel stream is fed a sub-stoichiometric amount of oxidant (air) in a single chamber, where the oxygen deficient POX reaction takes place in the presence of a catalyst. In another form of the direct POX pathway (shown in Figure 3), steam is added subsequent to the POX reaction to facilitate further reformation of the fuel stream by steam reformation. The air input of this configuration is adjusted to accommodate for the additional, endothermic steam reformation.

In the indirect POX pathway, three principle reactions generally take place: the combustion, steam reformation, and dry (CO_2) reformation. Dry or CO_2 reformation can be represented as:

$$C_nH_m + nCO_2 \rightarrow 2nCO + (\tfrac{m}{2})H_2$$

In this configuration, a different catalyst and reaction chamber is generally used for each reaction that takes place. In the first chamber a small and separate portion of the fuel stream is completely oxidized into combustion products, carbon dioxide, heat, and water. Subsequently, this combusted gas stream is fed into a chamber containing fresh fuel. With the aid of one or more catalysts (typically), the fresh fuel is reformed by the combustion products via steam and dry reformation. A direct type POX reformer may have a startup time on the order of a few minutes, whereas an indirect type POX reformer can have a startup time of an hour (Pastula et al. 2001).

Auto Thermal Reforming

Auto thermal reformers (ATR) have been developed primarily for operation with methanol and gasoline. This reformer type may be thought of as a hybrid of the partial oxidation and steam reformer types in that reactions from both reforma-

tion techniques take place. Steam is delivered to the reformation chamber with fuel and a sub-stoichiometric amount of oxidant (air):

$$C_nH_mO_p + x(O_2 + 3.76N_2) + (2n - 2x - p)H_2O \rightarrow nCO_2 + (2n - 2x - p + \tfrac{m}{2})H_2 + 3.76(x)N_2$$

The exothermic reaction of a small portion of the fuel and the oxygen provides heat for the endothermic steam reformation reaction. The ATR reaction is more selective to CO_2 than CO, which is its compatibility with the PEM fuel cell. One of the primary drivers of development for this reformation technique is that of the automotive application. Figure 4 shows a general schematic of autothermal reformation.

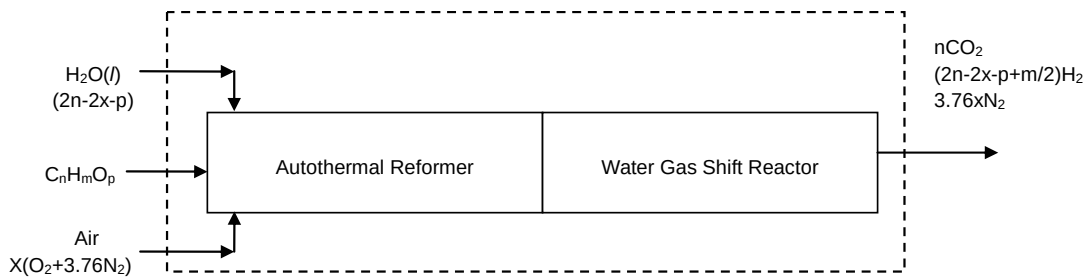

Figure 4. Autothermal reformation (Ahmed and Krumpelt 2001).

Thermal Decomposition

Thermal decomposition reformers (TDR) use heat such as with pyrolysis techniques, to break down higher hydrocarbon chains into their base components.

$$C_nH_m \rightarrow nC + (\tfrac{m}{2})H_2$$

This technique has a long history and has been used to convert relatively dirty fuels into clean fuels. However, its practicality for small-scale fuel cell systems is suspect.

Market Summary

Global Thermoelectric reports that steam reformation of natural gas has been widely used for commercial and residential applications. The wide use of steam reforming compared to partial oxidation is based in part on the fact that the par-

tial oxidation reaction produces less hydrogen per molecule than the steam reforming reaction, making it a less economical choice (Pastula et al. 2001).

The indirect technique of partial oxidation reforming has been used for remote applications since an input source of water is not necessary (Pastula et al. 2001). The direct technique of partial oxidation reforming has been shown to accommodate heavier fuels such as diesel and JP8, Minh et al. (2000). High H_2 and CO yields have been achieved (up to 70-80 percent low heating value in JP8). The syngas product generated to fuel a solid oxide fuel cell contained 11.7 percent H_2, 14.1 percent CO, 0.5 percent CO_2, 10 percent H_2O and 63.7 percent inert. Thermal cycling was also successfully achieved without significant performance degradation (Minh et al. 2000).

Researchers at the Massachusetts Institute of Technology (MIT) have used their plasmatron to reform various oils, including canola oil, into a hydrogen rich gas stream. Plasma technology used in this design is a low power, low current electrical discharge that is used to boost partial oxidation conversion of hydrocarbon fuels into hydrogen and CO (Bromberg et al. 2002).

The U.S. Department of Energy's Argonne National Laboratory has developed an autothermal reformer to generate a hydrogen rich gas primarily for automotive applications. Proprietary catalysts are used to support these reactions at about 700 °C. The reactor is reported to be 20 cm in diameter and is 50 cm long to generate enough hydrogen for a 10 kW fuel cell (Ahmed and Krumpelt 2001). Autothermal reformers are currently the technology of choice for transportation applications.

3 Application Considerations

There are several important parameters to consider in reformer selection. Consideration of input fuel properties is paramount, especially when designing for the reformation of long chain hydrocarbons. Dynamic operation is important to analyze given the slow start up or poor load following characteristics of some reformer technologies. Cost is also an important consideration. Each of these criteria is evaluated below.

Fuel Properties

The use of canola oil as feedstock for a fuel cell system was not found in the literature. Nor was the use of biodiesel as a fuel cell feedstock found in the literature. Therefore, the approach of this work was to identify reformer technologies most similar to the use of canola oil or a canola biodiesel application and to extrapolate an expected operation. Basic fuel properties were accumulated and compared. Table 1 lists the average empirical formula for various fuels.

The average empirical formula for canola oil was obtained from Idem et al. (1997), which was of the degummed and refined variety consisting mainly of unsaturated triglycerides. This canola oil stock (from CSP Foods, Saskatoon, Canada) also had a density of 928.8 kg*m^{-3}, a flash point of 63 °C, a surface tension of 29.2 dynes*cm^{-1}, and a pH of 7.0. The average empirical formula for 100 percent Soybean Methyl Ester (Biodiesel) was obtained from the National Biodiesel Board (2003a).

Table 1. Fuel properties.

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)	$C_{21}H_{28}O_2$
100% Rapeseed Biodiesel (REE)	$C_{22}H_{43}O_2$
100% Soy Biodiesel	$C_{18.8}H_{34.6}O_2$

Fuel generally needs to reach a gaseous state for efficient chemical conversion in the reformer. Liquid fuels are typically atomized and subsequently vaporized before reformation begins. This technique greatly reduces the potential for carbon deposition and enhances the reactant's level of mix. A pre-reformer can also be used to crack higher molecular chains into smaller ones, such as methane (CH_4), which is also done prior to injection into the primary reformer.

Reformer Degradation

Reformer degradation considerations such as sulfur poisoning and carbon deposition are crucial. It is generally accepted that fuel streams entering a fuel cell stack must contain very low levels of sulfur, typically below 0.1 ppm (Minh and Takahashi 1995). Canola oil has sulfur content ranging from 3 to 15 ppm (Przybyiski 2000). Biodiesel has a sulfur content of up to 0.05 percent by mass (National Biodiesel Board 2003b). Therefore, canola oil will require sulfur removal for use in most fuel cell systems.

Once desulfurized, the fuel stream is typically odorless making leakage of fuel or reformate hard to detect and creating a potential serious health, fire, and explosion hazard. Sulfur removal can be accomplished with a zinc oxide (ZnO) bed and an operating temperature of roughly 400°C and can have a significant (e.g., 0.1 atmosphere) pressure drop. Desulphurizer maintenance is necessary on a regular basis. Research is being conducted on removing sulfur from fuel while it is in liquid form, since a fuel cell system that has sulfur removed prior to reforming will see much lower sulfur concentrations than a system where sulfur is removed after reforming. In addition, reformer catalysts can be poisoned by sulfur.

Fouling is typically the deposition of unburnt hydrocarbons on the catalytic or heat transfer surfaces. Fouling is a major problem in fuel cell systems fueled by carbon-based fuels due to the lack of cleaning ability. Fouling not only blocks reactive sites in the reformer and fuel cell, but can also increase the pressure drop to the point of inoperability. Once carbon deposition has been initiated, a coke deposit will rapidly form and may completely obstruct the fuel feed line. Catalysts that inhibit carbon formation can be beneficial in the extreme case when operating on dry hydrocarbon fuels (Pastula et al. 2001). Reformate should also be stable at the stack operating temperature due to the fact that no current may be drawn at some instants in time, which makes carbon deposition more probable. In summary, managing carbon formation limits, as dictated by equilibrium thermodynamics rather than reaction kinetics, can prevent carbon formation (Hartvigsen 2001).

Disproportion of carbon monoxide can be achieved through the Boudouard reaction and is thermodynamically favored at low temperatures and high pressures. This is represented by the following formula:

$$2CO \rightarrow CO_2 + C$$

Carbon formation by hydrocarbon cracking is favored at high temperatures and low pressures, which can be represented by the following formula:

$$CH_4 \rightarrow C + 2H_2$$

Other carbon equilibrium reactions can also occur, which can be represented by the following formula:

$$CO_2 \rightarrow C + O_2$$

Carbon formation is also sensitive to feed heating rate, thus liquid fuels are often atomized using a point injector, vaporized in a heat exchanger, and then reformed before there is a chance to deposit carbon on any surface. Thermal gradients are often purposely designed into reformation reactors so that the fuel is not heated too fast (which would invite coke formation). In addition, liquid fuels are often atomized and vaporized because reaching a gaseous state is good for mixing and the accompanied high chemical conversion.

To further help prevent low temperature cracking of unsaturated, aromatic, or long chain hydrocarbons, they are commonly converted to methane in a pre-reformer before entry into the primary reformer. Pre-reformers convert less refractory molecules to methane and some syngas.

Prevention of carbon formation can also be accomplished by adjusting the steam to carbon ratio and oxygen to carbon ratio. Less coking and better reformation can be achieved when more steam is added. A steam ratio of nearly 2.0 is often required in steam reformers to ensure carbon is thermodynamically unstable under reformer conditions. Global Thermoelectric has reported the use of a moderate molar ratio of 1.8 to 2.5 mole H_2O / mole CH_4 in their steam reformer design. This safely avoids carbon formation when operating on natural gas (Pastula et al. 2001). However, adding more steam will decrease the partial pressure of hydrogen at the fuel cell anode, which decreases the fuel cell voltage generated, indicating that optimal steam content must be achieved.

Less coke formation and better reformation can also be achieved when more air or oxygen is added. In some fuel cell systems, depleted fuel is mixed with fresh fuel to provide more oxygen to suppress carbon deposition. However, as this re-

cycle process also returns additional carbon compounds (primarily CO_2) to the reformer, making the minimum steam requirements higher, and lessening performance. In addition, more oxygen in the reformer generally means that more fuel is being used for reformation process rather than for the electrochemical process in the fuel cell, thus, optimal oxygen content exists as well.

Reformer Dynamics

Coupling fuel reformers directly to fuel cell systems can require complex control design. This generally applies to larger, stationary designs, where rejected heat and spent fuel from the fuel cells is used in the reformer. This concept is generally used for relatively steady load profiles, because if the fuel cell requires additional fuel on short notice, the reformer may not be able to respond since a fair amount of its input comes from the fuel cell. Therefore, for widely varying load profiles, the fuel cell and reformer are normally separated both thermally and chemically. The drawback of this feature is that it is not as efficient as alternative designs.

The load following capability of low temperature fuel cell systems will generally be limited by the reformer system. In contrast, the load following capability of a high temperature fuel cell system could be limited by the fuel cell or the reformer, depending on the reformer type. Load following capability is generally limited by the thermal hydraulic design, rather than by reaction kinetics.

Reformer Cost

Reformate destined for consumption in high temperature fuel cells need not be completely converted to syngas. This is because reformation inside the fuel cell (internal reformation) is possible, so that up to 31 percent CH_4 can be used as fuel in some advanced SOFC designs (Forschungszentrum Jülich 2002). Internal reformation is basically a combination of the steam and water gas phase shift reactions. This technique is very desirable since it lessens reformer efficiency requirements, but it can create thermal stress problems. Therefore, cost is mostly a function of the components required for a given fuel cell system, i.e., low temperature fuel cell reformation will be rather expensive compared to high temperature fuel cell reformation.

When considering only the primary reformer and not the cleanup components necessary for low temperature fuel cell systems, reformer cost is expected to be a function of the catalyst type and loading. It is expected that steam reformers

represent the most cost effective technology since nickel is an effective steam reforming catalyst and is cheaper than platinum, ruthenium, iridium, and palladium.

Modularity and compactness of reformer designs are more amenable to the planar reformer design, whereas high-pressure containment and uniform reaction may be better suited with a tubular design. A modular and compact design would be desirable for commercialization considerations if enough units could be produced to make a significant cost impact.

4 Reformer Evaluation

The previous chapters have reviewed various fuel reformers with potential for successful application to canola oil or canola biodiesel applications. This chapter rates each reformer technology for its potential to reform canola oil or canola biodiesel into a high quality syngas. The reformer criteria used to make this selection were feasibility, applicability, availability, and cost.

- The *feasibility* criterion estimates the potential of each reformer to accomplish the stated objective. This criterion considers promising as well as discouraging attributes of the reformer types, and is not intended to be interpreted as scientific fact. There were no literature citations found detailing a method of reforming canola oil or canola biodiesel for a fuel cell system.
- The *availability* addresses the current marketplace status of the reformer type. This criterion is important because if an off-the-shelf product cannot be retrofitted for the canola oil application, it may cost many times more to obtain a reformer through custom design and manufacture. In addition, several commercial suppliers may exist for one reformer type, but perhaps only one supplier may exist for another; such limited supply could affect the cost of the reformer.
- The *applicability* criterion identifies general compatibility of the reformer with process conditions. Some reformer types have been developed for specific gas or liquid fuels while others are applicable for a wide range of fuels or fuel cells, and some have varied degrees of load following capability, etc.
- The *cost* criterion is an indication of the cost of one reformer technology relative to another. Some reformer types require an extensive amount of auxiliary equipment, or require rare and expensive noble metal catalysts that may require sophisticated deposition techniques. The assessment of costs for this report did not address the cleanup components for low temperature fuel cell systems.

Each reformer type was assigned a qualitative performance rating for each of the selected criteria. These qualitative ratings were Low Desirability (LD), Medium Desirability (MD), or High Desirability (HD), where HD is the best rating. Table 2 lists the qualitative ratings assigned to each reformer for each criterion, for canola oil and canola biodiesel applications.

Table 2. Reformer evaluation.

Parameter \ Type	Steam Reforming	Partial Oxidation Reforming	Autothermal Reforming	Thermal Decomposition Reforming
Feasibility	HD*	HD	MD	LD
Applicability	MD	HD	HD (PEM) MD(SO/MC)	MD
Availability	HD	HD	LD	LD
Cost	MD	HD	LD	No Data
*HD = High Desirability (best) / MD = Medium Desirability / LD = Low Desirability]				

Reformer technologies need to integrate well into the overall fuel cell power generation system. Frequently, a particular reformer technology will integrate well with a particular type of fuel cell technology. For example: steam reforming is widely used with proton exchange membrane, solid oxide and molten carbonate fuel cells; partial oxidation reforming is typically used with solid oxide fuel cells, but could also be used with molten carbonate fuel cells; and autothermal reforming is typically used with proton exchange membranes in transportation applications.

- The steam (SR) reformer was assigned a “High Desirability” score for the Feasibility criterion because research on reforming bio-oils for hydrogen production was found to be in progress (Garcia et al. 2000). The partial oxidation (POX) reformer was assigned a “High Desirability” score for the Feasibility criterion since Bromberg et al. (2002) reported successful demonstration on reformation of canola oil. The autothermal (ATR) reformer was given a “Medium Desirability” score for the Feasibility criterion since Ahmed and Krumpelt (2001) successfully demonstrated operation on gasoline. The thermal decomposition (TDR) reformer was given a “Low Desirability” score for the Feasibility criterion.
- The steam (SR) reformer was reported by Pastula et al. (2001) to be less suited for operation on heavier fuels and therefore was assigned a “Medium Desirability” score for the Applicability rating. The partial oxidation reformer has been designed for small-scale fuel cell systems, operating on diesel and JP8 (Minh et al. 2000), and is currently being designed for canola oil operation (Bromberg et al. 2002). Because of this, it was assigned a “High Desirability” Applicability rating. The autothermal reformer generally has a low CO yield and high CO_2 yield, and therefore was given a “High Desirability” rating for proton exchange membrane fuel cell applications and a “Medium Desirability” rating for solid oxide and molten carbonate fuel cell applications, indicating the inter-relationship of reformers and fuel cells. The thermal decomposition reformer is generally used for large-scale operation and therefore was given a “Medium Desirability” rating for the Applicability.

- The steam reformer was assigned a “High Desirability” score for the Availability criterion because of its established market position. The partial oxidation reformer was also assigned a given a “High Desirability” score for the Availability criterion because of its broad market acceptance. The autothermal reformer and thermal decomposition reformer were both assigned a “Low Desirability” score for Availability.
- The steam reformer was assigned a “Medium Desirability” score for the Cost criterion given its more complex design. The partial oxidation reformer was assigned a given a “High Desirability” score for the Cost criterion since it generally is a compact and simple design. The autothermal reformer was assigned a given a “Low Desirability” score for the Cost criterion. No Data was available from which to assign a Cost criterion rating for the thermal decomposition reformer technology.

5 Telephone Interviews – Industry and Academic

List of Organizations Contacted

Researchers contacted 26 companies, individuals, universities, or institutions involved in reformer technology manufacturing, development, or research (Table 3). Interviews explored the subjects' experience, and activities in reformer technology applications for canola (rapeseed) oil for use in fuel cell systems.

Table 3. Contact list.

Name	Address	Phone No.
Alchemix Corp.	8 Sundial Circle PO Box 1150 Carefree, AZ 85377	480-488-3388
Boeing	PO Box 2515 Seal Beach, CA 90740	714-372-4734 714-896-4770
Catalytica	430 Ferguson Drive Bldg 3 Mtn. View, CA 94043	650-940-6253
Chevron Texaco	Technology Ventures 3901 Briarpark Rd Houston, TX 77042	713-954-6257
Genesis Fueltech	4922 East Union Ave Spokane, WA 99203	509-534-5787
H2Gen	4740 Eisenhower Ave Alexandria, VA 22304	703-212-7444
Harvest Energy Technology	9253 Glenoaks Blvd. Sun Valley, CA 91352	818-767-3157
Hydrogen Source	60 Bidwell Road South Windsor, CT 06074	860-987-5000
HyRadix	175 West Oakton St. Des Plaines, IL 60018	847-391-1200
IdaTech	63160 Britta Street Bend, OR 97701	541-383-3390 434-522-5165
InnovaTek, Inc.	350 Hill St., Ste.104 Richland, WA 9932	509-375-1093
McDermott Tech.	Rt. 726, Mt. Athos Rd. PO Box 11435 Lynchburg, VA 24506	
Membrane Reactor	Technologies Ltd("MRT") 170 E. 3250 East Mall Vancouver, BC Canada V6T 1W5	604-822-4343

Name	Address	Phone No.
Mesufuel, Inc.	1001 Menaul Blvd NE Albuquerque, NM 87107	505-314-8144
NuElement	2323 N.30th St.Ste100 Tacoma, WA 98403	253-573-1780
Nuvera Fuel Cells	20 Acorn Park Cambridge, MA 02140	617-245-7500 06-6202-2221
Osaka Gas Co. Ltd	4-1-2 Hiranomachi Chuo-ku, Osaka 541-0046, Japan	
REB Rsrch & Cons.	25451 Gardner Plaza Oak Park, MI 48237	248-545-0155
UOP LLC	25 East Algonquin Rd. Des Plaines, IL 60017	847-391-2000
Wah Chang	PO Box 460 Albany, OR 97321	541-926-4211 (44) (0) 23 92 664911
Wellman CJB	Airport Service Road Portsmith, Hampshire PO3 5PG, England	
ZTEK Corp.	300 West Cummings Park Woburn, MA 01801	781-933-8339
Hydrogen Burner	19300 So. Susanna Road Comptom, CA 90221	310-900-0400
Umicore Protonics	US Fuel Cells Dev. Auburn Hills, MI 48326	248-340-1040 ext.269
U.S.D.A.	Oil Chemical Research 1815 N. University St Peoria, IL 61604-3902	309-685-4011
University of Regina	Regina Saskatawan Canada	306-585-4470

Findings of Interviews

The interviews with the above organizations revealed that:

- The manufacturing companies are working on products that have commercial value in the *immediate* future.
- The primary focus is on *fuels with short carbon chains*, i.e., gasoline, methanol, natural gas, etc., that are easy to reform to hydrogen.
- Established infrastructure is an important consideration to the types of fuels being considered, e.g., transportation and storage facilities for gasoline, methanol, natural gas, etc.
- All manufacturers indicated that they needed to make a reformer technology product that has the opportunity for an immediate return on their investments.
- All work being done with canola oil is being done on the bench scale size.
- The research organizations feel that they have the knowledge base to conduct canola oil reforming at commercial scale.

6 Conclusion

Based on the findings of the literature review performed for this report, the catalytic partial oxidation (POX) reformer appears to be the most applicable technology for canola (rapeseed) oil or canola (rapeseed) biodiesel reforming. Feasibility was determined to be a critical evaluation issue and it was concluded that the catalytic partial oxidation reformer has the most related experience and therefore the most potential to meet the expectations for canola (rapeseed) reformer / fuel cell application.

References

Ahmed, S., M. Krumpelt, "Hydrogen from Hydrocarbon Fuels for Fuel Cells," *International Journal of Hydrogen Energy* (2001), vol 26, pp 291-301.

Bromberg, L., D. Cohn, J. Heywood, A., and Rabinovich, *Onboard Plasmatron Generation of Hydrogen Rich Gas for Diesel Engine Exhaust Aftertreatment and Other Applications* (Massachusetts Institute of Technology, Cambridge, MA, 2002).

Forschungszentrum, Jülich, "New Milestone in Fuel Cell Research," *Institut fur Werkstoffe und Verfahren der Energietechnik* (Germany, 2002).

Garcia, L., R. French, S. Czernik, and E. Chomet, "Catalytic Steam Reforming of Bio-Oils for the Production of Hydrogen: Effects of Catalyst Composition," *Applied Catalysis* (2000), pp 201, 225-239.

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.

Hartvigsen, J. Personal Communication (2001).

Idem, R., Katikanei, S., Bakhshi, N., "Catalytic Conversion of Canola Oil to Fuels and Chemicals: Roles of Catalyst Acidity, Basicity and Shape Selectivity on Product Distribution," *Fuel Processing Technology* (1997), vol 51, pp 101-125.

Minh, N., A. Anumakonda, R. Doshi, J. Guan, S. Huss, G. Lear, K. Montgomery, E. Ong, and J. Yamanis. "Demonstration of Logistic Fueled Solid Oxide Fuel Cell Systems," *Fuel Cell Seminar 2000* (Portland, OR, 2000).

National Biodiesel Board, *Chemical Weight and Formula* (2003a), available through URL: http://www.biodiesel.org/pdf_files/Weight&Formula.PDF

National Biodiesel Board, *Specification for Biodiesel (B100)* (2003b), available through URL: http://www.biodiesel.org/pdf_files/BDSpec.PDF

Pastula, M., J. Devitt, R. Boersma, and D. Ghosh, "Fuel Processing Development at Global Thermoelectric Inc.," *Solid Oxide Fuel Cells VII*, H. Yokokawa, and S.C. Singhal, eds. (The Electrochemical Society, Inc, NJ, 2001).

Peterson, C., and T. Hustrulid, "Carbon Cycle for Rapeseed Oil Biodiesel Fuels," *Biomass and Bioenergy* (1998), vol 14, pp 91-101.

Przybyiski, R., *Canola Oil: Physical and Chemical Properties* (2000), available through URL: http://www.canola-council.org/

Zizelman, J., J. Botti, J. Tachtler, and W. Strobl, *Solid-Oxide Fuel Cell Auxiliary Power Unit: A Paradigm Shift in Electric Supply for Transportation* (Delphi Automotive Systems and The BMW Group, 2000).

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)
08-2004

2. REPORT TYPE
Final

3. DATES COVERED (From - To)

o4. TITLE AND SUBTITLE
Canola Oil Fuel Cell Demonstration:
Volume I – Literature Review of Current Reformer Technologies

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
John W. Adams, Craig Cassarino, Joel Lindstrom, Lee Spangler, Michael J. Binder, and Franklin H. Holcomb

5d. PROJECT NUMBER

5e. TASK NUMBER
CFE-B033

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Engineer Research and Development Center (ERDC)
Construction Engineering Research Laboratory (CERL)
PO Box 9005
Champaign, IL 61826-9005

8. PERFORMING ORGANIZATION REPORT NUMBER
ERDC/CERL SR-04-24

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Headquarters, U.S. Army Corps of Engineers (HQUSACE)
441 G St., NW
Washington, DC 20314-1000

10. SPONSOR/MONITOR'S ACRONYM(S)
ODDR&E

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
Copies are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

14. ABSTRACT

This literature review identifies fuel reformer technologies that may be pertinent for reforming canola / rapeseed oil and other agricultural biomass including biodiesel. A description of candidate reformers is presented, noting characteristics generally inherent to each configuration. A comparison of the identified reformers is accomplished by rating each reformer against a set of specific criteria, which is essential for attaining operating characteristics desired for canola / rapeseed oil given applications.

15. SUBJECT TERMS
fuel processing
energy efficient
fuel alternatives
fuel cells
biomass

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Michael J. Binder
Unclassified	Unclassified	Unclassified	SAR	32	19b. TELEPHONE NUMBER (include area code) (217) 373-7214

NSN 7540-01-280-5500

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18