CHEMINFO

Study of Technologies to Convert Biodiesel to Hydrocarbon Fuels

Final Report

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Natural Resources Canada
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Disclaimer

The overall purpose of this report is to provide background information to Natural Resources Canada regarding the advantages and disadvantages of technologies that convert fatty acid methyl ester (FAME) biodiesel to hydrocarbons. This report should not be used for business or any other purpose.

The report contains summaries of information from literature sources for the relevant technologies. It also contains summaries of opinions provided by biodiesel and other industry representatives.

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Acronyms and Abbreviations

Scientific Acronyms	
atm	atmosphere (a unit of pressure)
B100	biodiesel 100%
B5, B20	fuel with 5 and 20% biodiesel
bar	bar (a unit of pressure)
C	degrees Celsius (a unit of temperature)
CP	cloud point
FAME	fatty acid methyl ester (biodiesel)
g	gram(s)
GHG	greenhouse gas
h	hours
HC	hydrocarbon
HDRD	hydrogenation derived renewable diesel
HVO	hydrotreated vegetable oil
K	Kelvin (a unit of temperature)
kg	kilogram(s)
kPa	kilopascal (a unit of pressure)
MPa	megapascal (a unit of pressure)
PHSME	partially hydrogenated soybean methyl ester
PP	Pour point
s	second
Chemical Elements and Compounds	
Al_2O_3	aluminum oxide (alumina)
Ar	argon gas
$BaSO_4$	Barium sulfate
C	carbon
C-17	A carbon chain with 17 carbon atoms. The same nomenclature applies to all symbols having the form: C-##
CeO_2	cerium dioxide (ceria)
CH_3	methyl functional group
CH_4	methane
Co	cobalt
CO	carbon monoxide
CO_2	carbon dioxide
CO_2e, CO_2eq	carbon dioxide equivalent
Cu	copper
H_2 (g)	hydrogen gas
He	helium gas
ImS3-12	3-(1-dodecyl-3-imidazolio) propanesulfonate
Mo	molybdenum
N_2	nitrogen gas
Ni	nickel
O_2	oxygen gas
Pd	palladium
Pt	platinum
SO_x	sulfur oxides (so, so_2)

TiO_2	titanium dioxide (titania)
USY	ultra soluble y-type zeolite
Yb	ytterbium
ZrO_2	zirconium dioxide (zirconia)
ZSM-5	zeolite socony mobil – 5 (an aluminosilicate zeolite)
Organizations	
ADM	Archer Daniels Midland
ASTM	American Society for Testing and Materials
CGSB	Canadian General Standards Board
CRFA	Canadian Renewable Fuels Association

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1. Executive Summary

1.1 Introduction

Hydrogenation derived renewable diesel (HDRD) is a drop-in renewable fuel that possesses favourable blending and typically cold flow properties, when compared to biodiesel. For these reasons, according to a survey of refiners conducted by EcoRessources for Natural Resources Canada, its use by petroleum refiners is growing despite HDRD's higher cost compared to fatty acid methyl ester (FAME) biodiesel.[1] However, biodiesel is the leading renewable alternative to diesel produced and used globally.

The purpose of this report is to identify and assess FAME to hydrocarbon (HC) conversion technologies that are designed to modify FAME and produce a renewable hydrocarbon (HC) fuel similar to HDRD. In order to provide an assessment of the identified technologies, biodiesel producers in Canada, Europe, and the United States were contacted for their input. Industry associations were also contacted for input on the identified technologies. The report comprises two main sections: the first being a review of the technologies identified in the literature; and the second being a summary of the perspectives obtained from the interviews.

1.2 FAME to Hydrocarbon Conversion Technologies

The technologies identified fell into the following categories: partial hydrogenation, deoxygenation, hydrodeoxygenation, decarboxylation, and chemical reaction. All FAME to HC converting technologies identified in the study are currently at an early lab-scale stage of development. No pilot plants or operating plants using the technologies were identified. The focus of studies in the available literature, for the most part, was on reaction mechanisms and kinetics with some brief mention of fuel properties and cold-flow characteristics. The absence of any comparison or analysis of cold flow properties raises uncertainties about the potential of these technologies to address one of the main concerns with biodiesel facing some producers. Similarly, most studies made no remark about the properties of the new fuels produced. The absence of proven performance data in diesel engines or certification from national fuel standard boards is another impediment to the comparison of these new technologies. Moreover, only one study made any mention of costs associated with these new processes. The absence of economic information for these new technologies makes it difficult to evaluate their commercial potential or economic feasibility. The table below summarizes the technologies, incorporating the results of literature findings and input from industry representatives.

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[1] EcoRessources Consultants (2012) *An Update on Renewable Diesel Infrastructure in Canada*, Available at: http://oee.nrcan.gc.ca/sites/oee.nrcan.gc.ca/files/files/pdf/transportation/alternative-fuels/resources/pdf/Infrastructure_update_final_report_English.pdf

Table 1: Summary of FAME to Hydrocarbon Conversion Technologies

Description	Status	Costs	Advantages	Disadvantages
Partial Hydrogenation				
Wide variety of catalysts. Produces monounsaturated methyl esters.	University research / laboratory scale	Only the study by Moser (2007) addressed the costs of implementation. It was estimated to result in a change in production costs from ¢$53/L to ¢57/L, or 4 ¢/L (2007 period).	Similar to the well-established hydrogenation of edible oils. Conditions are milder than other technologies	H_2 (g) supply is required. High temperature and pressure equipment is needed along with a potentially expensive catalyst. Will address oxidative stability but will not improve the cloud point directly.
Deoxygenation				
Pd, Pt, catalysts formed linear alkanes while zeolite catalysts formed a mix of olefins	University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Produces mostly linear hydrocarbons. The studies by the University of Oklahoma used relatively inexpensive catalysts	These technologies had low yields and this was identified as a major concern for the economic viability of FAME producers.
Hydrodeoxygenation				
Ni, Ni-Cu, Ni-Mo catalysts showed good yields for linear alkanes	University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Very high conversion of starting FAME (~90%)	None of the studies reviewed mentioned an improvement in cold flow properties. Sensitive conditions and high temperatures led to rapid hydrocracking (formation of methane and short hydrocarbons)
Decarboxylation				
Pd catalyst. With one study on supercritical hexane solvent. Produces mostly linear alkanes.	University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Very high conversion (~90%), mostly linear alkane products	Very high pressures. High temperatures. Expensive Pd catalyst.
Chemical Reaction				
Addition of Formic acid, hydrogen peroxide to create epoxide functional groups on FAME.	University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Simple chemical reaction, no catalyst. Improves oxidative stability and maintains cold-flow properties.	Raw material costs unknown, fuel properties unknown

Source: Cheminfo Services, (2013)

1.3 Industry Input

Input on FAME to HC conversion technologies was sought from different participants in the biodiesel industry. These included:

- Canadian biodiesel producers (BIOX, Methes Energy, Rothsay Biodiesel);
- U.S. biodiesel producer (ADM Biodiesel);
- European biodiesel producers (Biopetrol Industries (Prolea), Verbio);
- Equipment/technology vendors (SRS International, BDR Technologies, Lurgi); and
- Canadian Renewable Fuels Association (CRFA).

Additional similar industry representatives and academic researchers were contacted for input. Some indicated that they would respond but no additional input was obtained in time for preparation of this report.

When presented with literature summaries of the conversion technologies, none of the biodiesel producers were aware of the identified technologies. Some had examined technologies to convert oil/triglycerides into hydrocarbons, but had not examined FAME to HC conversion options. Only one technology vendor was aware of the FAME to HC conversion technologies. The evaluation of the identified FAME to HC conversion technologies by industry representatives was generally negative. The uncertainties regarding costs, reliability, and fuel properties were major concerns.

1.4 Conclusions

FAME to HC conversion technologies present additional processing steps to FAME and consequently the following issues and uncertainties arise:

- additional capital and operating costs would be involved;
- there would likely to be some yield loss for the desirable fuel components;
- an alternated yield slate of products presents product separation challenges, and market challenges for selling (or using) non-fuel products;
- properties of HC fuel are uncertain, e.g., may not meet ASTM or CGSB standards;
- use of new materials (e.g., hydrogen) and catalysts presents infrastructure challenges at existing sites / operations;
- unproven cold flow properties of the HC product;
- increased energy use and greenhouse gas (GHG) emissions and associated sustainability concerns;

- there are alternatives to overcoming FAME biodiesel properties leading to market issues that are likely to be more cost-effective than FAME to HC conversion; and
- state of the technology advancement is lab-scale and full conclusions would require more research and development.

A major issue for existing FAME biodiesel producers for FAME to HC conversion is the anticipated increase in production costs. These firms are already challenged with thin margins. The narrow profit margins that FAME biodiesel producers operate with makes any additional process challenging unless the product can provide significant added value, or the process is shown to be inexpensive. There was no indication from the industry representatives contacted that these FAME to HC technologies could be incorporated to an existing facility without a total overhaul of existing plants, anticipated to be at high costs.

Moreover, the prevailing opinion of respondents that biodiesel (FAME) can strategically be incorporated in the fuel market (e.g., higher use in summer than winter) is another reason that biodiesel producers are not actively considering modifying their process.

2. Introduction

2.1 Background

This study was conducted in the context of lower than expected demand for Canadian FAME biodiesel and a growing preference[2] for HDRD in the fuels marketplace. HDRD has certain advantages in the marketplace over biodiesel such as:

- Available at much lower cloud point, making HDRD more flexible than FAME biodiesel for use in colder climates; and
- Blends from 5% to 100% can be used without any modification to existing storage or transportation infrastructure.[3,4]

Conventional biodiesel is a FAME, which has slightly different properties than petroleum-based diesel, and some differences with HDRD. Creating hydrocarbon fuels from FAME biodiesel requires extra processing steps to remove the ester group from the biodiesel using de-oxygenation and hydrogenation. A number of technologies to achieve this have been identified in scientific literature and are investigated in this report.

2.1.1 FAME Biodiesel

Conventional biodiesel (FAME) is a renewable fuel made from plant and animal oils/fats. The reaction mechanism used to transform these oils/fats into FAME is called transesterification. It essentially separates the triglyceride molecule into long fatty acid chains, and then adds a methyl group (CH_3) to the terminal oxygen atom of the acid. Although it is chemically different from petroleum diesel, it possesses the necessary properties to be used in various proportions in a conventional diesel engine with no modifications.

Biodiesel is produced in a relatively simple and well-established process and it possesses some advantageous properties such as lower SO_x emissions, improved engine lubricity, and improved fuel combustion[5]. However, some issues with biodiesel include its high cloud point and its limited shelf life. Long-term storage and storage with temperature

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[2] EcoRessources Consultants (2012) *An Update on Renewable Diesel Infrastructure in Canada*, Available at: http://oee.nrcan.gc.ca/sites/oee.nrcan.gc.ca/files/files/pdf/transportation/alternative-fuels/resources/pdf/Infrastructure_update_final_report_English.pdf

[3] U.S. Department of Energy, *Alternative Fuels Data Center*. Available at: http://www.afdc.energy.gov/fuels/emerging_green.html.

[4] Neste Oil, *Neste Green 100 diesel – a premium-quality fuel for today's engines.* Available at: http://www.nesteoil.com/default.asp?path=1,41,11991,12243,12335

[5] Personal interview.

variations can lead to biodiesel oxidation, causing the fuel to degrade[6]. These properties require storage and blending procedures (oxidation stability additive) that are adapted mainly to maintain a higher temperature for the biodiesel component of the blend in colder months. This has led to reluctance by some diesel blenders and petroleum refiners to adopt biodiesel. Despite this concern, studies have demonstrated that FAME meeting the CGSB B100 standard CAN/CGSB-3.520 B1-B5 (with an 8-hour oxidative stability limit) is suitable for use in Canada in terms of oxidative stability and cold flow properties.[7] A number of techniques and additives to improve the cold flow properties and oxidative stability of biodiesel are available to meet this standard[8].

2.1.2 Hydrogenation Derived Renewable Diesel (HDRD)

HDRD is also called hydrotreated vegetable oil (HVO), or simply renewable diesel. Its production process involves removing glycerine, oxygen groups, and unsaturation sites from vegetable oil to yield a saturated hydrocarbon (alkane), using very high temperatures and pressures as well as potentially expensive catalysts. This process is somewhat analogous to hydrotreatment (requiring hydrogen) of petroleum fractions to produce gasoline components.

Depending on the type of oil, the alkane molecules are generally between 15 and 19 carbon atoms long and are indistinguishable from the alkanes in petroleum diesel. Due to its chemical similarity to petroleum diesel, the two fuels are fully fungible[9]. It can also be produced with much lower cloud points than FAME. Neste Oil is the largest producer of HDRD in the world, with plants in Finland, Singapore, and the Netherlands. Neste offers HDRD with cold property grades from -5°C to -34°C [10]. The main disadvantages of HDRD are that it is more expensive than FAME, and that its GHG emissions reductions are generally not as good as those from FAME.

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[6] Natural Resources Canada. (2010). *Report on Technical Feasibility of Integrating an Annual Average 2% Renewable Diesel in the Canadian Distillate Pool by 2011*.Pg. 13. Available at : http://oee.nrcan.gc.ca/sites/oee.nrcan.gc.ca/files/pdf/transportation/alternative-fuels/programs/nrddi/report-2010/pdf/nrddi-final-report-e.pdf

[7] National Renewable Diesel Demonstration Initiative. (2010). *Demonstration of the Use if Biodiesel in Electric Generators in Remote Canadian Locations and Long term Storage in Gensets*. Available at: http://www.hydro.mb.ca/environment/energy_sources/genset_lts_study_final_report.pdf

[8] Climate Change Central (2009) *Alberta Renewable Diesel Demonstration* http://www.renewablediesel.ca/pdf/ARDD_Report_English.pdf

[9] U.S. Department of Energy, *Alternative Fuels Data Center*. Available at: http://www.afdc.energy.gov/fuels/emerging_green.html. Accessed on Feb.26 2013

[10] NExBTL renewable diesel production information guide. Available: http://www.nesteoil.com/binary.asp?GUID=542AF06E-FD19-4BC3-9159-28F3B390BA2E

2.1.3 Upgraded Biodiesel

Although there are no commercial products classified as upgraded biodiesel (FAME), a number of research groups have investigated technologies to upgrade FAME molecules into an improved fuel. Some research is focused on trying to develop a reaction similar to that used for HDRD but with milder process conditions. Other research is focused on modifying and improving the fuel properties by changing the FAME molecules. The impetus behind such research is to find a more cost effective process than HDRD to produce a renewable diesel fuel. A significant portion of the research in this field is also dedicated to upgrading oils and fats directly but these technologies were not part of the scope of this study.

2.2 Purpose of this Report

The purpose of this report is to provide a desktop assessment of technologies that can be applied to convert FAME biodiesel to hydrocarbons for use in transportation fuel markets. Since the identified technologies are currently at a lab scale, information to support the assessment involved a review of the published literature and input from biodiesel industry representatives.

2.3 Research Methodology

The methodology employed in the project involved two main elements, specifically:

(i) an internet search on new and existing technologies for the conversion of biodiesel to hydrocarbon fuels; and
(ii) conducting a survey of major biodiesel producers and other experts in Canada, the US, and the European Union in order to determine their perspective on these new technologies, and the likelihood/feasibility of their adoption.

A literature search of journal repositories was conducted using the following resources: Science Direct, Wiley Interscience, Springerlink, ACS Publications, IngentaConnect, and Google Scholar. A total of fifty (50) papers were obtained, out of which eighteen (18) were relevant. The relevant journal articles were reviewed and summarized in this report.

Telephone interviews of biodiesel industry representatives and other experts were conducted, from which nine phone interviews were completed. A questionnaire was prepared along with a summary table of the FAME conversion technologies. The questionnaire and summary table were used in the interviews and forwarded to the interviewees and other experts for input. Table 2 lists the organizations that were contacted.

Table 2: Organizations From Which Input Was Sought

Organization Contacted
Canadian Biodiesel Producers
BIOX
Methes Energy
Rothsay Biodiesel
Canadian Renewable Fuels Association (CRFA)
Consolidated Biofuels
U.S. Biodiesel Producers
ADM (USA)
REG, Renewable Energy Group
Imperium Renewables (Imperium Grays Harbor)
Green Earth Fuels LLC
Louis Dreyfuss Commodities
Renewable Biofuels Inc.
European Biodiesel Producers
Biopetrol Industries (Prolea)
Verbio
Biopetrol Industries Switzerland
Equipment/Technology Vendors
Lurgi (Germany)
SRS International (CA, USA)
BDR Technologies, Ottawa
Crown Ironworks (USA)
Researchers/Academics
University of Oklahoma,
United States Department of Agriculture

2.4 Structure of the Report

The report has been structured into two main sections. The first section consists of the summary of literature articles concerning FAME upgrading technologies. This section provides short summaries of the reviewed articles followed by a summary table detailing the advantages, disadvantages, costs, and development status of each technology grouping. The following section summarizes the telephone interviews conducted over the course of the project. The information gathered in these two phases of the project is synthesised in the conclusions and recommendations section. This section is intended to provide a representative perspective from industry on the issues identified in the terms of reference for the project.

3. FAME to Hydrocarbon Conversion Technologies

3.1 Introduction

This section reviews the relevant literature articles for FAME to hydrocarbon conversion technologies. The following table is a summary of the key points for each study including the catalyst, operating conditions, and products. This is followed with more detailed or focused summaries of each study with some perspectives relevant to the purpose of this study. Following each section is an assessment of each technology grouping based on the literature findings as well as industry input.

3.2 Summary of Key Features of Technologies

The following table summarizes the information on the identified technologies.

Table 3: Summary of Key Features of Each Technology Studied

Non-selective Deoxygenation					
Catalyst	**Feed**	**Operating Conditions**	**Products**	**Characteristics**	**Affiliated Researcher/Group**
ZSM-5 Alumino-silicate zeolite	Methyl octanoate	T= 673-773 K P= atmospheric	Wide distribution	High temperatures yielded mostly light hydrocarbon gases. Low temperatures yielded octanoic acid and condensation products.	Danuthai, T. 2009 U of Oklahoma
CsNaX zeolites	10% Methyl octanoate in methanol	T= 723 K P= atmospheric O_2/He atmosphere	a-heptene (13.7%), a-hexene (9.8%), octenes (2.7%), octanal (3.1%), pentadecanone (4.6%)	Mixture of unsaturated hydrocarbons and heavier condensation products. Conversion of ester is only 40%. Hydrogen not required.	Danuthai, T., Sooknoi T. 2008, 2011 U of Oklahoma
Pt/Al_2O_3, Pt/TiO_2	Methyl Stearate	1 wt% Pt/Al_2O_3 catalyst in flow of H_2; P=690 kPa, T = 598 K Time= 5 h	Heptadecane (>90%), 1-heptadecene, octadecane, heavy products, CO_2, CO and CH_4	Conversion of 60% on Pt. After 5 h, the conversion rate drops to 40% due to condensation reaction by-products. The presence of hydrogen greatly increases the selectivity and yield of linear alkanes. May requires downstream separation.	Do, P.T., 2009 Lobban, L. University of Oklahoma
Pd/C (alkaline)	Ethyl Stearate	T=593 K P=750 kPa N_2 Time = 6 h	n-heptadecane (46%), C-17 aromatics (36%), unsaturated C-17 (6%)	Conversion ~60%, after 6 hours ~ 40% Concentrated feeds of ethyl stearate over alkaline an Pd/C catalyst gave good n-heptadecane selectivity. Aromatic compound formation increased catalyst deactivation. Hydrogen helped suppress the deactivation due to coke formation.	Maki-Arvela, 2007 Abo Akademi University, Finland

<table>
<tr><th colspan="6">Non-selective Deoxygenation</th></tr>
<tr><th>Catalyst</th><th>Feed</th><th>Operating Conditions</th><th>Products</th><th>Characteristics</th><th>Affiliated Researcher/Group</th></tr>
<tr><td>Pd/C</td><td>Methyl oleate</td><td>T=300°C
P=1500 kPa
Time= 6 h</td><td>n-heptadecane (46%)
other C17 (50%)</td><td>Conversion=84%, possibly feasible for industrial scale-up</td><td>Snare, M. 2008, Abo Akademi University, Finland</td></tr>
<tr><th colspan="6">Hydrodeoxygenation</th></tr>
<tr><th>Catalyst</th><th>Feed</th><th>Operating Conditions</th><th>Products</th><th>Characteristics</th><th>Affiliated Researcher/Group</th></tr>
<tr><td>Ni/ZrO_2-CeO_2</td><td>Biodiesel FAME, rapeseed oil</td><td>T=553-603 K
P=500-2,000 kPa</td><td>Heptadecane, C15, C16, C6-C14 alkanes</td><td>Conversion ~100% over 250°C, ~80% alkane yield. At temperatures greater than 350°C, alkane yield drops as hydrocraking becomes dominant. No mention of cold flow properties.</td><td>Yakovlev, V.A. 2009</td></tr>
<tr><td>Ni-Cu/ZrO_2-CeO_2</td><td>Methyl oleate</td><td>T=290-320°C
P=1,000 kPa (H_2/Ar)</td><td>n-heptadecane (70-75% selectivity)</td><td>~90% conversion above 300°C. C12-C17 linear alkanes, water, and methane were produced. Increased temperatures caused an increase in conversion but also a rapid increase in selectivity towards the formation of methane. No mention of cold flow properties.</td><td>Dundich, V.O. 2010</td></tr>
<tr><td>NiMo/$Al_2O_{3,}$
CoMo/Al_2O_3</td><td>Methyl heptanoate</td><td>T=250°C
P=7,500 kPa H_2 or N_2</td><td>Saturated and unsaturated C_6 and C_7</td><td>>90% conversion. No mention of cold flow properties. Rapid catalyst deactivation from sulfur removal. Addition of a sulfur compound required.</td><td>Ryymin, E.M., Senol, O.I.</td></tr>
<tr><th colspan="6">Pyrolysis</th></tr>
<tr><th>Catalyst</th><th>Feed</th><th>Operating Conditions</th><th>Products</th><th>Characteristics</th><th>Affiliated Researcher/Group</th></tr>
<tr><td>N/A</td><td>Rapeseed oil FAME</td><td>T=550-850°C
P=atmospheric
Time= >1 second</td><td>Light C_1-C_{10} hydrocarbons with low yields of diesel range products, CO, CO_2, H_2 in the gas phase</td><td>Varitey of short chain and aromatic compounds. Only 5% yield of C3-C8 compounds and lower yields for heavier, diesel-range compounds.</td><td>Billaud F. 1995</td></tr>
</table>

Decarboxylation					
Catalyst	**Feed**	**Operating Conditions**	**Products**	**Characteristics**	**Affiliated Researcher/Group**
$Pd/BaSO_4$, supercritical hexane solvent	Methyl stearate	T=270^{o}C P=1,600 kPa (H_2) Time=3.5 h	96.6% heptadecane selectivity	Conversion ~ 99%. No mention of cold flow properties. No reported catalyst recycle issues although periodic rinsing is required)	Han, J. 2010
Pd/C (5%)	Methyl stearate	T=270–360 ^{o}C P= 1,700–4,000 kPa He-Ar, He-H_2 (5%)	n-heptadecane, other C17 hydrocarbons	|90% conversion after 3 hours. Mostly a study of reaction kinetics with little or no discussion on yield or product properties.	Snare, M. 2007
Partial Hydrogenation					
Catalyst	**Feed**	**Operating Conditions**	**Products**	**Characteristics**	**Affiliated Researcher/Group**
Pd-Pt/Yb-USY-Al_2O_3	4% fish oil FAME, 96% rapeseed FAME	80-120^{o}C, 500 kPa (H_2)	Monounsaturated, saturated FAME	Very low blend caused no change in pour point. Improved oxidative stability	Toba, M.
Ni-based hydrogenation catalyst (Nyosel 645)	Soybean oil FAME	T=170^{o}C P=100 kPa (H_2) Time = 1 h	Partially hydrogenated FAME	CP=3^{o}C better than some waste oil FAME. Estimated to result in a production cost increase of $0.04/L compared to conventional biodiesel	Moser, B.R.
Cu-Ni/Al_2O_3	Rapeseed oil FAME	T=180^{o}C P=600-2,000 kPa (H_2) (unknown uptake) Time=1-3 hours	Partially hydrogenated FAME (mostly 1 or 2 unsaturations)	80-90% C18:1 molecules, PP= -13 to -15^{o}C	Ravasio, N.
Pd/ImS3-12 nanoparticles, ionic liquid	Soybean oil FAME	T=27-60^{o}C P= 3,000-10,000 kPa (H_2)	Partially hydrogenated FAME (mostly 1 unsaturation)	Phase transition range (-40 to -9^{o}C), good catalyst recycle properties	Souza, B.S.
Chemical Reaction					
Catalyst/ reactants	**Feed**	**Operating Conditions**	**Products**	**Characteristics**	**Affiliated Researcher/Group**
Formic acid, hydrogen peroxide	FAME (poultry fat)	T=25^{o}C P=atmospheric Time=5 hours	FAME molecule with an epoxide group added over the carbon double bond sites	Improved cetane number and oxidative stability, preserved cold-flow properties	Wadumesthridge, K. et al. (2009)

3.3 Partial Hydrogenation

Numerous research groups have proposed partial hydrogenation as a method of upgrading conventional FAME biodiesel. Partial hydrogenation is a process similar to that used to produce HVO or HDRD that uses a catalyst and hydrogen gas to increase the degree of saturation of the FAME molecules. The main difference between this suggested process and the HDRD process is that the milder conditions leave the carbon-oxygen bonds intact and hydrogen is simply added to the carbon-carbon double bond sites on the FAME molecules. The suggested advantages of this process include less intensive process conditions (80-120°C and 100-500 kPa) with lower H_2 (g) consumption as compared to HVO processing. Moreover, since this process is similar to vegetable oil hydrogenation, it has been suggested that simple, existing equipment could be incorporated into current biodiesel plants to produce an upgraded product. The degree of saturation affects both the cold-flow properties and the oxidative stability. A more saturated molecule is more resistant to oxidation but possesses inferior cold-flow properties. Performing this partial hydrogenation thus requires fine control over the process to maximize oxidative resistance while minimizing the increase in cloud point.[11] This is especially true of biodiesel to be blended for use in colder Canadian climates.

The equipment used to carry out such reactions would be similar to hydrogenation equipment used in the production of edible oils. Dr. Makoto Toba from the Research Center for New Fuels and Vehicle Technology (a division of the National Institute of Advanced Industrial Science and Technology) has published papers on the subject. Currently, the dominant catalysts used for this reaction are Palladium, Platinum, or Ruthenium-based heterogeneous catalysts.

In addition to improving the final FAME properties, partial hydrogenation may have applications in the production of FAME from waste sources that were previously limited in use due to poor performance. [12]

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[11] Toba, M. et al. (2009). *Oxidative Degradation Behavious of Fatty Acid Methyl Ester in fish Oil biodiesel and improvement of oxidative stability by partial hydrogenation,* Journal of the Japan Petroleum Institute, Volume 52, Issue 6.

[12] Toba, M. et al. (2009). *Oxidative Degradation Behavious of Fatty Acid Methyl Ester in fish Oil biodiesel and improvement of oxidative stability by partial hydrogenation,* Journal of the Japan Petroleum Institute, Volume 52, Issue 6.

3.3.1 Literature Review

3.3.1.1 Toba, M. et al. (2009). Oxidative Degradation Behaviour of Fatty Acid Methyl Ester in Fish Oil Biodiesel and Improvement of Oxidative Stability by Partial Hydrogenation.

A study by Toba et al. demonstrated the partial hydrogenation of FAME produced from fish oil. The main objective for this study was to improve the oxidative stability of biodiesel from waste oils that have traditionally been discarded due to performance concerns. The catalyst employed was a Pd-Pt/Yb-USY-Al_2O_3 catalyst under a 500 kPa flow of hydrogen. This study may show promise for the potential use of waste oils for fuels. However, the partial hydrogenation process shows a distinct decrease in cold temperature performance for an already poorly performing fuel. The results of hydrogenating a 4% mixture of fish oil FAME with 96% rapeseed oil FAME caused the cloud point to increase from -4°C to 11°C. When mixed with petroleum diesel to form a B5 blend, the cloud point remained unchanged, largely because the total fish oil FAME volume fraction was so low.[13]

3.3.1.2 Bourazios et al. (2010). Catalytic Conversions in Green Aqueous Media: Part 4. Selective Hydrogenation of Polyunsaturated Methyl Esters of Vegetable Oils for Upgrading Biodiesel.

Bouriazos et al. (2010) also studied the partial hydrogenation of biodiesel with the goals of improving oxidative stability, maintaining cold-flow properties, and increasing combustion performance. The catalyst used was sodium triphenylphosphine trisulfonate (TPPTS). The study used an Rh/TPPTS aqueous catalyst in a 2-phase system to selectively hydrogenate methyl esters of linseed, soybean, and sunflower oil. The study briefly mentions the need for precise hydrogenation control in order to maintain an acceptable cloud point but this parameter is not a focus of the study.[14]

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[13] Toba, M. et al. (2009). *Oxidative Degradation Behavious of Fatty Acid Methyl Ester in fish Oil biodiesel and improvement of oxidative stability by partial hydrogenation,* Journal of the Japan Petroleum Institute, Volume 52, Issue 6.

[14] Bouriazos, A., Sotiriou, S., Vangelis, C., Papadogianakis, G. (2010). *Catalytic conversions in green aqueous media: Part 4. Selective hydrogenation of polyunsaturated methyl esters of vegetable oils for upgrading biodiesel*, Journal of Organometallic Chemistry, Volume 695, Issue 3.

3.3.1.3 Moser, B.R. et al. (2007). Evaluation of Partially Hydrogenated Methyl Esters of Soybean Oil as Biodiesel

The 2007 study by Moser et al. examines the partial hydrogenation of FAME while directly addressing the cold temperature performance. The reaction took place at 170°C under 100 kPa of H_2 (g) for one hour over a Ni-based hydrogenation catalyst (Nyosel 645). The pure, partially hydrogenated soybean methyl ester (PHSME) had a cloud point of 3°C which is higher than that of pure soybean oil FAME (0°C) but lower than that of most waste oil FAMEs (such as waste cooking oil, grease, and tallow). The study concluded that the oxidative stability of the fuel was improved and that it met the standards for both the US ASTM D6751 and EN 14214 standards. As mentioned by the author, there is no value for low-temperature performance in either of these standards but noted that these PHSME has a better cloud point (CP) and pour point (PP) than palm oil, tallow and grease methyl esters. The added capital and operating costs of such a process was estimated to result in a $0.04 per liter increase in production cost for the fuel but there was little discussion of how the added costs were calculated. [15]

3.3.1.4 Ravasio, N. et al. (2002). Environmental Friendly Lubricants Through Selective Hydrogenation of Rapeseed Oil Over Supported Copper Catalysts.

This study investigated partial hydrogenation as a means to improve both cold flow properties and oxidative stability. Although the focus of the study is on the production of lubricants, the products are suitable for use as a diesel additive and the author suggests their potential use for this application. The catalysts used were mixtures of copper and nickel on a silica support under high H_2 (g) pressures. One concern with hydrogenating oils or their esters is that decreasing the degree of unsaturation leads to an increase in cloud point temperature. The goal of partial hydrogenation for biodiesel is to improve oxidative stability by reducing the number of carbon-carbon double bonds. A fully saturated molecule, however, will have a cloud point well above 0°C that may be unacceptable for a diesel fuel. Another complication in these processes is the tendency for hydrogenation catalysts to promote isomerization of the molecules to a *trans* state; further reducing the fuel's cold flow properties. The goal is thus to reduce as much as possible the trienic and dienic fractions (3 and 2 unsaturations, respectively) while preventing the formation fully saturated molecules and *trans* isomerization. This study found that certain Cu containing catalysts showed promise in producing a final biodiesel with roughly 80-90% C18:1 (one unsaturation for an 18-carbon chain) molecules and a pour point of

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[15] Moser, B.R. (2007). *Evaluation of partially hydrogenated methyl esters of soybean oil as biodiesel,* Eur. J. Lipid Sci. Technol. 109 (2007) 17–24.

minus 13-15°C. The reactions were carried out under a 600-2000 kPa of H_2 (g) at a temperature of 180°C for 1-3 hours.[16]

3.3.1.5 Souza, B.S. et al. (2012). Selective Partial Biodiesel Hydrogenation Using Highly Active Supported Palladium Nanoparticles in Imidazolium-based Ionic Liquid.

The recent study by Souza et al. investigated the use of ionic liquids and surfactants, along with palladium nanoparticles as a heterogeneous catalyst for the partial hydrogenation of FAME. Similarly, to the 2002 study by Ravasio, the product contained high levels of C18:1 molecules with low C18:2 and C18:3 levels, showing little *trans* isomerization. The reactor conditions were 27-60°C at 3039-10,132 kPa of H_2 (g). It is unclear what the rate of consumption of H_2 is for this type of reaction. The discussion of cold-flow properties focuses on the fuel's phase transition but it makes no mention of its pour point and cloud point. The author mentions that the partially hydrogenated FAME retains the cold-flow properties of the starting FAME material.[17]

3.3.2 Summary

The table below provides a summary of our assessment of partial hydrogenation technology from our review of the literature and the results of our telephone interviews.

Table 4: Assessment of Partial Hydrogenation Technologies

Status	**Costs**	**Advantages**	**Disadvantages**
University research / laboratory scale	Only the study by Moser (2007) addressed the costs of implementation. It was estimated to result in a change from US \$0.53/L to US \$0.57/L For the most part, no cost assessment was identified in the literature or by the interviewed parties	Similar to the well-established hydrogenation of edible oils. Conditions are milder than other technologies	H_2 (g) supply is required. High temperature and pressure equipment is needed along with a potentially expensive catalyst. Will address oxidative stability but will not improve the cloud point directly.

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[16] Ravasio, N., et al. (2002). *Environmental friendly lubricants through selective hydrogenation of rapeseed oil over supported copper catalysts*, Applied Catalysis A: General, Volume 233, Issues 1–2.

[17] Souza, B.S., et al. (2012). *Selective partial biodiesel hydrogenation using highly active supported palladium nanoparticles in imidazolium-based ionic liquid*, Applied Catalysis A: General, Volumes 433–434, pages 109-114.

3.4 Deoxygenation

Deoxygenation is a broad term for any chemical reaction that removes oxygen from a substance (usually an organic compound). Deoxygenation can be divided as either selective or unselective based on the reaction mechanisms involved. Selective deoxygenation removes oxygen in the form of CO_2, CO, and H_2O while leaving the aliphatic hydrocarbon chain intact or with one fewer carbon atom. Unselective deoxygenation, on the other hand, is similar to hydrocracking and results in hydrocarbons, CO_2, and short-chain oxygenates. These processes tend to form a distribution of products and incur a loss of usable fuel compared to the starting mass of FAME. When describing these mechanisms, the terms decarboxylation (COOH), decarbonylation (CO), and deacetylation (CH_3CO) are often used and refer to the type of functional group being removed from FAME.[18]

Research has indicated that Pd/C catalysts can perform the decarbonylation/ decarboxylation of biodiesel to produce hydrocarbons. The major drawback of this catalyst is that CO is produced in the reaction that will poison the Pd catalytic sites. To counteract catalyst deactivation, a higher hydrogen partial pressure is required in the reaction vessel.[19] Other potential candidate catalysts to perform this reaction are solid base catalysts such as low-silica zeolites containing highly polarizable cations (Caesium, for example). Zeolites are microporous alimino-silicate minerals that are used as absorbents and in ion exchange beds. They are widely used in the hydrocracking process for the petroleum industry. They are useful and versatile heterogeneous catalysts that can be modified to exhibit both acidic and basic chemical behaviour depending on the preparation methods used. These catalysts are not susceptible to CO poisoning and can operate under lower hydrogen partial pressures.[20]

3.4.1 Literature Review

3.4.1.1 Sooknoi, T., et al. (2008). Deoxygenation of Methylesters Over CsNaX.

It has been demonstrated by T. Sooknoi et al. that a cesium (Cs)-containing sodium (Na) zeolite (CsNaX) catalyst is potentially suitable for converting FAME into hydrocarbons.

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[18] Kubičková, I., Kubička, D., (2010). *Utilization of Triglycerides and Related Feedstocks for Production of Clean Hydrocarbon Fuels and Petrochemicals: A Review*, Waste and Biomass Valorization, Volume 1, Issue 3.

[19] Danuthai, T., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., Resasco, D.E. (2009). *Conversion of methylesters to hydrocarbons over an H-ZSM5 zeolite catalyst.* Applied Catalysis A: General, Volume 361, Issues 1-2.

[20] Danuthai, T., et al. (2011). *Effect of extra-framework cesium on the deoxygenation of methylester over CsNaX zeolites,* Applied Catalysis A: General, Volumes 409-410, Pages 74-81

The X in the catalyst formula above denotes the type of crystal structure of the zeolite.[21] The authors used methyl octanoate co-fed with methanol for a gas phase reaction to simulate the reactions of FAME molecules. Methly octanoate is a methyl ester of octane and is thus a shorter analogue to FAME. The reaction was carried out under atmospheric pressure at a temperature of 425ºC for 2 hours. The atmosphere was an O_2/He (g) mixture and there were numerous complex reaction pathways under these conditions that yielded several products. The authors found that the major products were hexenes (23.7%), heptenes (39.4%), and octenes (16.4%). In addition to the three predominant products, a number of by-products were also produced from side-reactions. Although the main by-products are mostly hydrocarbons with one fewer carbon atom than the feedstock, they are all unsaturated hydrocarbons (or alkenes). The conversion of methyl octanoate was maintained at around 40% when using methanol as a solvent in a He (g) atmosphere. Methanol is crucial in the reaction because it provides a source of hydrogen for the reaction and prevents the formation of undesired by-products. In other words, they contain at least one carbon-carbon double bond. It is unclear whether theses alkenes possess the necessary properties to be blended with petroleum diesel. In order to form saturated hydrocarbons, H_2 (g) must be added in a hydrogenation reaction. It is stated that this process is more environmentally favourable since it uses methanol instead of H_2 (g) in the reaction. It should be noted that methanol is itself a by-product of fossil fuels since the predominant production of methanol occurs via the reaction between carbon monoxide and hydrogen, which are by-products of the steam reformation of methane. Regarding the industrial application of such a process, certain key pieces of information are still missing to evaluate this technology such as catalyst regeneration methods as well as product separation.[22]

3.4.1.2 Danuthai, T., et al. (2011). Effect of Extra-Framework Cesium on the Deoxygenation of Methylester over CsNaX Zeolites.

This study is an extension of this group's previous 2008 study and investigated the effect of cesium (Cs) loading on the zeolite catalyst. The reaction conditions were similar to the previous study and the authors varied the amount of extra-framework Cs on the catalyst to vary the acid-base properties. Increasing the amount of Cs led to increased basicity, caused a preference toward decarbonylation, and improved the catalyst stability. The reaction was carried out at atmospheric pressure at 425ºC for 2 hours. The feed was methyl octanoate in a methanol solvent fed into the reactor as vapour. As in the previous study, the methanol is a critical additive in order to preserve the catalyst activity and supply hydrogen for the deoxygenation reactions. The CsNaX20 catalyst showed the best

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[21] Htun, M.M.H. et al. (2012). *Preparation of Zeolite (NaX,Faujasite) from Pure Silica and Alumina Sources*, International Conference on Chemical Processes and Environmental issues

[22] Sooknoi, T., Danuthai, T., Lobban, L.L., Mallinson, R.G., Resasco, D.E. (2008). *Deoxygenation of methylesters over CsNaX*, Journal of Catalysis, Volume 258, Issue 1.

stability, remaining at 40% conversion after 300 minutes on stream. The results are generally positive in this study, however, it is unclear how the results would change when using FAME molecules that are much heavier and less volatile than methyl octanoate.[23]

3.4.1.3 Danuthai, T., et al. (2009) Conversion of Methylesters to Hydrocarbons Over Zn-Modified H-ZSM-5 Zeolite Catalyst.

The same group that used CsNaX catalysts to investigate FAME deoxygenation also tested H-ZSM5 acid zeolite catalyst to perform the same reaction. The reactions also used methyl octanoate with a methanol solvent in the gas phase. The reactions occurred at atmospheric pressure at 500°C for 2 hours. Although the discussions are favourable for the use of such a process, the results are less promising. The main products are short chain hydrocarbons (C2 to C4) and long condensation products with traces of aromatics. The product distribution is so wide at all process conditions that the losses in conversion likely outweigh any potential property upgrading gains. The 2008 study using CsNaX zeolites or Pd-based catalyst was much more promising.[24]

3.4.1.4 Do, P.T. et al. (2009). Catalytic Deoxygenation of Methyl-Octanoate and Methyl-Stearate on Pt/Al2O3

This study used both methyl stearate and methyl octanoate to model the deoxygenation of FAME. Several types of catalysts and catalyst loadings were examined and the optimal catalyst for the study was found to be a 1 % wt Pt/Al_2O_3 catalyst in a tetradecane solvent. The reaction was carried out at 690 kPa and 325°C for 5 hours. The results for the liquid-phase conversion of methyl stearate showed a conversion of 64%. The main product was heptadecane (>90% selectivity) with a yield of 42 % after 5 hours. The dominant reaction path was suggested to be decarbonylation due to the absence of chain shortening. Changing the reaction atmosphere from hydrogen to helium resulted in a drop in methyl stearate conversion from 64% to 42%. This decrease is believed to be due to faster catalyst deactivation in the absence of hydrogen.[25]

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[23] Danuthai, T., et al. (2011). *Effect of extra-framework cesium on the deoxygenation of methylester over CsNaX zeolites,* Applied Catalysis A: General, Volumes 409-410, Pages 74-81

[24] Danuthai, T., et al. (2009). *Conversion of Methylesters to Hydrocarbons Over Zn-Modified H-ZSM-5 Zeolite Catalyst*, Catalysis Letters, Volume 132, Pages 197-204.

[25] Do, P.T. et al. (2009). *Catalytic Deoxygenation of Methyl-Octanoate and Methyl-Stearate on Pt/Al2O3,* Catalyst Letters, Volume 130, Issues 1-2.

3.4.1.5 Mäki-Arvela, et al. (2007). Catalytic Deoxygenation of Fatty Acids and Their Derivatives.

This study from Finland is one of several studies published by the researchers Paivi Maki-Arvela, Iva Kubickova, Mathias Snare, Kari Erainen, and Dmitry Yu. Murzin. As with several papers examined in the context of this report, the feed conversion in these reactions was low (13%) since the main objective of the study was to characterize the reaction kinetics and reaction paths. Further research on commercial feasibility is required before making any judgement on this reaction technique. In order to model FAME, ethyl stearate was used as the feed with an alkaline Pd/C catalyst. The reaction conditions were 320°C under 750 kPa for 6 hours. The dominant product was n-heptadecane (46%), however a substantial amount of C17 aromatics (36%) and C17 unsaturated (6%) compounds were also formed. The study found that increasing the alkalinity of the catalyst increased the reaction rate of the ester and increased the selectivity towards the formation of n-heptadecane. In the experiments using acidic catalysts, the dominant product was stearic acid. The authors claim that the first step in the reaction to form a deoxygenated fuel is the formation of stearic acid. Only under basic conditions will stearic acid further react to form n-heptadecane: a saturated hydrocarbon.[26]

3.4.1.6 Snare, M. et al. (2008), Catalytic Deoxygenation of Unsaturated Renewable Feedstocks for Production of Diesel Fuel Hydrocarbons.

This study is related to the previous study by Maki-Arvela (2007) and was performed by the same research group. The reactions occurred at 300°C, under 1500 kPa in an atmosphere of 5% H_2 (g) in argon (Ar) gas. Methyl oleate was employed as a model molecule for FAME. The study was conducted at a feed conversion rate of under 20%. The products were similar to the previous study: n-heptadecane and other C17 hydrocarbons. After 6 hours, the methyl oleate conversion was 84%. This study also focused predominantly on the deoxygenation of fatty acid compounds. The researchers attempted to model industrial process conditions by using a flow reactor loaded with the same catalyst in the absence of a solvent. The feed used was stearic acid however, so no accurate conclusions can be drawn for a methyl ester feed.[27]

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[26] Mäki-Arvela, et al. (2007). *Catalytic Deoxygenation of Fatty Acids and Their Derivatives,* Energy Fuels, Volume 21, Issue 1. 21.

[27] Snare, M. et al. (2008), *Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons,* Fuel, volume 87.

3.4.2 Summary

The table below provides a summary of our assessment of deoxygenation technologies from our review of the literature and the results of our telephone interviews.

Table 5: Assessment of Deoxygenation Technologies

Status	Costs	Advantages	Disadvantages
University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Produces mostly linear hydrocarbons. The studies by the University of Oklahoma used relatively inexpensive catalysts.	These technologies had low yields and this was identified as a major concern for the economic viability by FAME producers.

3.5 Hydrodeoxygenation

Hydrodeoxygenation is differentiated from the previous deoxygenation examples due to the reaction mechanism. This type of reaction involves high H_2 gas pressures as the principal method of removing oxygen. The oxygen is typically removed in the form of H_2O or CO.

3.5.1 Literature Review

3.5.1.1 Dundich, V.O. et al. (2010). Nickel Catalysts for the Hydrodeoxygenation of Biodiesel

Dundich et al. investigated the upgrading of FAME using a Ni-Cu catalyst on a CeO_2-ZrO_2 support. The reaction was carried out in a fixed-bed reactor at 290-320ºC under a 1,000 kPa atmosphere of H_2 and Ar. The results of this study are promising and report the main products as linear alkanes (C_{12}-C_{17}), methane and water. Other studies regarding solid base catalysts produced a wider range of products with much lower levels of alkanes. Starting with a feed of methyl oleate (a typical biodiesel component), the main product obtained was heptadecane with 70-75% selectivity.[28]

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[28] Dundich et al. (2010). Nickel *Catalysts for the Hydrodeoxygenation of Biodiesel*, Kinetics and Catalyst, Volume 51, Issue 5.

3.5.1.2 Yakovlev, V.A. (2009). Development of New Catalytic Systems for Upgraded Bio-Fuels Production from Bio-Crude-Oil and Biodiesel

This study tested a variety of catalysts for the hydrodeoxygenation of FAME. This process is similar to that used in petroleum refineries in the hydrotreater unit. The catalyst employed at refineries are sulfided hydrodesulfurization catalysts (sulfided Co–Mo/Ni–Mo supported on AlO_2). These catalysts cannot be used on FAME because of its tendency to remove sulfur from the catalyst surface and deactivate it. The authors used FAME produced from rapeseed oil as a model biodiesel mixture. The reactions were carried out at temperatures between 250-400°C and at pressures between 500-2,000 kPa under a flow of 50% H_2 in Ar. The results were promising, showing close to 100% biodiesel conversion with 75% selectivity towards C17 alkane products. The other products included 5% each C6-C14, C15, and C16 hydrocarbons. The catalyst of choice was a Cu-Ni mixture supported on ZrO_2/CeO_2. Although other catalysts without copper showed higher C17 selectivities, their biodiesel conversion was low at 280°C. Increasing the temperature in catalysts without Cu cause rapid methanization of FAME and complete conversion to methane (CH_4). The disadvantage with this technology is that is requires high H_2 partial pressures and would require a large supply of hydrogen gas.[29]

3.5.1.3 Senol, O.I. et al. (2007). Reactions of Methyl Heptanoate Hydrodeoxygenation on Sulphided Catalysts

In this study, Senol et al. employed an existing type of hydrotreatment catalyst: $Ni-Mo/Al_2O_3$ and $Co-Mo/Al_2O_3$. The reaction was carried out in a continuously stirred batch reactor (CSTR). The study is concerned with the deoxygenation of bio-oil compounds but it uses methyl heptanoate, a methyl ester, as a model compound. The NiMo catalyst produced mostly hydrocarbons and exhibited a higher ester conversion than the CoMo catalyst. The main products and their respective selectivities were heptanes (44%) and hexanes (33%) as well as some heptenes, hexenes and heptanoic acid. This indicates a preference towards saturated hydrocarbons over unsaturated hydrocarbons, which is a desirable feature for the purposes of this study. After an initial drop in ester conversion, the reactions over Ni-Mo catalysts remained steady at around 80% and showed good long-term stability. After long reaction times, sulfide products begin to appear and a slow decrease in catalyst activity was observed.[30]

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[29] Yakovlev, V.A. et. al. (2009). *Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel.* Catalysis Today, Volume 144, Issues 3-4.

[30] Senol, O.I., et al. (2007). *Reactions of Methyl Heptanoate Hydrodeoxygenation on Sulphided Catalysts*, Journal of Molecular Catalysis A: Chemical, volume 268.

3.5.1.4 Ryymin, E.M., et al. (2009). Insight to Sulfur Species in the Hydrodeoxygenation of Aliphatic Esters Over Sulfided NiMo/g-Al2O3 Catalyst.

This study was primarily concerned with the deoxygenation of bio-oils however, the model compound used was methyl heptanoate. Since methyl heptanoate has also been used in studies to model FAME, the results were considered in this study. The most promising reaction used a sulphided Ni-Mo catalyst on an Al_2O_3 support at 7,500 kPa and 250°C in a H_2 (g) atmosphere. Under these conditions nearly all of the feed material was consumed (>90% conversion) and the main products were hexenes, heptenes, n-hexane, and n-heptane. 1-heptanoic acid and 1-heptanol are formed as intermediate compounds before a subsequent reaction to form hydrocarbons. These compounds are also formed when using the less active catalysts in the study or when using an inert atmosphere or a lower H_2 partial pressure. The importance of H_2 (g) in the formation of hydrocarbons is noted in the study.[31]

3.5.2 Summary

The table below provides a summary of our assessment of hydrodeoxygenation technologies from our review of the literature and the results of our telephone interviews.

Table 6: Assessment of Hydrodeoxygenation Technologies

Status	Costs	Advantages	Disadvantages
University research/ laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Very high conversion of starting FAME (~90%)	None of the studies reviewed mentioned an improvement in cold flow properties. Sensitive conditions and high temperatures led to rapid hydrocracking (formation of methane and short hydrocarbons)

3.6 Decarboxylation

Decarboxylation is a chemical reaction in which a carboxyl group is removed from a molecule (often a carboxylic acid), releasing CO_2. When performed on a methyl ester, decarboxylation results in a long hydrocarbon chain, CO_2, and a methyl compound from

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[31] Ryymin, E.M., et al. (2009). Insight to sulfur species in the hydrodeoxygenation of aliphatic esters over sulfided NiMo/g-Al2O3 catalyst, Applied Catalysis A: General, Volume 358.

the original methyl ester. These reactions are distinguished from the previous types since the conditions are such that decarboxylation is the only reaction mechanism involved.

3.6.1 Literature Review

3.6.1.1 Han, J. et al. (2010). Palladium-Catalyzed Decarboxylation of Higher Aliphatic Esters: Towards a New Protocol to the Second Generation Biodiesel Production.

The authors achieved 99.5% conversion of methyl stearate over 5%Pd/BaSO4 catalyst. The H_2 partial pressure was 1,600 kPa with a reaction time of 3.5 hours at a temperature of 270°C. The solvent was hexane, which existed in a supercritical state at the reaction conditions. The conversion of methyl stearate was 99.5% and the yield of heptadecane was 96.6% indicating a very effective method for producing hydrocarbons. The equipment required to carry out this reaction include an autoclave, high-pressure pumps, a supply of hydrogen, separation equipment (flash vessel/distillation column), and the catalyst.[32] When the reaction was complete, 5%Pd/BaSO4 catalyst was deposited at the bottom of the autoclave. The catalyst was separated by filtration, washed sufficiently with hexane, and then dried in an oven at 70°C for 0.5 hours. The catalyst was recovered and reused in the next run without further activation treatment.[33]

3.6.1.2 Snare, M. et al. 2007, Production of Diesel Fuel From Renewable Feeds: Kinetics of Ethyl Stearate Decarboxylation.

In this 2007 study, the authors used ethyl stearate as a model compound for FAME with a Pd/C catalyst. The reaction took place in an autoclave between 270 – 360°C at 1,700-4,000 kPa in a solvent (n-dodecane). The atmosphere was comprised mostly of inert He or Ar gas with 5% H_2 (g). In this study, n-heptadecane was the primary product along with other C17 molecules. The conversion of methyl stearate was low however, and after a reaction time of 60 minutes, the molar fraction of methyl stearate in the vessel was roughly 84%. The focus of this study was on kinetic modelling of the reaction and not on process feasibility so these results may differ in industrial applications. Further studies by this author are also examined in this report. According to the authors, the production of unsaturated hydrocarbons should be avoided due to their lower cetane numbers, chemical stability, and tendency to form aromatic hydrocarbons. The second part of this study was dedicated to the numerical modeling of reaction kinetics. This study is useful in its illustration of the complex reaction network involved in a catalytic reaction such as this.

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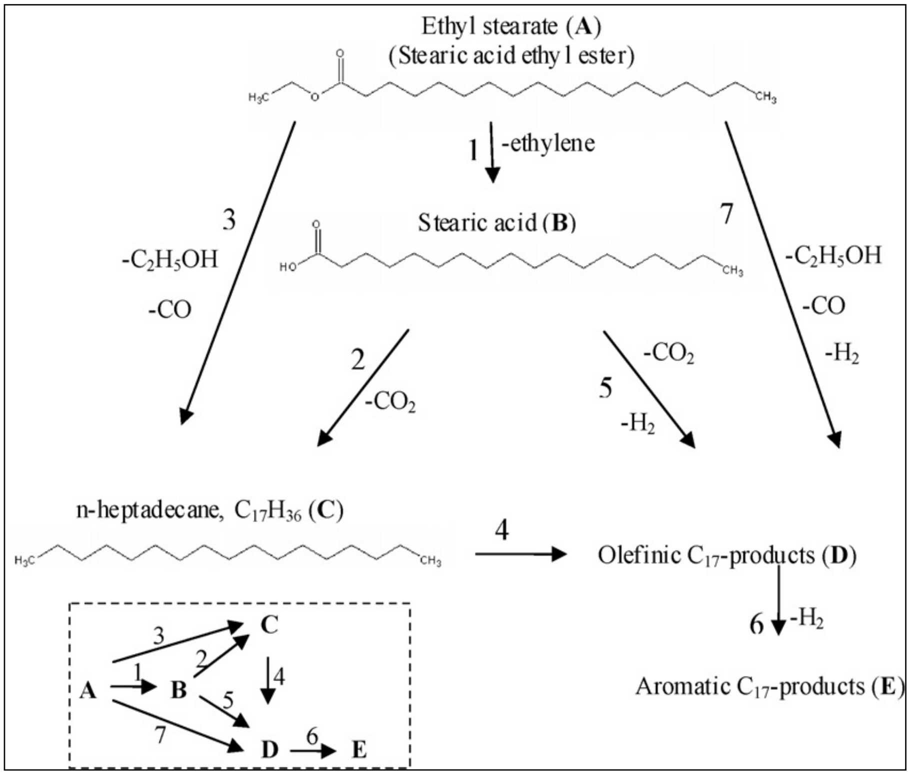
[32] Han, J., et al. (2010). *Palladium-catalyzed decarboxylation of higher aliphatic esters: Towards a new protocol to the second generation biodiesel production*, Green Chemistry, Issue 3

[33] Han, J., et al. (2010). *Palladium-catalyzed decarboxylation of higher aliphatic esters: Towards a new protocol to the second generation biodiesel production*, Green Chemistry, Issue 3.

The figure below was taken from the study to show the suggested reaction routes in the formation of various products.[34]

Figure 1: Suggested Reaction Mechanism, Snare, M. 2007[35]



Source: Snare, M. et al. (2007). *Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation,* Chemical Engineering Journal, Volume 134 pages 29–34

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[34] Snare, M. et al. (2007). *Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation,* Chemical Engineering Journal, Volume 134 pages 29–34.

[35] Snare, M. et al. (2007). *Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation,* Chemical Engineering Journal, Volume 134 pages 29–34.

3.6.2 Summary

The table below provides a summary of our assessment of decarboxylation technologies from our review of the literature and the results of our telephone interviews.

Table 7: Assessment of Decarboxylation Technologies

Status	Costs	Advantages	Disadvantages
University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Very high conversion (~90%), mostly linear alkane products	Very high pressures. High temperatures. Expensive Pd catalyst.

3.7 Chemical Reaction

One relevant study was identified that involved examination of a simple chemical reaction to upgrade biodiesel properties.

3.7.1 Literature Review

3.7.1.1 Wadumesthridge, K. et al. (2009). Effects of Partial Hydrogenation, Epoxidation, and Hydroxylation on the fuel Properties of Fatty Acid Methyl Esters.

This study compares the effects of hydrogenation, epoxidation, and hydroxylation on the various properties of poultry fat biodiesel. The final comparison examined the following fuel properties: acid number, water content, viscosity, cloud point, pour point, oxidation stability, higher heating value, cetane number, and lubricity. Since these reactions do not result catalytic cleavage of functional groups, the yield of all reactions remains high (>90%). The hydrogenation reaction was carried out over a standard Pd/C catalyst for 2 hours at 120^{o}C and 405 kPa. The epoxidation reaction was carried out at room temperature and atmospheric pressure for 5 hours in the presence of formic acid, and hydrogen peroxide. The separation stage involved the use of hexane as a solvent and a sodium bicarbonate wash. Finally, the hydroxylation reaction employed an osmium tetraoxide "Ad mix-α" catalyst in the presence of water, tert-butyl alcohol, sodium sulfite, and methylene chloride. The extraction stage employed hexane solvent to remove FAME from the aqueous phase. A final separation stage is required to isolate the product from hexane. The reaction occurs at room temperature under atmospheric pressure and requires 18-24 hours using the conditions just described. As expected, hydrogenation yielded improved oxidative stability and cetane number but reduced cold flow properties. Hydroxylation cause a significant increase in lubricity but the time required for the reaction and its complexity makes this route less favourable for industrial applications. Epoxidation was observed to be a promising method to improve the cetane number and oxidative stability of the fuel while leaving the cloud point unchanged and maintaining good lubricity.[36]

3.7.2 Summary

The table below provides a summary of our assessment of the technology described above from our review of the literature and the results of our telephone interviews.

Table 8: Assessment of the Epoxidation Technology

Status	Costs	Advantages	Disadvantages
University research / laboratory scale	Unknown. No cost assessment was identified in the literature or by the interviewed parties.	Simple chemical reaction, no catalyst is required. Improves oxidative stability and maintains cold-flow properties.	Requires a supply of non-commodity chemicals. Reaction time of five hours may be considered too long.

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[36] Wadumesthridge, K., Salley, S.O., Ng, K.Y.S., (2009). *Effects of partial hydrogenation, epoxidation, and hydroxylation on the fuel properties of fatty acid methyl esters,* Fuel Processing Technology, Volume 90, Issue 10.

4. Industry Input on FAME to Hydrocarbons Conversion Technologies

4.1 Introduction

Industry representatives and other experts were interviewed via phone calls. In addition to phone interviews, interviewees were emailed a questionnaire and information package containing a summary table of the reviewed technologies. Their assessment and other input on technologies was requested. Respondents provided general input on conversion technologies, and several respondents provided input for the individual technologies.

4.2 Awareness of FAME Conversion Technologies

The perspective on new technologies to convert FAME into hydrocarbons appears to be relatively homogeneous across the biodiesel industry. Due to the relatively unknown and unproven nature of the technologies identified in this study, no biodiesel producer interviewed was aware of any of the new technologies. All FAME producers were aware of HDRD/HVO and some had been researching similar technologies. For all producers where this was the case, it was indicated that the processes were deemed unfeasible or not economical. Only one equipment vendor was aware of processes designed to produce hydrocarbon fuels directly from biodiesel (FAME) but only as early-stage research technologies.

4.3 Technical and Cost Input on FAME Conversion Technologies

One common concern among respondents with respect to FAME conversion technologies was that adding additional reaction stage(s) to a biodiesel plant would be economically unfeasible. Several respondents indicated that it might be more favourable to operate such a process using a triglyceride or oil as a feedstock rather than a methyl ester. The benefit of using FAME as a feedstock was not evident to respondents given that it already requires significant costs to obtain it and that research is actively being pursued to make hydrocarbons directly from oils and triglycerides.[37]

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[37] Personal interview.

The main concern from the point of view of biodiesel producers is whether or not the additional capital cost and yield loss are justified simply to improve the cold flow properties of biodiesel. This opinion is based on biodiesel producers experience as well as some studies, such as the National Renewable Diesel Demonstration Initiative and the Alberta Renewable Diesel Demonstration, that show biodiesel can be used in cold Canadian climates. HDRD/HVO fuels may possess better cold-flow properties but their production is not currently economical for small producers. Some biodiesel industry respondents expressed interest in a "drop-in" or "hydrocarbon" renewable fuel and one respondent indicated that an economic path to manufacture them may develop if the appropriate policy and funding support is established.[38]

Several studies used methyl octanoate, a short-chain methyl ester, as a model compound. One survey response indicated that the results of studies using this model compound might not translate when using longer chain fatty acids. In addition, a straight chain, saturated hydrocarbon would have significantly a worse cloud point and pour point than the starting methyl ester. In order to remedy this, a subsequent isomerization step would be required in addition to the previous deoxygenation step.[39]

4.4 Perspectives on HDRD/HVO

All parties interviewed were aware of the increased competition for biodiesel from HDRD/HVO but offered varying opinions on the severity of the threat and therefore the need or value of converting biodiesel to hydrocarbons. One respondent pointed out that there is a trade-off between investing in biodiesel blending/storage infrastructure and purchasing HDRD at a premium cost.

Most HDRD/HVO is currently being produced in Finland, Singapore, and the Netherlands. While HDRD is being used in Canada and the United States, the choice to purchase biodiesel or imported HDRD is largely dependent on which option is more economical for a petroleum refiner, in a given location, at a given point in time.

The Canadian biodiesel industry expects that as biodiesel infrastructure becomes more widespread in Canada, the blending concerns will be less important and petroleum refiners will choose to use more domestic biodiesel.

According to one respondent, the development of technologies similar to renewable diesel in Canada has been slowed due to the intellectual property rights of current

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[38] Personal interviews.
[39] Personal interview.

HDRD/HVO producers. In an interview with another respondent, it was indicated that an HDRD-type facility was being built in Louisiana using a novel resin-based catalyst.[40,41]

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[40] Personal Interview.

[41] Dynamic Fuels LLC, Available at: http://www.dynamicfuelsllc.com/

5. Conclusions

5.1 Introduction

For this study, a number of new technologies to convert biodiesel (FAME) into hydrocarbons were reviewed and summarized. The technologies were presented to biodiesel producers and industry experts in order to evaluate their potential and to determine the industry's perspectives in regards to these technologies. Those who provide input had a negative assessment of the technologies. The key conclusions drawn from this study are outlined below.

5.2 Loss of Yield

All identified technologies will incur a yield loss due to side reactions. The loss of final product could strain the economics of small biodiesel producers. It was indicated that the reaction to produce FAME from oils results in a small loss of yield and that additional yield losses would be undesired. Only if the new product could be sold at a significantly higher price could this yield loss be justified. The highest conversion rates observed in the studies was 90% and even this rate was viewed as not feasible. Most studies indicated that catalyst performance was an issue. Poor catalyst performance may cause a decrease in product yield over time.

5.3 Added Equipment, Capital, and Operating Cost

Additional equipment may include high pressure/temperature reactors, pumps, and separation vessels. If hydrogen gas is required, it may be supplied by a small natural gas reformer, delivered in cylinders, or provided via pipeline. A supply by pipeline could only occur if the facility was located close to a large natural gas reformer such as those found at petroleum refineries. In cases where complete conversion is not achieved, equipment is needed to separate the unreacted feed and recycle it back into the process. If undesired components are present, they must also be separated and discarded. This separation equipment will incur additional capital and operating costs. The added equipment costs were not obtained from industry interviews and rarely mentioned in the literature. Only one study made any mention of costs associated with these new processes. The absence of any economic evaluation of these new technologies made it very difficult to evaluate their potential. The prevailing opinion given by respondents was that the types of reactions described in the literature would necessitate a complete overhaul of an existing biodiesel facility. As a result, unless a technology is proven to add significant value, such a process is unlikely to be adopted but an existing biodiesel facility.

5.4 Unproven Fuel Properties

The engine performance and fuel storage characteristics were not discussed in the reviewed articles. A major factor in considering any new technology is the certification of the fuel by the Canadian General Standards Board (CGSB), American Society for Testing and Materials (ASTM), the European Committee for Standardization, or the German Institute for Standardization (DIN). In the identified literature, it was often claimed that the resulting products would perform adequately in diesel engines but only one report mentioned that their fuel met the standards specified by ASTM D6751 and EN 14214. Before any consideration is given to a new fuel mixture, it must be proven to meet these standards. It should also be proven to have superior blending and cold flow properties in order to provide an incentive for biodiesel producers to consider changing their process. The positive attributes of the linear alkane fuels identified in some studies are their expected blending properties. Due to their chemical similarity to petroleum diesel, these compounds can be incorporated into the existing fuel infrastructure. Where a mixture of products are produced, the blending characteristics were not clear from the consulted sources.

5.5 Uncertain Cold Flow Properties

Although most research articles claim FAME to HC conversion technologies address cold flow issues, some respondents indicated that linear alkanes (as produced in most of the deoxygenation reactions) would worsen the cold flow properties of the fuel. In order to use these linear alkanes, a subsequent isomerization step is required in order to produce a product with more favourable cold flow properties. If such a step were in fact required, it would incur additional equipment and hydrogen gas.[42] Few of the identified studies directly measured the cold flow properties of the fuel.

5.6 Concerns About Sustainability

All identified conversion technologies require additional energy and chemical inputs, and result in direct and indirect (lifecycle) greenhouse gas and other emissions. For some technologies, hydrogen gas is required, which would likely be produced from the steam reformation of methane - a fossil fuel. The same situation arises in technologies where

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[42] Personal interviews.

methanol is required since it is produced primarily from synthesis gas, a product of the steam reformation of methane.[43]

In addition, respondents described the removal of the ester group as redundant. A considerable amount of energy and chemicals are invested in the process of oil transesterification to FAME. Most of the interviewed parties viewed a process overhaul in order to produce a hydrocarbon directly from vegetable oil as preferable. The additional energy and non-renewable chemical consumption of the identified technologies might degrade the environmental sustainability profile of the fuel.

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[43] Methanol Institute (http://www.methanol.org/)

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7. Appendix

7.1 Questionnaire / Discussion Guide

The following questions served as a discussion guide for the interviews conducted by Cheminfo Services.

- Have you considered modifications to produce a hydrocarbon fuel instead of FAME?
    - What is the status of the upgrade? Conceptual stage, design stage, abandoned?
    - What type of equipment, infrastructure, and costs are associated with the upgrades?
- As part of our study, we have reviewed scientific literature regarding biodiesel (FAME) upgrading technology. We have supplied a table with a broad summary of the technologies that were identified.
    - Regarding the products, do you have any comments regarding their storage, handling, and use?
    - Regarding the operating conditions, do you have any comments regarding the type of equipment required and whether or not this is feasible for a biodiesel plant? Ex. high-pressure reactor, distillation column.
    - Regarding the catalysts/reactants/solvents, do you have any comments regarding the cost/feasibility of using these materials in addition to your current process inputs?
    - Are you aware of any other process that might produce a hydrocarbon fuel or a biodiesel with improved cold-flow and blending properties?
- Given your current operating status, could you justify any additional capital and operating costs to upgrade your facility? How sensitive is the operation to changes in feedstock costs/sales price?

Who designed your facility? Who supplies your major equipment?