Innovative Canadian Process Technology for Biodiesel Production

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Abstract

The need for increasing renewable and alternative energy in the global energy mix has been well recognized by Governments and major scientific forums to reduce climate change impact for this living planet. Biodiesel has very high potential for GHG emission reduction. An innovative process developed in Canada provides a solution to mitigate the feedstock, yield and quality issues impacting the industry. The BIOX process uses a continuous process which reduces reaction times, provides > 99% yield of high quality biodiesel product. The process is feedstock flexible and can use cheaper higher FFA non-edible feedstock providing a sustainable approach for biodiesel production.

Keywords: Biodiesel, Continuous process, High free fatty acid feedstock

1 Introduction

The World Energy Outlook 2009 [1] predicts in its Reference Scenario that fossil fuels will still dominate the global primary energy mix for several decades to come. It, however, also predicts that consumption of biofuels will rise strongly in the transportation sector. Some of their findings in the Outlook Executive Summary that are relevant to introduce this paper are restated below:

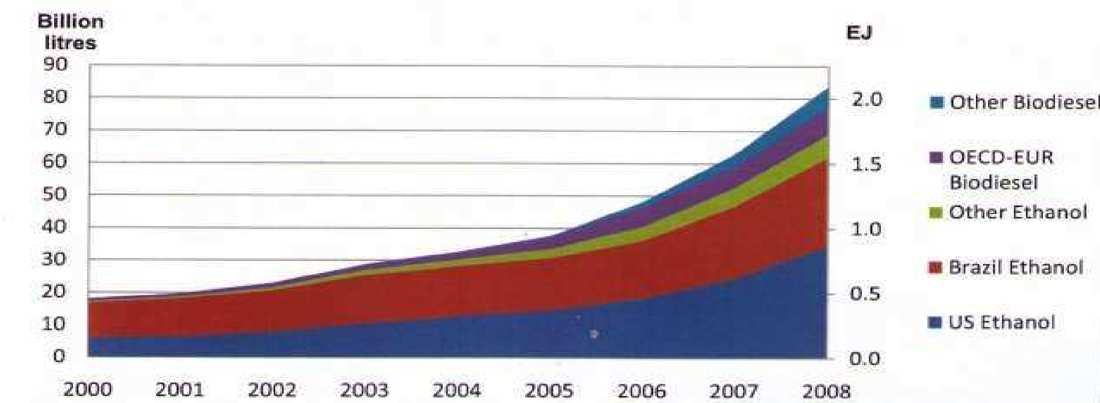
- "Continuing on today's energy path, without any change in government policy, would mean rapidly increasing dependence on fossil fuels, with alarming consequences for climate change and energy security.
- These trends would lead to a rapid increase in the concentration of greenhouse gases in the atmosphere.
- Measures in the transportation sector to improve fuel economy, expand biofuels and promote the uptake of new vehicle technologies – notably hybrid and electric vehicles – lead to a big reduction in oil demand.
- The use of non-hydro modern renewable energy technologies (including wind, solar, geothermal, tide and wave energy, and bioenergy) sees the fastest rate of increase in the Reference Scenario."

The World Energy Outlook 2009 450 Scenario [2] projects biofuels to provide 9% (11.7 EJ) of the total transport fuel demand (126 EJ) in 2030. In the *Blue Map Scenario [3]* of *Energy Technology Perspectives 2008 [4]* that extends analysis until 2050, biofuels provide 26% (29 EJ) of total transportation fuel (112 EJ) in 2050.

Biodiesel is a clean burning, non toxic, biodegradable and renewable biofuel that can be used to substitute diesel fuel fully or in blends. It can be made virtually from any oil or fat feedstock. Biodiesel is considered to be an environmentally friendly fuel and offers a viable alternative to fossil fuels mainly in the transportation sector. According to Joe Jobe, CEO National Biodiesel Board (NBB), biodiesel has one of the best energy balances and one of the best Greenhouse Gas (GHG) reductions [5]. US Environmental Protection Agency (EPA), as part of Renewable Fuel Standard 2 (RFS2), approved biodiesel as an Advanced Biofuel [6].

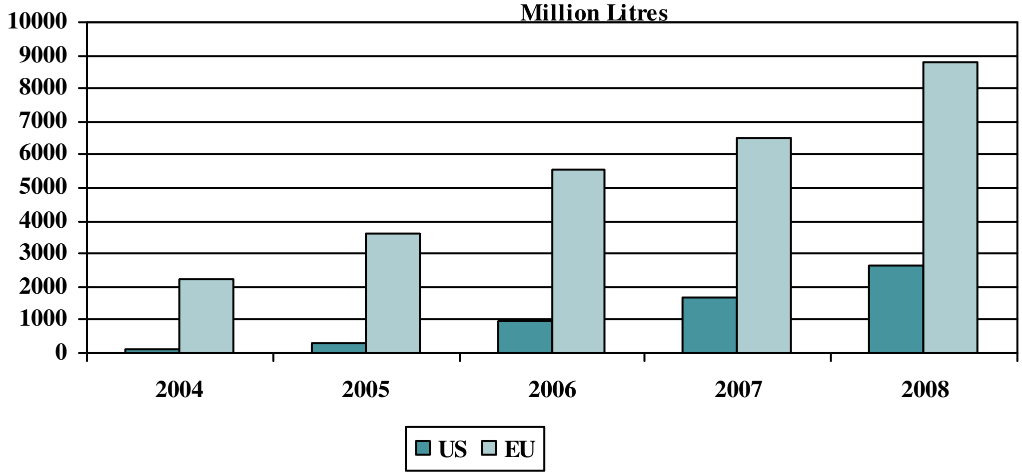
Global biofuel production has had a spectacular growth in the first decade of this 21st century. Figure 1.1 shows the growth of biofuels from Year 2000 to 2008 and Figure 1.2 shows the growth of biodiesel in the US and EU from 2004 to 2008.

Figure 1.1
Biofuel Production



Source: IEA [7]

Fig. 1.2
US/EU Biodiesel Production
Million Litres



Source: NBB and EBB

Total global biodiesel production in 2008 was of the order of 13.6 billion litres whereas the total Canadian production in the same year was 126 million litres (source CRFA).

The development of the global biofuel industry has been largely fuelled by governments through mandates, targets and various mechanisms of support such as subsidies, mainly for energy security [8]. Mitigating climate change is another major driver. Despite the impressive growth in biodiesel production, the capacity utilization of the industry in general has been very poor (from 26% in US to 37% in EU in 2008). There are several issues that have impacted the capacity utilization of the biodiesel industry. The primary issues are related to feedstock costs and process technology limitations. Other issues include the economic climate in recent years and poor planning for some of the projects in the developing industry.

This paper discusses the key drivers that will sustain the growth of biodiesel production, the key issues facing the biodiesel industry and a description of the BIOX continuous process technology which can mitigate some of these issues.

2 Biodiesel Demand Drivers

Major drivers fuelling the biodiesel demand are as follows:

- Increasing energy security
- Reducing environmental emissions
- Government mandates and incentives

2.1 Increasing Energy Security

Energy security can be described as "the uninterrupted physical availability at a price which is affordable while respecting environment concerns" [9]. As stated earlier, the International Energy Agency (IEA) predicts primary dependence on fossil fuels, mainly oil, for decades to come. Current known reserves are restricted to a limited number of countries. Any limitations arising in the supply of oil from any of the key oil producing nations impact global energy security.

Several steps are being taken worldwide to improve global energy security. These include:

- improving energy efficiencies
- increasing storages
- natural gas storage and liquefaction
- timely investments for energy supply in line with economic development
- diversification of energy sources including growth of renewable energy

Biodiesel production can be distributed more widely among many nations using domestically available resources. Governments around the world are instituting policies to encourage new ways of producing energy domestically from renewable resources to:

- reduce dependence on imported fossil fuels
- extend existing fossil fuel reserves
- improve domestic energy security

2.2 Reducing Environmental Emissions

Exhaust Emissions

Several studies have been conducted to determine the exhaust emission changes in combusting biodiesel or blends in diesel engines. The results tend to vary from study to study.

For the purpose of this paper, data on regulated exhaust emissions is taken from the 2002 study performed by the United States EPA on the impacts of biodiesel on exhaust emissions. This technical report assembles a large quantity of pre-existing data from various test programs and presents a statistical analysis of the trends found therein [10]. The results of this analysis are compared with the results of the 100,000 mile transit bus evaluation performed by the United States National Renewable Energy Lab (NREL) in which the emissions of buses fuelled on a B20 blend were compared to those running on neat petroleum diesel. [11]

The results are summarized in Table 2.1.

Table 2.1
Impact of Blending Biodiesel on Regulated Emissions

Emission	B20 Biodiesel EPA Analysis [10]	B20 Biodiesel NREL Analysis [11]
CO	-11.0%	-23.6%
THC	-21.1%	-28.1%
PM	-10.1%	-18.6%
NOx	+2.0%	-4.85%

Greenhouse Gas (GHG) Emissions

GHGs in Canada are regulated by the Clean Air Act. The primary emission of concern is carbon dioxide; however, included in the category of GHG are hydro fluorocarbons, chlorofluorocarbons, methane and nitrous oxides.

The advantage provided by biodiesel usage lies not only in a reduction of tailpipe emissions as indicated above, but in a reduction of the emission of greenhouse gases (such as CO2) throughout the entire lifecycle of the fuel. This includes considerations such as carbon dioxide taken up into the canola, soy (etc) during growth, gases sequestered in the soil and emissions during transportation and fuel processing.

Several Life Cycle Assessments (LCA) completed for biodiesel show a wide range of net GHG savings compared to diesel fuel. The variations in LCA results depend on the feedstock, process technology, location and several other factors including varying assumptions and methodical constraints. The 1998 study done by Sheehan et al jointly for the US Department of Agriculture and the US Department of Energy [12] assessed a net life cycle reduction of 78.4% in CO2 emissions when compared to petroleum diesel. The study also stated that biodiesel yields 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle (FER). More recent studies by these Departments predict LCA savings of 66% to 74% in GHG emissions [13] and revised FER of 4.4 to 4.56 [14]. US EPA has approved classification of soy and animal fat based biodiesel as Advanced Biofuels achieving greater than 50% LCA reduction in GHG emissions [15].

GHGenius is a model developed by Natural Resources Canada to analyze overall carbon dioxide emissions. The model considers factors such as fertilizer use, seed crushing for plant feedstock and transportation. The most recent report considers seven biologically based diesel alternatives: three plant based biodiesels (canola, soy and palm), two animal based biodiesels (tallow and yellow grease) and two types of biodistillate (SuperCetane from canola and from tallow). It also includes information on the emissions of GHGs other than CO2, namely methane, nitrous oxide, chlorofluorocarbons and hydro fluorocarbons. The emissions values for these compounds are expressed in terms of equivalent tonnes of CO2. The greenhouse gas reductions that result from the blending of these seven fuels are included in Table 2.2.

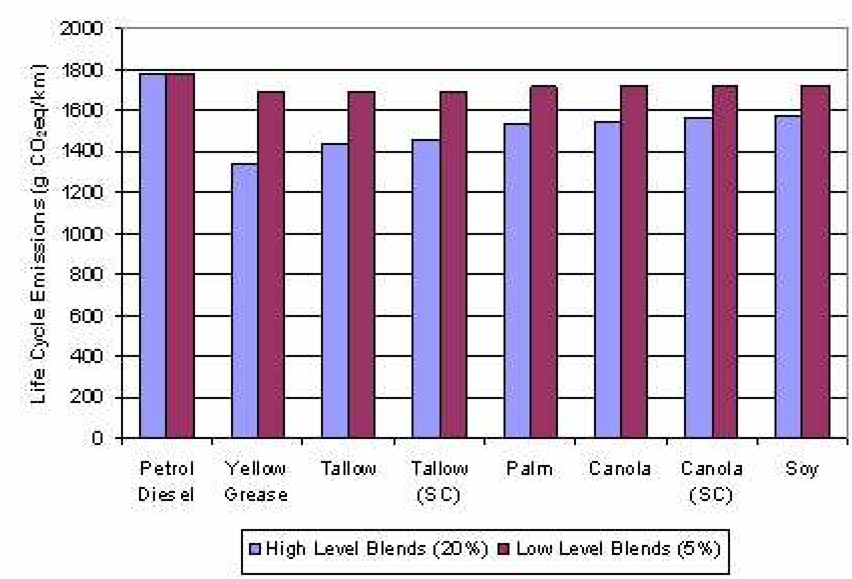
Table 2.2
Reduction of CO_2 Equivalent per kilometer of Biodiesel Blend compared to Ultra Low Sulphur Diesel (ULSD)

Biodiesel	% Reduction at 5% Blending	% Reduction at 20% Blending
Canola Biodiesel	3.2	12.9
Soy Biodiesel	2.8	11.4
Palm Biodiesel	3.4	13.8
Tallow Biodiesel	4.7	18.8
Yellow Grease Biodiesel	4.8	19.3
Canola SuperCetane	3.0	11.9
Tallow SuperCetane	4.4	17.9

Source: [16]

It can be seen that the most significant reduction in emissions occurs from the use of yellow grease to make biodiesel. The comparative effects of the different fuels on lifecycle GHG emissions are also illustrated in Figure 2.1. The values are given in emissions of CO2 equivalent per kilometer driven in a heavy-duty vehicle.

Figure 2.1: Total Life Cycle Emissions in grams CO2 equivalent per kilometer for various feedstock and blending levels. [16]



2.3 Government Mandates and Incentives

Biodiesel production is being supported by Governments worldwide by approving mandates and incentives. Some of the major support being provided by the Governments of Canada, EU and US are as follows:

- Governments in Canada, the US and the EU are promoting the production and use of renewable fuels via Producer Payments, Renewable Fuel Blending Standards and/or Tax Exemptions
- As part of the Clean Air Act, the Government of Canada has mandated a 2% biodiesel blend by 2011 (Bill C-33)
- The Renewable Fuels Standard Program (RFS-2) in the United States mandates 5% renewable fuel content in the fuel pool (gas & diesel) starting in 2010 with a minimum of 1 billion gallons annually in the diesel pool by 2012
    - U.S. 2009 and 2010 combined mandate of 1.15 billion gallons
- The European Union's Clean Energy Directive mandates 5.75% renewable fuel content by 2010 by each member state

3 Biodiesel Issues

3.1 Feedstock

Feedstock is key to successful production of biodiesel, as ultimately it is an issue between renewable vs. finite. Feedstock is the major cost item in the biodiesel production. Biodiesel can be made from any oil or fat feedstock including:

- Vegetable/seed oils: Canola, castor, copra, corn, cottonseed, flaxseed, mustard, palm, peanut, rapeseed, sesame, soybean, sunflower
- Other oils: Camelina, jatropha, linseed
- Algae oils
- Animal fats: Chicken grease, fish oil, lard, tallow
- Used/Blended oils/fats: Used restaurant oils, yellow grease

A study completed last year by the Renewable Energy Group (REG) produced biodiesel from 34 different oils and fats [17] and evaluated their characteristics.

The use of a feedstock by a biodiesel production facility depends on its price and suitability for the process technology in use. Oils and fats are primarily triglycerides of fatty acids. Some of the oils and fats listed above such as animal fats, used oils, yellow grease and some others contain a higher percentage of FFA which is detrimental to the use of standard technology of trans-esterification of triglycerides.

The majority of biodiesel currently produced worldwide utilizes higher cost seed oil as feedstock due to physical location and technological limitations. Seed oils such as soy, canola and rapeseed that contain very low levels of FFA are currently more expensive than animal fats and used/blended oils and fats.

In recent years there has been much debate on *Food vs. Fuel* concerning the risk of diverting farmland or crops for biofuel production which could impact the food supply on a global scale. There are arguments being presented from both sides but it has been demonstrated that biodiesel production has had a minimal impact on food prices or availability as yet. The NBB factsheet indicates that US biodiesel production only used 12% of US soybean in 2007. Out of this soybean 81% of the yield is protein rich feed that enters the market for human consumption or animal feed [18].

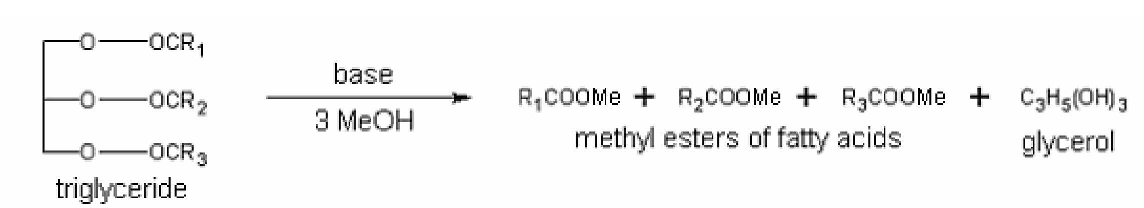
The NBB fact sheet [18] estimates the availability of biodiesel feedstock in the US in 2016 to be over 20 billion litres. NBB estimates include current feedstock (soy, canola, sunflower, tallow, yellow grease), their future expansions, as well as new sources such as corn oil from ethanol plants, camelina, restaurant grease and white grease. A significant amount of research and development is being completed in developing sustainable production of algae oils for biodiesel production as algae oils require the least amount of land area per unit of oil extracted. Canada is a net exporter of oils and fats and can easily meet the requirements of the domestic biodiesel industry.

The projections for feedstock availability show adequacy for some years to come but it is important that the biodiesel industry considers sustainability in its future growth. The share of non-food oils and fats in the feedstock mix should be increased in a sustainable manner. In addition, new sources of feedstock including algae oils need to be developed.

3.2 Process Technology

The production of biodiesel is performed through a chemical process known as transesterification. Transesterification specifically refers to the transformation of fats or oils into specific esters. [19] When producing biodiesel, it is vegetable oil in particular that is being converted into monoalkyl monoesters. A general reaction scheme for a transesterification reaction is shown in Figure 3.1. It can be noted that the structure of any alkyl esters that is produced depends on the groups initially attached to the fat or oil molecules (triglyceride) denoted by R1, R2 and R3. The glycerol produced as byproduct is immiscible with biodiesel (methyl esters) and is separated.

Figure 3.1
Transesterification Reaction



Transesterification of triglycerides is a very slow reaction and needs a catalyst such as a base to improve the reaction rate. Methanol does not have good miscibility with oils/fats. As such transesterification requires significant agitation and multiple stages to improve yield. The reaction can be done batchwise or continuously, but standard process is more commonly done batchwise due to the lack of homogeneity in the oil/fat and methanol mixture. If such reaction systems are not properly designed or operated correctly, yield and the quality of the product are impacted adversely.

Another issue, which has technological significance for the biodiesel industry, is the presence of FFA in the feedstock. FFA saponifies the base and thus hinders the transesterification reaction from proceeding and creates difficulty in biodiesel – glycerol separation. A majority of the biodiesel production facilities use this standard technology which is limited in the use of higher FFA cheaper feedstock. The maximum amount of FFA acceptable in the feedstock for the standard process is generally less than 1%. Some plants are pretreating the higher FFA feedstock by caustic refining/stripping and then recover FFA by acidulation for sale as another byproduct. This, however, reduces the overall yield of biodiesel per unit of feedstock as some triglycerides are lost with the soaps during caustic stripping.

4 BIOX Continuous Process

An innovative continuous process for the production of biodiesel from higher FFA feedstock was developed in Canada at the University of Toronto. The patented process was acquired by BIOX and a commercial demonstration plant was built in Hamilton, Ontario, Canada in 2006. The plant is running at full production capacity (67m litre nameplate production capacity, 60m litre output target including maintenance downtime). Since April 2007, the plant has been using 100% animal fats, yellow grease, and other greases as feedstock. The biodiesel produced meets or exceeds ASTM D 6751 and EN14214 specifications. BIOX is a BQ 9000 certified producer of biodiesel.

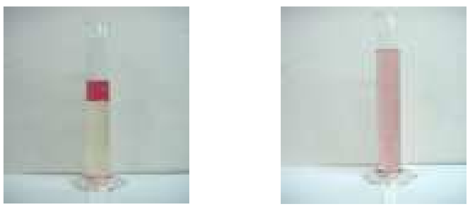
The BIOX Process discussed in this section provides the following benefits:

- Innovative technology using a proprietary and patented process
- Uses acid esterification of FFA in the feedstock to convert them into biodiesel to get almost full conversion of FFA and triglycerides
- Capable of converting lower cost feedstock with no change to the chemical process or increase in production costs while achieving yields of >99%
- Uses less energy and less time than traditional processes
    - Total process takes less than 90 minutes
    - Continuous versus batch production process
    - Chemically efficient
    - Performed at near-ambient temperature and atmospheric pressure

The BIOX Process uses a cosolvent with methanol for mixing with oils/fats. The cosolvent helps in forming a homogeneous phase for the mixture facilitating the transesterification reaction. The formation of the homogeneous phase reduces the need for extensive agitation, multiple batch reactors and extensive reaction time (minutes instead of hours), and improves the yield and product quality. Figure 4.1 shows the formation of the single phase when cosolvent is used and a basic process flow diagram of the BIOX Process.

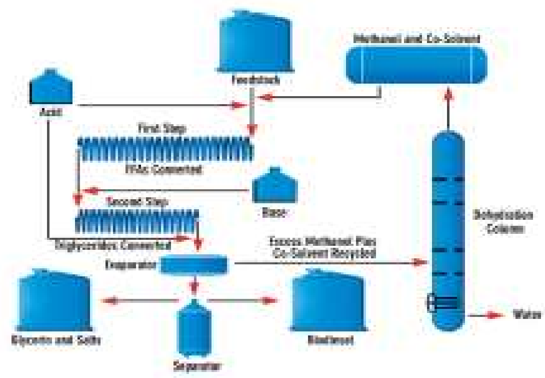
Fig. 4.1
Biox Process Flow Diagram

Cosolvent advantage



Methanol/Oil   With Cosolvent

Process Flow Diagram



The BIOX Process uses continuous acid catalyzed esterification of FFA by methanol to produce biodiesel by the following reaction:

$$FFA + CH_3OH \overset{Acid}{=} Methyl\ Ester + H_2O$$

The BIOX Process as such can use less expensive feedstock, such as tallow or yellow grease that are characteristically high in free fatty acids (FFA). The resultant product mixture continues on to the base catalyzed transesterification of triglycerides.

The multi-feedstock used by the BIOX Process provides inherent technological flexibility in the process to make more sustainable choices in regards to the use of appropriate feedstock. The process is ready for using future feedstock including algae oils.

Other features of the BIOX Process are as follows:

- Modular plant design and assembly with standardized engineering of components reduces on site setup times
- Small footprint (less than 10,000 sq m process area)
- Outdoor processing provides higher safety and significantly reduced risks
- Produces distilled biodiesel superior in quality and appearance when compared to standard biodiesel separated by decantation

Traditionally, biodiesel companies build plants near seed oil sources and away from end user markets (industrial centres), compounding their technical dependence on a single feedstock source. Enabled by its feedstock flexibility, plants based on the BIOX Process can be located within the industrial/distribution hubs which offer favourable transport logistics, thereby improving access to both the widest variety of potential feedstock and industrial consumers of petroleum diesel (end users), and creating significant economic advantages.

BIOX Hamilton Plant

5 Conclusions

The need for increased production of biofuels has been recognized worldwide to increase domestic energy security within nations and to reduce GHG emissions. Biodiesel produced from oils and fats has one of the highest GHG reduction potentials and very high energy output to input ratio. The biodiesel industry is being supported and promoted by most Governments. Biodiesel production has increased significantly in the past decade but the industry is suffering from poor capacity utilization. Key issues impacting the industry are related to feedstock and process technology. Most of the biodiesel plants around the world use batch process technology for transesterification of triglycerides in oils/fats. These processes are limited in the use of cheaper feedstock that has higher Free Fatty Acid content. This impacts the economic well-being of the industry. An innovative continuous Canadian process is owned and being used by BIOX that has the advantage of using cheaper higher FFA feedstock, reducing reaction time significantly compared to batch traditional processes, and providing greater than 99% yield of a high quality product. The multi feedstock capability to produce advanced biofuel in a more sustainable manner makes the BIOX Process ready to propel the growth of the biodiesel industry.

References

1 World Energy Outlook 2009, Reference Scenario, IEA/OECD

2 World Energy Outlook 2009, 450 Scenario, IEA/OECD (This Scenario models future energy demand in light of a global long term CO_2 concentration in the atmosphere of 450 ppm)

3 IEA/OECD: This Scenario models future energy demand to 2050 with same 450 ppm target

4 Energy Technology Perspectives - 2008, IEA/OECD

5 National Biodiesel Board: News Bulletin - Feb. 10, 2010. Speech at NBB 2010 conference

6 US Environmental Protection Agency: RFS 2 - February 2010 Bulletin

7 Towards sustainable production and use of resources: Assessing Biofuels, - 2009, UNEP

8 Sustainable Production of Second Generation Biofuels - 2010, IEA/OECD

9 IEA Website > By Topic > Energy Security - 2010

10 A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions – 2002, US EPA

11 100,000 Mile Evaluation of Transit Buses Operated on Biodiesel Blends(B20) – 2006, National Renewable Energy Laboratory, US Department of Energy

12 Sheehan J. et al: An overview of Biodiesel and Petroleum Diesel Life Cycles – 1998, US Department of Agriculture and US Department of Energy

13 Huo H. et al: Life Cycle Assessment of Energy and Greenhouse Gas Effects of Soybean Derived Biodiesel and Renewable Fuel – 2008

14 Pradhan A. et al: Energy Life Cycle Assessment of Soybean Biodiesel – 2009, Argonne National Laboratory, US Department of Agriculture

15 US Environmental Protection Agency: RFS 2 - February 2010 Bulletin

16 $(S \& T)^2$: Sensitivity Analysis of GHG Emissions from Biofuels in Canada – Prepared for Natural Resources Canada, Office of Energy Efficiency

17 Sanford S. D. et al: Feedstock and Biodiesel Characteristics Report – 2009, Renewable Energy Group

18 National Biodiesel Board: Biodiesel Feedstock Supply

19 Zhang Y. : Biodiesel Production from Waste Cooking Oil: Process Design and Technological Assessment – 2003, Bioresource Technology