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A Brief Literature Overview of Various Routes to Biorenewable Fuels from Lipids for the National Alliance for Advanced Biofuels and Bio-products (NAABB) Consortium

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1.0 Introduction

Methods of producing renewable transportation fuels are currently the focus of numerous large research efforts across the globe. Renewable fuel produced from algal lipids is one aspect of this research that could have profound implications on future transportation fuel requirements. However, technical challenges remain in several areas of algal-lipid-based fuels. These challenges include the identification and development of robust and productive algal species as well as extraction methods to recover the produced lipids. Not the least of these technical challenges is the conversion of the algal lipids to fungible fuels. This brief literature review focuses primarily on state-of-the-art “downstream” applications of producing fuel from fats and lipids, which can be applied to ongoing research with algae-derived lipids.

Algae lipids (oil) are similar to other oils in that three acyl groups are coupled to a glycerol “back bone.” The acyl groups are typically 14-22 carbons in length and have varying degrees of unsaturation from 0 to 6 double bonds.¹ The three acyl groups attached to the glycerol backbone are commonly referred to as triacyl glycerides, or TAGs. There are currently two major routes to producing diesel fuel from TAGs. First, the most common and commercially practiced method is to remove the acyl chains from the glycerol backbone using methanol as a co-reactant and a homogenous catalyst via a mechanism known as transesterification. Transesterification results in molecules known as fatty acid methyl esters, or FAMEs, which are widely used as biodiesel.

An alternate processing route for producing diesel fuel from algae-derived lipids is through deoxygenation. TAGs can be directly deoxygenated, or hydrolysis of the fatty acid chains could first be performed with subsequent deoxygenation of the fatty acids. FAMEs may also be deoxygenated. Deoxygenation can be performed through several different mechanisms. Hydrodeoxygenation is a mechanism that utilizes hydrogen to produce saturated alkanes and water as products. Hydrodeoxygenation can be applied to TAGs, FAMEs, and/or free fatty acids (FFAs). Catalytic decarboxylation of TAGs, FAMEs or FFAs can also be performed, resulting in oxygen removal through the production of CO₂. The feed stock molecules can also be non-selectively cracked or pyrolyzed. Regardless of the mechanism, the goal of deoxygenation is to produce hydrocarbon chains without oxygen present. In contrast to FAMEs which contain oxygen present in the ester group, deoxygenated hydrocarbons are expected to be essentially oxygen free.

For clarity, it is important to distinguish between the terms “biodiesel” and “renewable diesel.” Knothe² recently published a review with an excellent commentary on the usage of these terms. Knothe describes FAMES as “biodiesel” and oxygen-free hydrocarbons produced by hydrotreating TAGs as “renewable diesel.” Similar to Knothe, the current review will use the term biodiesel to describe FAMES. In contrast to Knothe, renewable diesel will be used to describe all diesel-range deoxygenated hydrocarbons produced from TAGs, FAMES or FFAs by *any* mechanism, including hydrotreating, selective catalytic decarboxylation, cracking or pyrolysis. Green diesel, which is another term that appears commonly in the literature, should be considered analogous to renewable diesel in the current review.

After the initial discussion of terminology, the review by Knothe proceeds into a discussion on the pros and cons of both biodiesel and renewable diesel. Smith et al.³ also recently published a review on different sources and technologies pertaining to biodiesel and renewable diesel. Other reviews that the authors have found particularly helpful include the discussion on biodiesel by Ma and Hanna,⁴ a review on various hydrotreating and cracking methods by Huber and Corma,⁵ and the more encompassing reviews by Lestari et al.⁶ and Kubickova and Kubicka.⁷ These reviews cover a large amount of published data in great detail and are invaluable to those working in the area of oil and lipid conversion to fuels.

2.0 Biodiesel

Biodiesel is commercially produced from TAG's with methanol added as a co-reactant and NaOH added as a homogenous basic catalyst. In the conventional process, the lipid feedstock must have very low FFA content because the basic NaOH will cause the FFAs to saponify into fatty acid salts (soap). Ma and Hanna⁴ reviewed the production of biodiesel with an emphasis on the transesterification mechanism. Meher et al.⁸ also reviewed the transesterification mechanism for the production of biodiesel. Knothe et al.⁹ published an overview of biodiesel with respect to economics, technical challenges and engine performance issues.

An alternative to the transesterification mechanism is the esterification mechanism, which can convert FFAs as well as TAGs to biodiesel. Lam et al.¹⁰ recently reviewed homogenous, heterogeneous and enzymatic catalysts capable of converting used cooking oil, which has a high concentration of FFAs, into biodiesel. Di Serio et al.¹¹ reviewed both acidic and basic heterogeneous catalysts. Iyer¹² recently applied for a patent for a process utilizing cationic and anionic exchange resins as acidic and basic catalysts, respectively. A single-step solid-acid-catalyzed process from feeds with high FFA concentrations was reported by Baig et al.¹³ State-of-the-art catalysts such as functionalized

mesoporous silicas were reviewed by Mbaraka and Shanks¹⁴ and continue to be of interest as demonstrated by the recent publication by Ngo et al.¹⁵

3.0 Renewable Diesel

Renewable diesel produced via catalytic hydrotreating of various lipid feedstocks is a process that has recently been commercialized by several companies. The Neste Oil NExBTL process produces renewable diesel by hydrotreating vegetable oils or waste fats, resulting in a 40-80% lifecycle reduction in CO₂ depending on the feedstock.¹⁶ Neste Oil recently opened a plant in Singapore using NExBTL technology that will produce more than 800,000 tons per year of renewable diesel from feedstocks such as palm oil and waste animal fat.¹⁷

The UOP/Eni Ecofining¹⁸ process is based on the hydrotreating of TAGs and/or FFAs, which results in deoxygenation via hydrodeoxygenation and decarboxylation.^{19,20} After the hydrotreating step, an isomerization process is performed to produce an isoparaffin rich diesel fuel. The renewable diesel product produced by the Ecofining process (termed “green diesel” by the authors) was reported to be economically competitive with biodiesel based upon a life cycle analysis reported in a 2009 publication.²¹

Dyanmic Fuels, which is a joint venture between Syntroleum and Tyson Foods, recently opened a plant in Geismar, LA for the production of renewable diesel from non-food grade animal fats.²² The animal fat includes beef tallow, pork lard, chicken fat and greases. Syntroleum reported that the carbon footprint of the renewable diesel produced at the plant is 75% below petroleum diesel. The plant is designed to produce up to 75 million gallons of renewable fuel per year.

Valero also recently announced that a new plant at its St. Charles Refinery in Norco, LA will be utilized to convert used cooking oil and animal fat into renewable diesel via hydrogenation and isomerization processes.²³ The fat and oil feedstocks will be supplied by Darling International, who is Valero’s partner in the venture. The new plant is slated to begin construction in the second or third quarter of 2011.

Several other independent groups have also investigated hydrotreating various lipids and fats to produce fuels. Simacek et al.²⁴ recently reported the utilization of hydrorefining NiMo/alumina catalysts to hydroprocess rapeseed oil. At a pressure of 7 MPa H₂ and temperatures above 310°C, the main products were C₁₇ and C₁₈ hydrocarbons. Many of the reports in the academic and patent literature use traditional hydrotreating catalysts such as sulfided CoMo or NiMo based catalysts.²⁵⁻⁴⁴ Hydrotreating

lipid feedstocks in general has generated a large number of recent patents and patent applications.⁴⁵⁻⁵⁴ Of particular interest is a recent patent published by Day and Franklin⁵⁵ on the catalytic hydroprocessing of microalgal oils.

More technical aspects on the kinetics and thermodynamics of the hydrotreating various feedstocks are also available in the open literature.⁵⁶⁻⁵⁹

Aatol et al.⁶⁰ reported on the performance of diesel engines with fuels produced via hydrotreating vegetable oil at the SAE International conference in Chicago in 2008. More recently, Simacek et al.⁶¹ reported on the fuel properties of hydroprocessed rapeseed oil. Similarly, the fuel properties of a fuel produced by hydrocracking petroleum vacuum distillate containing rapeseed oil was evaluated by Simacek and Kubicka.⁶²

Selective catalytic deoxygenation via a decarboxylation mechanism has been an active area of recent research.⁶³⁻⁶⁵ In contrast to the hydrodeoxygenation mechanism, decarboxylation does not require a stoichiometric level of H₂ consumption to produce renewable diesel. Current state-of-the-art catalysts for selective catalytic deoxygenation typically utilize noble metal supported catalysts, with Pd being the most common. While TAGs^{66, 67} and FAMES^{66, 68-72} have been studied, much of the effort to date on selective deoxygenation to produce fuels has been on FFA feedstocks. FFAs could be produced via the hydrolysis of TAGs to produce one mole of glycerol and three FFA chains. Maier et al.⁷³ published an early account of the gas-phase decarboxylation of shorter chain (C₇ and C₈) fatty acids over Pd and Ni. More recently, the Murzin group at Abo Akademi in The Netherlands has led a substantial effort on the deoxygenation of FFAs to produce diesel fuel focusing primarily on Pd on carbon catalysts to produce renewable diesel.^{71, 74-84}

As evidenced by some reports, improvement in Pd-based catalysts in continuous operation may be necessary because some reports suggest they are hindered by rapid deactivation. Maki-Arvela et al.⁷⁴ reported that the deactivation of a Pd catalyst while decarboxylating lauric acid may have been due to poisoning by the product gases (CO and CO₂) and/or coking. Currently, the best continuous conversion in the literature appears to be about 40% conversion of stearic acid to heptadecane after 92 hr of time on stream at 360°C with a “commercial Pd/C catalyst” as reported by Lestari et al.⁷⁶

FFAs may also be partially deoxygenated via ketonization over basic catalysts. Renz⁸⁵ recently reviewed this process as it relates to several feeds. The ketonization reaction is a bimolecular process whereby one mole each of CO₂ and water is rejected and a ketone is formed from the original fatty acid

molecules. For example, two stearic acid molecules may react to form 1 mole of CO₂ and H₂O, but the resulting ketone is a symmetrical C₃₅ ketone. Thus, the resulting hydrocarbon is not completely deoxygenated. Additionally, the C₃₅ molecule would require further processing such as hydrocracking and isomerization to obtain a diesel-like fuel.

The non-selective removal of oxygen from fats and lipids via pyrolysis or cracking has also been studied. TAGs,^{5, 86-115} FAMES,¹¹⁶⁻¹²⁰ and FFAs¹²¹⁻¹²³ have all been studied as feedstocks for cracking and pyrolysis reactions. Pyrolysis and cracking reactions have typically been studied on acidic materials, although alumina^{117, 123} and basic⁹¹ catalysts such as MgO and CaO, and even Na₂CO₃¹¹⁵ have also been studied. Cracking and pyrolysis reactions, which take place at elevated temperatures between 300-500°C, typically result in a distribution of molecules after treatment with varying amounts of less desirable short chain hydrocarbons. Additionally, many of the reports focused on cracking and pyrolysis mechanisms are performed with the goal of producing a lower boiling range fuel such as gasoline because cracking reduces the chain length and, thus, increases the volatility of the produced fuels.

4.0 Summary

Algae-derived lipids hold vast potential as a sustainable source for transportation fuels, especially diesel. Biodiesel produced by transesterification or esterification reactions as well as renewable diesel produced by deoxygenation mechanisms are both promising methods for transforming the initial algal-lipid feedstocks into a source of fuel. All of the routes to algal-lipid derived fuel possess unique research challenges. Ensuring that these fuels provide maximum economic, environmental and political impact should continue to be a significant focus of work and collaboration in the future.

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