L12

AQUATIC BIOMASS: DOWNSTREAM TECHNOLOGIES TO FAMES

Angela Dibenedetto
UNIVERISTY OF BARI AND CIRCC

Campus Universitario
University of Bari
70126 BARI - IT
a.dibenedetto@chimica.uniba.it

Angela Dibenedetto is Associate Professor at the University of Bari-UNIBA (IT) - Department of Chemistry. Her scientific interests are focused on carbon dioxide utilization in synthetic chemistry, catalysis, coordination chemistry and organometallic chemistry, green chemistry, marine biomass production by enhanced carbon dioxide fixation, marine biomass as source of fuels and chemicals applying the Biorefinery concept.
Actually she is director of the Interdepartmental Centre on Environmental Methodologies and Technologies–METEA at UNIBA.
In 2001 she was the winner of the RUCADI Prize on "Better Carbon Management - An Intelligent Chemical Use of CO_2" delivered by ACP-Belgium, Carburos Metalicos-Spain and ENIChem-Italy. Author of over 80 scientific papers on carbon dioxide utilization published in international Journals since 1995 and several book Chapters. She was Invited speaker at several international conferences.

Abstract

Aquatic biomass is currently considered as an ideal third generation biodiesel (biofuel) feedstock as they do not compete with food and feed crops and can produce higher amount of oil than the terrestrial biomass. The cultivation of algae is also very attractive because of its potential to fix atmospheric CO_2 into biomass and for enhanced biological fixation.
Several options can be considered to produce different kinds of biofuel such as biodiesel, bioethanol or biogas. In this presentation several technologies will be discussed for the conversion of aquatic biomass into biodiesel.

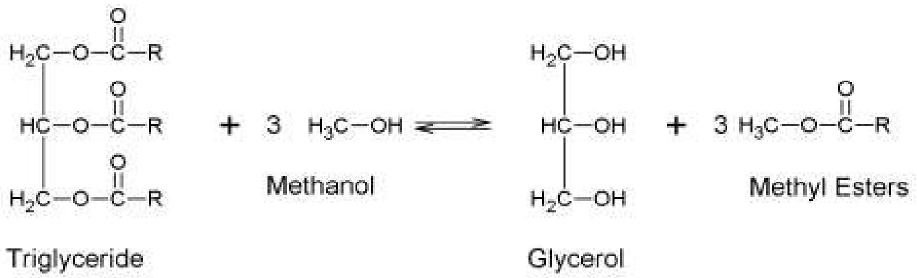
Introduction

There is a strong interest in the production and use of liquid biofuels [1, 2]. First generation biofuels have been mainly extracted from food and oil crops, including rapeseed, sugarcane, sugar beet, and maize [3]. Vegetable oils and animal have also been used applying conventional technologies [4]. The use of first generation biofuels has generated a lot of controversy, mainly due to their impact on global food markets and food security, especially with regards to the most vulnerable regions of the world economy. This has raised pertinent questions about their potential to replace fossil fuels and the sustainability of their production [5]. Currently, about 1% (14 million hectares) of the world's available arable land is used for the production of biofuels, providing 1% of global transport fuels. Clearly, increasing that share to anywhere near 100% is impractical owing to the severe impact on the world's food supply and the large areas of production land required [6]. The advent of second generation biofuels is intended to produce fuels from the whole plant matter of dedicated energy crops or agricultural residues, forest harvesting residues or wood processing waste [5], rather than from food crops.

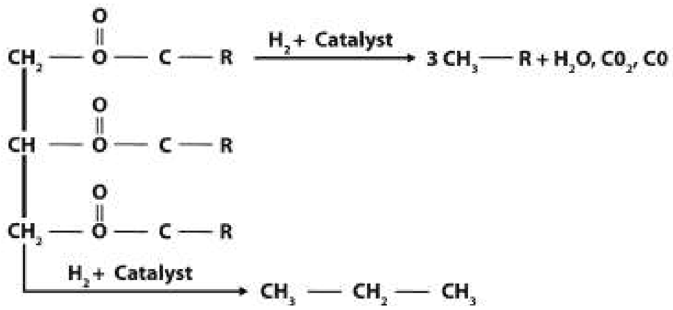
Based on current knowledge and technology projections, third generation biofuels specifically derived from aquatic biomass are considered to be a technically viable alternative energy resource that is devoid of the major drawbacks associated with first and second generation biofuels.
Micro- and macro-algae are photosynthetic organisms with simple growing requirements (light, CO_2, N, P, and K) that can produce lipids, proteins and carbohydrates in large amounts over short periods of time. These products can be processed into both biofuels and valuable co-products. In this lecture I will focus on dow-stream technologies for FAMEs production from algae.

Discussion

Several technologies have been developed for algae production that should replicate and enhance the optimum natural growth conditions using different type of cultivation (open pond, photobioreators).
To obtain oil from algae, it is important to concentrate them and then the oil can be extracted. Usually the conventional technologies use organic solvents which recover about 90% of the oil present in the biomass [7].
Supercritical carbon dioxide can also be used to extract oil [8]. Alternatively extraction can be carried out using microwave and ultrasound.
Other conversion technologies include the thermochemical conversion, where biomass in the absence of oxygen and at high temperature can be converted into various fuels including char, oil and gas. The process can be subdivided into pyrolysis and thermochemical liquefaction [9]. The former is executed at high temperature (350-530°C) at which a liquid, a gaseous and a solid fraction are produced. This process requires drying of the biomass while in the latter wet biomass is treated at lower temperature and high pressure (about 300 °C and 10 MPa). The bio-oil from the processing is composed of all organic compounds in the algae including lipids as well as proteins, fibers, and carbohydrates and therefore gives a higher yield than compared with the content of accumulated lipids in the algae cells.
The extracted oil is converted into biodiesel through the transesterification process during which it is transformed into alkyl methyl esters and glycerol. Such process is usually run in homogeneous conditions using NaOH or $NaOCH_3$ as promoters.



An interesting approach is the catalytic extraction that uses heterogeneous catalysts for an in situ transesterification in which lipids are released as methyl esters [10].
Algae in general produce oils rich of free fatty acids (FFAs) (up to 20%) that rises the problem of the catalyst. In general a two step process is adopted. Bifunctional catalysts are wished for the contemporary transesterification of lipids and esterification of FFAs [11]. Also, algae produce oils rich in polyunsaturated FFAs. These are more easily oxidated and the revelant biodiesel are not likely to meet the international standards [12]. To meet the biodiesel fuel quality standards (EN14214) the amount of poli-unsaturated species in algal oil can be reduced by partial catalytic hydrogenation.
An alternatively route for conversion bio-oil is its reaction with hydrogen over a catalyst followed by isomerization to produce a targeted mixture of alkanes, water, CO_2 and CO.



The alkane mixture can be fractionated to produce a synthetic kerosene jet fuel and hydrogenation-derived renewable diesel (HDRD) or green diesel.
The glycerol moiety derived from lipids can be converted to various compounds, among which fuels derivatives and added value chemicals.

Conclusions

Algal oil can be obtained from harvested biomass and can be converted into biodiesel, HDRD and synthetic jet fuel. Innovative technologies are welcome for an efficient conversion of biooil.

References

1. M. Bender, Potential conservation of biomass in the production of synthetic organics. Resources conservation and recycling **2000**, 30:49–58; Demirbas M.F. Current technologies for biomass conversion into chemicals and fuels. *Energy Sour Part A* **2006**, 28, *1181–1188*.
2. B. Kamm, P.R. Gruber, M. Kamm, Biorefinery industrial processes and products, *Status and future direction, vols. 1 and 2*. Weinheim:Wiley-Verlay Gmbtt and Co KGaA; **2006**.
3. FAO. The state of food and agriculture 2008. New York: *Food and Agriculture Organization*; **2008**.
4. FAO. Sustainable bioenergy: a framework for decision makers. *United Nations Energy*; **2007**.
5. A.Moore, Biofuels are dead: long live biofuels-part one. *New Biotechnology* **2008**, 25(1), 6–12.
6. IEA. World energy outlook 2006. Paris: International Energy Agency; **2006**.
7. N. Nagle, P. Lemke, Microalgal fuel production processes: Analysis of lipid extraction and conversion methods. Annual review Meeting Solar Energy Institute, Golden, CO **1989**, May 3-4.
8. A. Dibenedetto, T. Colonna, M. Carone, M. Aresta, C. Fragale, Production of biodiesel from macroalgae by supercritical CO_2 extraction and thermochemical liquefaction, *Environ.Chem Lett*, **2005** 3: *136–139*.
9. A. Demirbas, Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management* **2000**, 41: *633-646*.
10. M. Aresta, A. Dibenedetto, M. Ricci ENI Patent H10008, **2010**.
11. A. Dibenedetto, C. Pastore, L. di Bitonto, A. Colucci and M. Aresta *Energy and environmental Science submitted*
12. Y. Chisti, Biodiesel from microalgae, *Biotechnology Advances* **2007**, 25(3) *294-306*.

Acknowledgements

Part of this project has been funded by ENI.