Trends in Renewable Energy
OPEN ACCESS ISSN: 2376-2144
MINI-REVIEW futureenergysp.com/index.php/tre

Standards and Protocols for Characterization of Algae-Based Biofuels

Changyan Yang[1, 2*], Bo Zhang[1*], Chang Cui[1], Jinsheng Wu[1], Yigang Ding[1], Yuanxin Wu[1]

1: Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Key Laboratory of Novel Chemical Reactor and Green Chemical Technology, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Hubei, China
2: Hubei Key Laboratory for Processing and Application of Catalytic Materials, Huanggang Normal University, Hubei, China

Received April 23, 2016; Accepted May 1, 2016; Published May 4, 2016

Recently, algae have been considered as the third-generation biofuel feedstock, which can be converted to the precursor chemicals of drop-in fuels via either the algal lipid upgrading (ALU) pathway or the hydrothermal liquefaction (HTL) pathway. These precursors could be further processed and upgraded to fuels. This article reviews the standards and protocols that are suitable for characterization of drop-in algal biofuels. Applicable ASTM standards and European standards (EN) were summarized. The protocols that have been used by researches and the National Institute of Standards and Technology were also introduced.

Keywords: Algae-Based Biofuels; ASTM Standards; European Standards (EN); Drop-in Algal Biofuel; Algal Lipid Upgrading (ALU); Hydrothermal Liquefaction (HTL)

Introduction

Algae are a big variety of photosynthetic organisms, while microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that can grow rapidly and live in harsh conditions due to their unicellular or simple multicellular structure. It is estimated that more than 50,000 species exist, but only a limited number of algal species have been studied and analyzed [1]. Microalgae have the ability to mitigate greenhouse gases, and some species can accumulate oil with a high productivity, thereby having the potential for applications in producing the third-generation of biofuels [2].

During the past decade, government agencies and the private sector had shown tremendous interests in algae related studies. Thus, the algal technologies for biofuels production have been greatly advanced [3]. The algal biofuel production cost was significantly reduced, and the advanced process options for the conversion of algal biomass into biofuels and bioproducts have been developed [4]. Currently, there are two approaches that were suggested by the US Department of Energy as the promising technologies for algal biomass conversion. The first approach is call the algal lipid upgrading (ALU) pathway, in which algal oils are extracted from the biomass via high-pressure homogenization with hexane [5]. This approach was further improved by combining with a biological conversion route that converts carbohydrates in algae to ethanol. Therefore, an integrated biorefinery process for ALU pathway was established [6]. The second technique is via the hydrothermal liquefaction (HTL) pathway that produces a water-insoluble bio-crude oil by using treatments at high pressure (5-20 MPa)

*Corresponding author: ychy1969@163.com, bzhang_wh@foxmail.com

and at the temperature range of 250-450°C [7, 8]. Other techniques, such as pyrolysis [9] and gasification [10, 11], were also applied for converting algae to biofuels. However, these techniques have not been extensively studied yet, because of their inherent problems.

The products from ALU and HTL are crude algal oil and bio-crude oil, respectively. Due to the low selectivity of two pathways, both products contain impurities like heteroatoms, oxygenated compounds, and nitrogenated compounds. In order to synthesize algae-based drop-in fuels, it requires upgrading processes (such as cracking and hydrogenation) to improve the fuel quality [12]. This article reviews the standards and protocols that are suitable for characterization of algae-based biofuels.

Standards and Protocols for Characterization of Algae-Based Fuels

Drop-in fuels, which are a mixture of different hydrocarbons, include gasoline, diesel, and aviation fuel (*i.e.* jet fuel). The hydrocarbons of gasoline contain typically 4-12 carbon atoms (C4-C12), while diesel contains between 12 and 20 carbon atoms per molecule (C12-20) [13]. The molecules of the aviation fuel have a carbon number range of C8-C16 [14].

Characterization of drop-in algae biofuels should follow the national or international standards. Gasoline (*i.e.* Unleaded petrol) is the fuel derived from petroleum that meets the requirements of the standards ASTM D4814 in the USA [15] and EN 228 in Europe [16], and the diesel needs to meet the standards of ASTM D 975 [17] and EN 590 [18]. The EN 590:2013 is applicable to automotive diesel fuel containing up to 7.0 % fatty acid methyl esters (FAMEs). Biodiesel is defined in the standard EN 14214 as FAMEs only [19], while US biodiesel is comprised of mono-alkyl esters of long-chain fatty acids derived from animal fats or vegetable oil as shown in the ASTM D6751 [20]. The standard specifications of aviation turbine fuels are available in ASTM D1655 [21] and ASTM D7566 [22]. According to ASTM 7566-11, up to 50% bio-derived synthetic fuels can be blended into conventional jet fuel [23].

Besides using the ASTM or EN standards, algal biofuels were characterized using various analytic protocols by researchers. Organic chemicals were identified by using the gas chromatography-mass spectrometry (GC-MS). Elemental analyses for carbon, hydrogen, nitrogen, and sulfur contents were determined using a CHNS/O analyzer. The H/C ratio is a useful indicator for the saturation extent of the aromatics in upgraded oils [24]. Alternately, sulfur and other minerals can be measured by ICP-OES. The higher heating value (HHV) can be calculated with the DuLong formula according to elemental analyses [25], or directly measured using an oxygen bomb calorimeter.

Because the oil products still contain compounds that cannot be identified by the GC-MS, more detailed analyses may be necessary. Following the ASTM D1319 method, hydrocarbon types in the oil can be determined by fluorescent indicator adsorption [26]. The similar identification can also be done by the carbon-13 NMR [27]. The boiling point distribution of oil samples can be obtained by performing fast simulated distillation analysis according to the ASTM D7169 [28]. Alternately, the ASTM D2887 is applicable to oil products with a boiling point between 55°C-538°C [29].

Aforementioned methods have been successfully applied to analyzing upgraded algal fuels. Scientists at the National Institute of Standards and Technology (NIST) combined methods of distillation curve method, NMR, and GC-MS to evaluate the properties of an algal-based hydrotreated renewable diesel [30]. Additional test methods including measuring the speed of sound, the cloud point, density, the cetane index, the storage stability, and the oxidation stability were also developed [31]. The combustion of this algal diesel has been tested in a diesel engine along with petroleum diesel [32].

ACKNOWLEDGMENTS

We are grateful for the support from the School of Chemical Engineering and Pharmacy at the Wuhan Institute of Technology.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

REFERENCES

[1] Richmond, A. (2008). *Handbook of microalgal culture: biotechnology and applied phycology*, John Wiley & Sons.

[2] Chisti, Y. (2007). Biodiesel from microalgae. *Biotechnology Advances*, 25(3), 294-306. DOI: 10.1016/j.biotechadv.2007.02.001

[3] Picardo, M., de Medeiros, J., Monteiro, J., Chaloub, R., Giordano, M., and de Queiroz Fernandes Araújo, O. (2013). A methodology for screening of microalgae as a decision making tool for energy and green chemical process applications. *Clean Technologies and Environmental Policy*, 15(2), 275-291. DOI: 10.1007/s10098-012-0508-z

[4] NAABB (2014). National Alliance for Advanced Biofuels and Bioproducts Synopsis. *http://www.energy.gov/sites/prod/files/2014/07/f18/naabb_synopsis_report_0.pdf*. (accessed on 5/2/2016)

[5] US Department of Energy (2013). Algal Lipid Upgrading. *https://www1.eere.energy.gov/bioenergy/pdfs/algal_lipid_upgrading.pdf*. (accessed on 5/2/2016)

[6] Dong, T., Knoshaug, E. P., Davis, R., Laurens, L. M. L., Van Wychen, S., Pienkos, P. T., and Nagle, N. Combined algal processing: A novel integrated biorefinery process to produce algal biofuels and bioproducts. *Algal Research*. DOI: 10.1016/j.algal.2015.12.021

[7] Zhang, B., Keitz, M., and Valentas, K. (2008). Thermal Effects on Hydrothermal Biomass Liquefaction. *Applied Biochemistry and Biotechnology*, 147(1-3), 143-150. DOI: 10.1007/s12010-008-8131-5

[8] Guo, Y., Yeh, T., Song, W., Xu, D., and Wang, S. (2015). A review of bio-oil production from hydrothermal liquefaction of algae. *Renewable and Sustainable Energy Reviews*, 48, 776-790. DOI: 10.1016/j.rser.2015.04.049

[9] Miao, X., Wu, Q., and Yang, C. (2004). Fast pyrolysis of microalgae to produce renewable fuels. *Journal of Analytical and Applied Pyrolysis*, 71(2), 855-863. DOI: 10.1016/j.jaap.2003.11.004

[10] Stucki, S., Vogel, F., Ludwig, C., Haiduc, A. G., and Brandenberger, M. (2009). Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. *Energy & Environmental Science*, 2(5), 535-541. DOI: 10.1039/b819874h

[11] Duman, G., Uddin, M. A., and Yanik, J. (2014). Hydrogen production from algal biomass via steam gasification. *Bioresource Technology*, 166, 24-30. DOI: 10.1016/j.biortech.2014.04.096

[12] Zhao, C., Bruck, T., and Lercher, J. A. (2013). Catalytic deoxygenation of microalgae oil to green hydrocarbons. *Green Chemistry*, 15(7), 1720-1739. DOI: 10.1039/c3gc40558c

[13] Advanced Motor Fuels (2015). Diesel and gasoline. *http://www.iea-amf.org/content/fuel_information/diesel_gasoline#gasoline*. (accessed on 5/2/2016)

[14] Chevron Products Corporation (2007). Aviation Fuels Technical Review. *https://www.cgabusinessdesk.com/document/aviation_tech_review.pdf*. (accessed on 5/2/2016)

[15] ASTM D4814 (2015). *Standard Specification for Automotive Spark-Ignition Engine Fuel*, ASTM International, West Conshohocken, PA. DOI: 10.1520/D4814-15A

[16] British Standards Institution (2013). *BS EN 228:2012 Automotive fuels. Unleaded petrol. Requirements and test methods*, BSI.

[17] ASTM D975 (2015). *Standard Specification for Diesel Fuel Oils*, ASTM International. DOI: 10.1520/D0975-15B

[18] British Standards Institution (2013). *BS EN 590:2013 Automotive fuels. Diesel. Requirements and test methods*, BSI.

[19] British Standards Institution (2013). *BS EN 14214:2012+A1:2014. Liquid petroleum products. Fatty acid methyl esters (FAME) for use in diesel engines and heating applications. Requirements and test methods*, British Standards Institution, London, UK.

[20] ASTM D6751 (2015). *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*, ASTM International, West Conshohocken, PA. DOI: 10.1520/D6751-15A

[21] ASTM D1655 (2015). *Standard Specification for Aviation Turbine Fuels*, ASTM International, West Conshohocken, PA. DOI: 10.1520/D1655-15C

[22] ASTM D7566 (2015). *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*, ASTM International, West Conshohocken, PA. DOI: 10.1520/D7566-15A

[23] Popov, S., and Kumar, S. (2013). Renewable fuels via catalytic hydrodeoxygenation of lipid-based feedstocks. *Biofuels*, 4(2), 219-239. DOI: 10.4155/bfs.12.89

[24] Elliott, D. C., and Schiefelbein, G. F. (1989). Liquid hydrocarbon fuels from biomass. *papers of the American Chemical Society*, 34(4), 1160.

[25] Mason, D. M., and Gandhi, K. N. (1983). Formulas for calculating the calorific value of coal and coal chars: Development, tests, and uses. *Fuel Processing Technology*, 7(1), 11-22. DOI: 10.1016/0378-3820(83)90022-X

[26] ASTM D1319 (2014). *Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption*, ASTM International, West Conshohocken, PA.

[27] Elliott, D. C. (2007). Historical Developments in Hydroprocessing Bio-oils. *Energy & Fuels*, 21(3), 1792-1815. DOI: 10.1021/ef070044u
[28] ASTM D7169 (2011). *Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography*, ASTM, West Conshohocken, PA.
[29] ASTM D2887 (2015). *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*, ASTM International, West Conshohocken, PA.
[30] Hsieh, P. Y., Widegren, J. A., Fortin, T. J., and Bruno, T. J. (2014). Chemical and Thermophysical Characterization of an Algae-Based Hydrotreated Renewable Diesel Fuel. *Energy & Fuels*, 28(5), 3192-3205. DOI: 10.1021/ef500237t
[31] Fu, J., and Turn, S. Q. (2014). Characteristics and Stability of Neat and Blended Hydroprocessed Renewable Diesel. *Energy & Fuels*, 28(6), 3899-3907. DOI: 10.1021/ef500544p
[32] Luning Prak, D. J., Cowart, J. S., Hamilton, L. J., Hoang, D. T., Brown, E. K., and Trulove, P. C. (2013). Development of a Surrogate Mixture for Algal-Based Hydrotreated Renewable Diesel. *Energy & Fuels*, 27(2), 954-961. DOI: 10.1021/ef301879g