Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 56 (2013) 591 – 596

Procedia Engineering

www.elsevier.com/locate/procedia

5th BSME International Conference on Thermal Engineering

Influence of fatty acid structure on fuel properties of algae derived biodiesel.

Muhammad Aminul Islam[1*], Godwin A. Ayoko[1], Richard Brown[1], Doug Stuart[5], Kirsten Heimann[2,3,4]

[1]*Faculty of Science and Engineering, Queensland University of Technology, Brisbane, Queensland 4001, Australia*

[2]*School of Marine and Tropical Biology, James Cook University, Townsville, Queensland 4811, Australia*

[3]*Centre for Sustainable Fisheries and Aquaculture, James Cook University, Townsville, Queensland 4811, Australia*

[4]*Centre for Biodiscovery and Molecular Development of Therapeutics, James Cook University, Townsville, Queensland 4811, Australia*

[5]*EchoTech Biodiesel, Narangba, Queensland 4505, Australia*

Abstract

Physical and chemical properties of biofuel are influenced by structural features of fatty acid such as chain length, degree of unsaturation and branching of the chain. A simple and reliable calculation method to estimate fuel property is therefore needed to avoid experimental testing which is difficult, costly and time consuming. Typically in commercial biodiesel production such testing is done for every batch of fuel produced. In this study 9 different algae species were selected that were likely to be suitable for subtropical climates. The fatty acid methyl esters (FAMEs) of all algae species were analysed and the fuel properties like cetane number (CN), cold filter plugging point (CFPP), kinematic viscosity (KV), density and higher heating value (HHV) were determined. The relation of each fatty acid with particular fuel property is analysed using multivariate and multi-criteria decision method (MCDM) software. They showed that some fatty acids have major influences on the fuel properties whereas others have minimal influence. Based on the fuel properties and amounts of lipid content rank order is drawn by PROMETHEE-GAIA which helped to select the best algae species for biodiesel production in subtropical climates. Three species had fatty acid profiles that gave the best fuel properties although only one of these (*Nannochloropsis oculata)* is considered the best choice because of its higher lipid content.

Selection and peer review under responsibility of the Bangladesh Society of Mechanical Engineers

Keywords: Microalgae; fatty acid; fuel property; biodiesel; PROMETHEE-GAIA.

Nomenclature

FAME	Fatty acid methyl ester
CN	Cetane number
CFPP	Cold filter plugging point (^{0}C)
KV	Kinetic viscosity (mm^2/sec)
HHV	Higher heating value (MJ/kg)
MCDM	Multi-criteria decision method

*Corresponding author.

Email address: ma.islam@qut.edu.au

1877-7058 © 2013 The Authors. Published by Elsevier Ltd.
Selection and peer review under responsibility of the Bangladesh Society of Mechanical Engineers
doi:10.1016/j.proeng.2013.03.164

1. Introduction

A systematic analysis of the fatty acid composition and comparative fuel properties are very important to select the best species for biodiesel production. The particular culture system may significantly influence the algal lipid content and fatty acids structure. The most common fatty acid profiles of algae consist mainly of Palmitic (Hexadecanoic_C16:0), Stearic (octadecanoic_C18:0), Oleic (Octadecenoic_C18:1), Linoleic (Octadecadienoic) and Linolenic (Octadecatrienoic_C18:3) acids [1].Along with these major fatty acids there are varieties of fatty acids in minor amounts which have some influence on fuel property. However there is no single fatty acid that is responsible for any particular fuel property.

The cetane number related to the ignition quality decreases with a decreasing chain length, increased branching, and increased saturation in the fatty acid chain. The higher the cetane number, the better the ignition quality whereas saturated esters, which are advantageous for cetane number possess poor cold-flow properties. Unsaturated, especially poly unsaturated fatty esters improve the cold-flow because of their lower melting points which are desirable but also lower the cetane number and oxidation stability which is undesirable for fuel [2].

These fatty acids have a direct impact on the chemical and physical properties of biofuel. There are methods we can use to derive the fuel properties like cetane number (CN), cold filter plugging point (CFPP), kinematic viscosity (KV), density and higher heating value (HHV) from the fatty acid composition, without experimental tests which can avoid the cost of test and time. The cetane number calculated by ASTM976 is too low when there is a higher number of saturated acids in the ester mixture and a higher number in the mixture with high levels of poly unsaturated acids. Klopfenstein proposed to calculate cetane number based on individual fatty acids [3] which is difficult, expensive and time consuming.

In this study few simple and reliable methods are utilized to estimate some important fuel properties. Cetane number is calculated using Krishnankura [4] proposed method which depends on iodine value and saponification value proposed by Kalayasiri et al.[5]. The degree of unsaturation (DU), long chain saturation factor (LCSF) and cold filter plug point (CFPP) were calculated from fatty acid composition following Remos [6] proposal. L.F.Remirez [7] proposed to calculate physical properties including kinematic viscosity, density, and higher heating value (HHV) from mass fraction of fatty acids.

Selection of species for biodiesel production depends on fuel properties and oil content along with engine performance and emission characteristics. There are multiple-criteria to determine the suitable algae species for biodiesel. A review of the MCDM literature revealed that the PROMETHEE-GAIA approach provides quite useful and clear guidelines for the preferred decision [8] in comparison to other MCDM. The significant advantage of PROMETHEE-GAIA is that it facilitates a rational decision making process which is achieved by virtue of a decision vector that directs the decision makers towards 'preferred' solutions [9].

This study applies the PROMETHEE-GAIA algorithm to a calculated data set containing chemical and physical properties of algae derived from fuel and lipid content of nine different algae species. The fatty acids composition is used as criterion along with fuel properties and lipid content to find the influence of individual fatty acids on fuel properties.

2. Materials and methodology

2.1 Algae culture, lipid content and fatty acid methyl ester (FAMEs) analysis

This study was undertaken to characterise suitable species of Algae for biofuel production. There were nine different species including; NQAIF034 *Amphidinium* sp., NQAIF038 *Biddulphia* sp., NQAIF031 *Phaeodactylum tricornutum*, NQAIF284 *Picochlorum* sp., NQAIF010 *Nannochloropsis oculata, NQAIF254 Extubocellulus* sp., NQAIF294 *Scenedesmus dimorphus,* NQAIF301 *Franceia* sp. and NQAIF303 *Mesotaenium* sp. Each was taken from different growth media but from the same growing environment to investigate their total lipid content and FAME profile using a gas chromatography (GC). There are many successful extraction processes in a laboratory setting but large scale systems in the commercial setting are yet to be developed. In this work, hexane extraction processes are followed in the NQAIF laboratory at James Cook University (JCU) in Townsville, Australia. The composition of fatty acid methyl ester (FAME) analysed from the identified peak on GC standard curve for nonadecanoic (C19:0) acid methyl ester is prepared to quantify the FAME from the GC peak. After concentration is calculated from the peak the fatty acid composition is calculated and shown in percentage in table 1.

2.2 Calculation of fuel properties from fatty acid composition

There are many useful methods proposed by researchers to estimate fuel properties from its fatty acid profile. An equation has been proposed by Klopfenstein [3] to estimate cetane number for individual fatty acids. In this case however we use Krisnangkura [4] proposed equation to estimate the cetane number (CN) of algae oil methyl ester based on their saponification value (SV) and iodine value (IV). Kalayasiri et al.[5] presented equations to estimate the SV and IV from fatty acid methyl ester composition. Ramos et al.[6] proposed equations to calculate the degree of unsaturation (DU) based on the amount of mono unsaturated and poly unsaturated fatty acids whereas the long chain saturation factor (LCSF) and cold filter plugging point (CFPP) lending more weight to the composition of fatty acids with long chains.
Recently Ramirez [7] proposed some empirical equations to estimate cetane number and three physical properties of methyl ester including kinetic viscosity, density and higher heating value. These properties were calculated based on molecular weight and degree of unsaturation of FAME.

Table 1: Fatty acid compositions of nine different algae species (g/100g of fatty acids).

Fatty acid	*Amphidinium* sp.	*Bidulphia* sp.	*Phaeodactylum tricornutum*	*Picochlorum* sp.	*Nannochlopsis oculata.*	*Extubocellulus* sp.	*Scenedesmus dimorphos*	*Franceia* sp.	*Mesotaenium*.sp.
C8:0	0.0	0.0	0.0	0.1	0.2	0.0	0.0	0.0	0.0
C10:0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
C12:0	0.0	0.5	0.0	0.0	0.4	0.0	0.0	0.0	0.0
C13:0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C 14:0	0.8	21.4	3.3	0.5	5.8	6.6	0.5	0.6	0.5
C 15:0	0.0	2.2	0.4	0.3	0.5	0.4	0.4	0.6	0.5
C 15:1	0.0	0.0	0.0	0.0	0.0	0.0	2.3	2.2	2.3
C 16:0	35.7	23.6	23.6	16.8	32.2	25.6	15.8	12.9	13.4
C16:1 (7)	1.1	33.2	48.2	1.2	29.6	60.6	1.6	1.4	1.3
C 16:1 (9)	0.0	0.0	0.0	0.0	0.0	0.0	3.6	5.9	4.8
C16:2 (7,10)	0.0	1.7	1.4	5.1	0.0	2.7	2.1	1.5	2.2
C16:2 (9,12)	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.8	0.7
C 17:0	0.0	0.0	0.0	0.4	0.4	0.0	0.4	0.5	0.5
C16:3 (cis 6,9,12)	0.0	4.4	4.3	3.5	0.0	0.0	0.5	0.7	0.6
C16:3 (7, 10, 13)	0.0	0.0	0.0	0.0	0.0	0.0	1.6	1.3	1.8
C16:4 (4,7,10,13)	0.0	0.0	0.0	0.0	0.0	0.0	15.6	17.0	16.4
C 18:0	4.1	0.8	0.8	3.4	1.0	0.9	0.6	0.5	0.6
C 18:1 (9)	19.4	1.5	3.6	15.5	20.1	3.2	7.1	4.4	5.7
C 18:1 (x)	0.0	0.6	2.3	0.0	0.0	0.0	1.8	2.3	1.9
C 18:2 (cis - 9,12)	0.0	0.0	0.0	35.8	1.3	0.0	12.8	8.5	11.8
C18:3 all cis 6,9,12	0.0	0.0	0.0	14.9	0.0	0.0	1.0	1.2	1.0
C 18:3 (all cis - 9,12,15)	0.0	0.0	0.0	0.0	0.0	0.0	25.0	32.3	30.4
C18:4 (6,9,12,15)	0.0	0.0	0.0	0.0	0.0	0.0	3.5	3.7	3.1
C20:0	5.7	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0
C 20:2 (cis - 11,14)	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.0
C20:5(allcis)5,8,11,14,17)	11.9	9.6	12.1	0.0	8.3	0.0	0.0	0.9	0.8
C22:6	20.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C 24:0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.8	0.0
C 24:1 (cis - 15)	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0

2.3 The PROMETHEE-GAIA analysis

Most MCDM problems involve several criteria. As a result, the solution of the problem exists in a multi-dimensional space. The GAIA (Graphical Analysis for Interactive Assistance) component of the PROMETHEE-GAIA algorithm performs Principal Component Analysis (PCA) to reduce the dimensionality of the problem to 2 spatial dimensions (called the GAIA plane) for visual interpretation of the problem.

Unlike PCA, PROMETHEE-GAIA has a critical difference in that it provides a decision vector for the analyst. This enables the decision maker to view different alternatives in the GAIA plane, and to be directed towards preferred solutions by the decision vector. The theory of the PROMETHE-GAIA algorithm is well described in literature [8-16].

In this study some estimated biodiesel properties (cetane number, iodine value, cold filter plugging point, kinetic viscosity, density and higher heating value) are analysed with PROMETHEE-GAIA to select the most suitable species for biodiesel production.

3. Results and discussion

Some fuel properties derived from their fatty acid profile by few estimation methods are shown in table 2. Based on these fuel properties and lipid content, suitable algae species need to be chosen for biodiesel production. These MCDM problems have been considered in nine different criteria (five chemical and three physical properties of fuel and lipid content) to select the suitable one from nine different algae species for biodiesel production. All criteria are weighted equally.

Table 2: Derived chemical and physical properties of fatty acid methyl ester.

Criteria		Algae species								
(Fuel property)	Standard	*Amphidinium* sp.	*Bidulphia* sp.	*Phaeodactylum tricornutum*	*Picochlorum* sp.	*Nannochlopsis oculata.*	*Extubocellulus* sp.	*Scenedesmus dimorphos*	*Franceia* sp.	*Mesotaenium* sp.
LCSF	↓	11.3	2.7	2.8	5.5	3.7	3	3.8	3.1	1.6
CFPP(^{0}C)	-5 to -13	19.1	-7.9	-7.8	0.7	-4.8	-7	-4.6	-6.7	-11
IV	120 ↓	159	87.9	114	135	80.6	65.1	183.7	205.5	202
SV		188.2	210	204	195	203	209	195.7	197.5	200
CN_1	51min	39.5	52.5	47.3	44	55	57.8	32.9	27.7	28.3
CN_2	51min	42.9	54.6	50.3	49.0	57.9	60.9	37.1	33.3	33.4
KV (mm2/sec)	1.9-6.0	4.1	3.7	3.7	4.0	4.2	3.9	3.6	3.5	3.4
Density(g/cm3)	0.88-0.89	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
HHV(MJ/Kg)	40	40.3	40.0	39.8	39.9	39.8	40.1	40.2	40.4	40.2
%Lipid DW^{-1}	↑	18.9	24.9	21.7	30.5	41.0	27.6			

CN_1: Cetane number derived by Krishnangkura's method [4]. CN_2: Cetane number derived by Ramirez's method [7].

Iodine value is an indicating parameter of the degree of saturation in fuel which influences the fuel viscosity and cold filter plugging point. The lower the iodine value is the higher CN which means better the fuel and vice versa[17].

Figure 1 presents the relation of fuel properties for each fatty acid. The dependence of long chain saturated factor (LCSF) and cold filter plugging point (CFPP) are the same with fatty acids. SV and CN are associated with the following fatty acids C16:1,7; C8:0; C20:2,c11,14; C12:0; C16:1,9; C13:0; C14:0; C18:0; C18:2allc6,9; and C20:5allc5 whereas IV is fairly allied with fatty acids C10:0; C16:2,9,12; C16:3c6,9,12; C19:0cis; C17:0; C22:0; C24:1c15; C16:2,7,10; C24:0; and C18;1x. LCSF, CFPP are positively related with the following fatty acids C16:0; C18:2c9,12; C18:3,7,10,13; C18:3allc9, C18:4,6,9,12,15; C15:0; C15:1m C18:1,9; and C16:4,4,7,10,13 even though they are showing opposite in the graph. This happened because of the negative value of CFPP. The more the negative value means more closely depends on these fatty acids in the opposite direction. IV and CN are oppositely related with fatty acids.

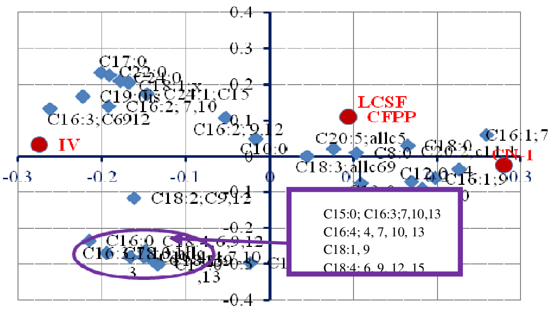


Fig.1. Loadings plot from PROMETHEE data based on fatty acids and fuel chemical properties only.

The relation of fatty acids and physical properties of fuel which are derived by Ramirez's method are shown in figure 2. The following fatty acids, C16:0; C18:3allc9; C16:3,7,10,13; C18:1,9: C15,0; C18:4,6,9,12,15; C16;4,4,7,10,13; C15:1; and C18:2c9,12 have negative influence on KV and CN. HHV and density are associated with the following fatty acid: C170, C220, C190is, C163c6912, C162710, C162912, C181x, C241c15, and C240. CN and KV has positively influenced the fatty acids C10:0; C13:0; C18:0; C16:1,9; C16:1,7; C14:0; C12:0; C18:3allC69, and C20:5allc5. Density is inversely related to the CN and KV of fuel.

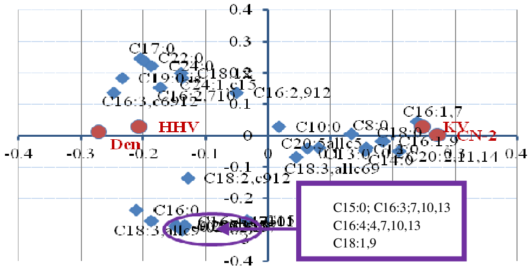
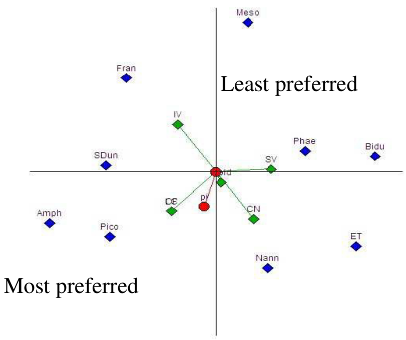


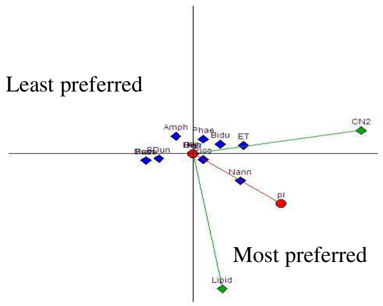
Fig.2. Loadings plot for PROMETHEE based on fatty acids and fuel physical properties only.

In the process of suitable species selection, multiple fuel properties and lipid content is considered for PROMETHEE-GAIA analysis and graphically presented in figure 3(a) and (b). Figure 3(a) shows a clear view of *Nannochlopsis oculata* and is most likely the best choice considering the fuel chemical properties and lipid content. Variance explained by the first two PCs is 93.99%; all variables were maximised and modelled using the usual preference function.



(a)

Fig.3(a). GAIA plot based on fuel chemical properties and lipid only.



(b)

Fig.3(b). GAIA plot based on fuel physical properties and lipid only

Graphical presentation of algae species selection influenced by the fuel physical properties and lipid content is shown in figure 3(b). In interpreting these results, the length of the decision vector (pi) is critical, as a longer decision vector indicates a greater decision making power. Initially the usual preference function was used and the decision vector was shorter therefore linear preference function is used and a stronger decision vector is found. Variance explained by the first two PCs is 100%; all variables were maximised (which means higher variable values are preferred) and modelled using linear preference function and the standard for each as the preference threshold. . Regardless the preference function used, the *nannochlopsis oculata* is chosen to be the best algae species for biodiesel production

4. Conclusion

In commercial biodiesel production it is essential to reduce cost and time with efficient processes. This work provides much needed support to optimise biodiesel production from algae. Our main aim was to investigate the influence of each fatty acid to fuel properties. The higher the poly unsaturated fatty acid, the higher the IV value and lower the cetane number. Kinematic viscosity is highly associated with saturated fatty acids whereas higher heating value increases with higher saturated fatty acids. The process of selecting the best species depended on the fuel properties which PROMETHEE-GAIA provides a clear graphical representation.

Acknowledgement

The author acknowledge NQAIF (North Queensland Algal Identification/culturing Facility), JCU, for their support throughout this work. Author also acknowledge for the financial support from QUT post graduate research scholarship.

References

[1] G. Knothe, "Improving biodiesel fuel properties by modifying fatty ester composition," *Energy Environ. Sci.,* vol. 2, pp. 759-766, 2009.

[2] G. Knothe, "“Designer” Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties†," *Energy & Fuels,* vol. 22, pp. 1358-1364, 2008.

[3] W. Klopfenstein, "Estimation of cetane index for esters of fatty acids," *Journal of the American Oil Chemists' Society,* vol. 59, pp. 531-533, 1982.

[4] K. Krisnangkura, "A Simple Method For Estimation of Cetane Index of Vegetable Oil Methyl Esters," *JAOCS,,* vol. VoL 63, no . 4 1986.

[5] P. J. Kalayasiri, N. Krisnangkura, K., "Survey of seed oils for use as diesel fuels," *Journal of the American Oil Chemists' Society,* vol. 73, pp. 471-474, 1996.

[6] M. J. Ramos, C. M. Fernandez, A. Casas, L. Rodriguez, and A. Perez, "Influence of fatty acid composition of raw materials on biodiesel properties," *Bioresource Technology,* vol. 100, pp. 261-268, 2009.

[7] J. E. R.-R. Luis Felipe Ramírez-Verduzco , Alicia del Rayo Jaramillo-Jacob, "Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition," *Fuel,* 2011.

[8] M. Behzadian, R. Kazemzadeh, A. Albadvi, and M. Aghdasi, "PROMETHEE: A comprehensive literature review on methodologies and applications," *European Journal of Operational Research,* vol. 200, pp. 198-215, 2010.

[9] J. P. Brans and B. Mareschal, "The PROMCALC & GAIA decision support system for multicriteria decision aid," *Decision support systems,* vol. 12, pp. 297-310, 1994.

[10] J. P. Brans and B. Mareschal, "PROMETHEE methods," *Multiple criteria decision analysis: state of the art surveys,* pp. 163-186, 2005.

[11] J. P. Brans, P. Vincke, and B. Mareschal, "How to select and how to rank projects: The PROMETHEE method," *European Journal of Operational Research,* vol. 24, pp. 228-238, 1986.

[12] M. Dağdeviren, "Decision making in equipment selection: an integrated approach with AHP and PROMETHEE," *Journal of Intelligent Manufacturing,* vol. 19, pp. 397-406, 2008.

[13] W. De Keyser and P. Peeters, "A note on the use of PROMETHEE multicriteria methods," *European Journal of Operational Research,* vol. 89, pp. 457-461, 1996.

[14] P. Karande and S. Chakraborty, "Application of PROMETHEE-GAIA method for non-traditional machining processes selection," *Management science,* vol. 2, 2012.

[15] B. Mareschal and J. P. Brans, "Geometrical representations for MCDA," *European Journal of Operational Research,* vol. 34, pp. 69-77, 1988.

[16] J. P. B. a. P. Vincke, "A PREFERENCE RANKING ORGANISATION METHOD (The PROMETHEE Method for multiple criteria Decision-Making)," *Management science,* vol. 31, pp. 647-656, 1985.

[17] S. C. P V Rao, Richard Brown, Kai-Shen Wu, " Influence of iodine value on combustion and NO_x characteristics of a diesel engine. ," p. 0451, 2010.