Production of Biodiesel from Seeds of Moringa oleifera (Drumstick Plant) and Determination it's Quality Parameters By

Mahboob Ali Kalhoro, Gulzar Hussain Jhatial, Santosh Kumar, Sadia Ferheen, Noor-Ul-Aqsa, Amanat Ali and Syed Najam Ul Islam

ISSN 0970-4973 (Print) ISSN 2319-3077 (Online/Electronic)

Index Copernicus International Value IC Value of Journal 4.21 (Poland, Europe) (2012) Global Impact factor of Journal: 0.587 (2012)

J. Biol. Chem. Research Volume 31 (1) 2014 Pages No. 520-525

Journal of Biological and Chemical Research

(An International Journal of Life Sciences and Chemistry)

Published by Society for Advancement of Sciences®

Biol. Chem. Research. Vol. 31, No. 1: 520-525 (2014) (An International Journal of Life Sciences and Chemistry) Ms 31/1/52/2014, All rights reserved ISSN 0970-4973 (Print) ISSN 2319-3077 (Online/Electronic)



Dr. Mahboob Ali http:// www.jbcr.in jbiolchemres@gmail.com info@jbcr.in

RESEARCH PAPER

Accepted: 21/03/2014 Revised: 15/03/2014

Received: 10/01/2014 Production of Biodiesel from Seeds of Moringa oleifera (Drumstick Plant) and Determination it's Quality Parameters

Mahboob Ali Kalhoro, Gulzar Hussain Jhatial, Santosh Kumar, Sadia Ferheen, *Noor-UI-Aqsa, Amanat Ali and Syed Najam UI Islam

Fuel Research Centre, PCSIR Karachi, 1 PRC, PCSIR Labs Complex, Karachi, Pakistan *Chemistry Department, University of Karachi, Pakistan

ABSTRACT

Biodiesel processing and quality are closely related. Biodiesel is technically competitive and have technical advantages compared to conventional petroleum Diesel fuel. Biodiesel has become more attractive recently because of its environmental benefit. The processes used to refine the feedstock and convert it to biodiesel determine whether it will meet the applicable specifications. This paper will describe the processing and production of biodiesel and how this determines its quality. The emphasis has been processing of biodiesel by reacting oil of Moringa oleifera with methanol and the standardized its guality with the AST M method. The Flash point, closed cup, Water and sediment, Kinematic viscosity at 40°C, Sulfated ash, Total Sulfur, Copper strip corrosion, C-tane number, Carbon residue, Acid number, Free glycerin, Total glycerin, Phosphorus and Vacuum distillation end point, 145 °C, 0.050%, 4.25 mm2/s, 0.020%, 0.04%, No.3, 49, 0.03%, 0.55 mg KOH/g, 0.02%, 0.22%, 20 ppm and 352°C respectively have been determined.

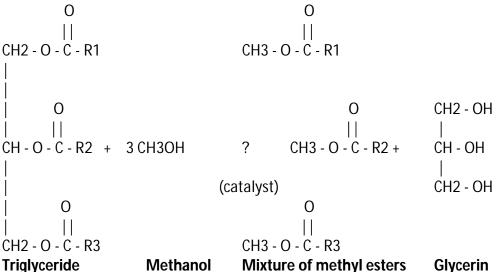
Key Word: Biodiesel, Moringa oleifera, Qulity parameters and Determination.

INTRODUCTION

Moringa oleifera (synonym: Moringa pterygosperma) is the most widely cultivated species of the genus *Moringa*, which is the only genus in the family Moringaceae. The commonly it is called drumstick tree (National Research Council, 2008). The yields of oil derived from the seed kernels has been estimated 250 liters per hectare (Radovich, T., 2009), whereas Rashid et, al. (2010) reported that Moringa seed oil has potential for use as a Biodiesel.

Published by Society for Advancement of Science[®]

Biodiesel is produced by chemically reacting a fat or oil with an alcohol, in the presence of a catalyst. The product of the reaction is a mixture of methyl esters, which are known as *biodiesel*, and glycerol, which is a high value co-product. The process is known as *transesterification*, as shown in the equation below, where R1, R2, and R3 are long hydrocarbon chains.



There are only five chains that are common in most vegetable oils and animal fats (others are present in small amounts). The relative amount of the five methyl esters determines the physical properties of the fuel, including the C-tane number, cold flow, and oxidative stability. While virtually all commercial biodiesel producers use an alkali-catalyzed process for the Transesterification process, other approaches have been proposed including acid catalysis (M.Canakci et al, 1999) and enzymes (L.A. Nelson et al; 1996, Y. Shimada et al; 1999, Y. Watanabe et al; 2002, W.H. Wu et al; 1999). The use of acid catalysts has been found to be useful for pre treating high free fatty acid feed stocks but the reaction rates for converting triglycerides to methyl esters are very slow. Enzymes have shown good tolerance for the free fatty acid level of the feedstock but the enzymes are expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification (ASTM International, West Conshohocken, PA (2002). Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area (Y. Shimada et al; 1999, Y. Watanabe et al; 2002, W.H. Wu et al; 1999).

Alkali-catalyzed Transesterification

This processes involved in biodiesel production from feedstock containing low levels of free fatty acids (FFA). It includes soybean oil, canola (rapeseed) oil, and the higher grades of waste restaurant oils. Alcohol, catalyst, and oil are combined in a reactor and agitated for one hour at 60°C. Smaller plants often use batch reactors by W.D. Stidham et al (2000) but larger plants (> 4 million liters/yr) use continuous flow processes involving continuous stirred-tank reactors or plug flow reactors (G. Assman et al; 1996).

Water may be added to the reaction mixture after the transesterification is complete to improve the separation of glycerol (G. Assman et al; 1996 and T. Wimmer, 1995]. Saka and Kusiana (2001, 2004), Dasari et al. (2003), and Diasakou et al. (2004), claim that it is possible to react the oil and methanol without a catalyst, which eliminates the need for the water washing step. However, high temperatures and large excesses of methanol are required. Kreutzer (1984) has described how higher pressures and temperatures (90 bar, 240°C) can transesterify the fats without prior removal or conversion of the free fatty acids. Boocock et al. (2003, 2001) have developed a novel technique for accelerating the transesterification reaction rate. During its early stages, the transesterification reaction is limited by the low solubility of the alcohol, especially methano I, in the oil. Boocock proposes the addition of a co solvent to create a single phase and this greatly accelerates the reaction so that it reaches substantial completion in a few minutes. The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high free fatty acid feed stocks. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids, as shown in the following reaction.

| Sodium soap Acid | Fatty acid Salt | |
|----------------------|------------------|--|
| Na+ -O - C - R + HCI | HO -C - R + NaCI | |
| | | |
| 0 | 0 | |

The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process.

Acid Catalyzed Pretreatment

Special processes are required if the oil or fat contains significant amounts of FFAs. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstock, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to this feedstock, the free fatty acids react with the catalyst to form soap and water as shown in the reaction below:

| 0 | | 0 | | |
|--------------|-----|--------------|---|-----|
| | | | | |
| HO - C - R + | КОН | K+ -O -C - R | + | H2O |

Fatty AcidPotassium HydroxidePotassium soapWaterUp to about 5% FFAs, the reaction can still be catalyzed with an alkali catalyst but additional
catalyst must be added to compensate for that lost to soap. The soap created during the
reaction is either removed with the glycerol or is washed out during the water wash.

When the FFA level is above 5%, the soap inhibits separation of the glycerol from the methyl esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl esters as shown in the following reaction:

| Fatty Acid Metha | anol | Methyl ester | Water | |
|--|------|---------------------------|-------|--|
| (H2SO4) HO – C – R + CH3OH Catalyst | | CH3 – O – C – R + H2O | | |
| 0 | | 0 | | |

MATERIAL AND METHODS

500 gm Seeds of *Moringa oleifera* plant were collected and sun-dried for two days, after that, the dried seeds were crush to obtain small solid particles and dipped in 1.0 liter of dried nhexane for the oil extraction. The extraction was carried out in a Soxhlet apparatous for 4 h. The extraction was carried out in order to determine the oil content. All of the experiments were carried out using a 2.5 L round-bottomed glass flask. The resultant solution was separated from solvent by distillation. The solvent was reused in the next batch of extraction.

| Table 1. | | | | | |
|-------------------------------|-------------|------------------|------------------|--|--|
| Parameter | Method ASTM | Limits | Moringa oleifera | | |
| Flash point, closed cup | D93 | 130 °C min | 145 °C | | |
| Water and sediment | D 2709 | 0.050 max % | 0.050% | | |
| Kinematic viscosity at 40°C | D 445 | 1.9 – 6.0 mm2/s | 4.25 mm2/s | | |
| Sulfated ash | D 874 | 0.020% max | 0.020% | | |
| Total Sulfur | D 5453 | 0.05% max | 0.04% | | |
| Copper strip corrosion | D 130 | No. 3 max | No. 3 | | |
| C-tane number | D 613 | 47 min | 49 | | |
| Carbon residue | D 4530 | 0.05% max | 0.03% | | |
| Acid number | D 664 | 0.8 mg KOH/g max | 0.55 mg KOH/g | | |
| Free glycerin | D 6584 | 0.02% | 0.02% | | |
| Total glycerin | D 6584 | 0.24% | 0.22% | | |
| Phosphorus | D 4951 | 10 ppm | 20 ppm | | |
| Vacuum distillation end point | D 1160 | 360 °C max | 352°C | | |

Table 1. Shows the property values required for a mixture of methyl esters to be considered biodiesel. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability.

Finally, the sample was dried in an oven (100 $^{\circ}$ C) until constant weight and 195 ml of oil has been obtained.

100 ml of oil was introduced in a thermostated. Reactor and heated at 62 °C and after that, methanol (10 wt % dry basis) in which sodium hydroxide (0.1 wt% dry basis) had been previously dissolved was added to the reactor. Reaction was conducted at the same temperature for four hours with constant stirring at 110 rpm. The reaction mixture was cooled to room temperature. Finally, the bottom layer of glycerin was separated from the mixture of biodiesel, which was then washed with water to remove the methanol excess and the traces of catalyst (Lang et al., 2001).

RESULTS AND DISCUSSION

These works has to carried out the transesterification process and determine the properties of biodiesel obtained from Moring oil which was followed by the process of oil extraction. In table, the Flash point, closed cup, Water and sediment, Kinematic viscosity at 40°C, Sulfated ash, Total Sulfur, Copper strip corrosion, C-tane number, Carbon residue, Acid number, Free glycerin, Total glycerin, Phosphorus and Vacuum distillation end point, 145 °C, 0.050%, 4.25 mm2/s, 0.020%, 0.04%, No.3, 49, 0.03%, 0.55 mg KOH/g, 0.02%, 0.22%, 20 ppm and 352°C respectively have been determined by ASTM methods and achieved the interested fruitful results which meets the biodiesel limits values.

CONCLUSIONS

Biodiesel is an important new alternative transportation fuel. It can be produced from many vegetable oil or animal fat feeds tocks. Conventional processing involves an alkali catalyzed process but this is unsatisfactory for lower cost high free fatty acid feeds tocks due to soap formation. These techniques have even been extended to allow biodiesel production from feeds tocks. Adherence to a quality standard is essential for proper performance of the fuel in the engine and will be necessary for widespread use of biodiesel.

ACKNOWLEDGEMENTS

The authors are thankful to Mr. Zahid Ali for the collection of seeds.

REFERENCES

- American Society for Testing and Materials, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, ASTM International, West Conshohocken, PA (2002).
- D.G.B. Boocock, 2001. "Single-Phase Process for Production of Fatty Acid Methyl Esters from Mixtures of Triglycerides and Fatty Acids," Canadian Patent No. 2,381,394.
- D. Kusdiana and S. Saka, 2001. "Kinetics of Transesterification in Rapeseed Oil to Biodiesel Fuel as Treated in Supercritical Methanol," Fuel 80, 693-698.
- G. Assman, G. Blasey, B. Gutsche, L. Jeromin, Jr. Rigal, R. Armengand, and B. Cormary, 1996. "Continuous Progress for the Production of Lower Alkayl Esters," US Patent No. 5,514,820.
- L.A. Nelson, T.A. Foglia, W.N. Marmer, 1996. "Lipase Catalyzed Production of Biodiesel," JAOCS, 73(8):1191-1195.

- Lang X., Dalai A.K., Bakhshi N.N., Reaney M.J. and Hertz P.B. 2001. Preparation and characterisation of biodiesels from various bio oils, Bioresour. Technol. 80, 53-62.
- M.A. Dasari, M.J. Goff, and G.J. Suppes, 2003, "Non-Catalytic Alcoholysis Kinetics of Soybean oil," JAOCS, (80), 189-192.
- M. Canakci and J.H. Van Gerpen, 1999. "Biodiesel Production via Acid Catalysis," Transactions of the ASAE, 42(5):1203-1210
- M. Diasakou, A. Louloudi, and N. Papayannakos, 1998. "Kinetics of the Non-Catalytic Transesterification of Soybean oil," Fuel, 77, 1297-1302.
- National Research Council 2006. <u>"Moringa"</u>. *Lost Crops of Africa: Volume II: Vegetables*. Lost Crops of Africa **2**. National Academies Press. <u>ISBN 978-0-309-10333-6</u>. Retrieved 2008.
- Radovich, T. 2009. <u>"Farm and Forestry Production and Marketing Profile for Moringa (Moringa oleifera)"</u>. Permanent Agriculture Resources (PAR), PO Box 428, Holualoa, Hawai'i 96725, US. Retrieved 20-11-2013.
- Rashid Umer Anwar, Farooq Moser, Bryan R. Knothe, Gerhard 2008. "Moringa oleifera oil: A possible source of biodiesel". *Bioresource Technology* **99** (17): 8175–9.
- S.Saka and D. Kusdiana, 2001. "Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol," Fuel 80, 225-231.
- T. Wimmer, 1995. "Process for the Production of Fatty Acid Esters of Lower Alcohols," US Patent No. 5,399,731.
- U.R. Kreutzer, 1984. "Manufacture of Fatty Alcohols Based on Natural Fats and Oils," JAOCS, 61(2):343-348.
- W.D. Stidham, D.W. Seaman, and M.F. Danzer, 2000. "Method for Preparing a Lower Alkyl Ester Product from Vegetable Oil," US Patent No. 6,127,560.
- W.H. Wu, T.A. Foglia, W.N. Marmer, J.G. Phillips, 1999. "Optimizing Production of Ethyl Esters of Grease Using 95% Ethanol by Response Surface Methodology," JAOCS 76(4):517-521.
- W. Zhou, S.K. Konar, and D.G.B. Boocock, 2003. "Ethyl Esters from the Single-Phase Base-Catalyzed Ethanolysis of Vegetable Oils," JAOCS, 80 367-371.
- Y. Shimada, Y. Watanabe, T. Samukawa, A. Sugihara, H. Noda, H. Fukuda, 1999. "Conversion of Vegetable Oil to Biodiesel Using Immobilized *Candida Antarctica* Lipase," JAOCS, 76(7):789-793.
- Y. Warabi, D. Kusdiana, and S. Saka, 2004. "Reactivity of Triglycerides and Fatty Acids of Rapeseed Oil in Supercritical Alcohols," Bioresource Technology, 91, 283-287.
- Y. Watanabe, Y. Shimada, A. Sugihara, H. Noda, H. Fukuda and Y. Tominga, 2000 "Continuous Production of Biodiesel Fuel from Vegetable Oil Using Immobilized Candida Antarctica Lipase," JAOCS, 77(4):355-360.

Corresponding author: Dr. Mahboob Ali Kalhoro, Fuel Research Centre, PCSIR Karachi 1 PRC, PCSIR Labs Complex, Karachi, Pakistan. **Email:** <u>kalhoro786pk@yahoo.com</u>