Synthesis of Ethyl Ester (Biodiesel) From Linseed Oil, Using Transesterification Double Step Process (TDSP)

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ABSTRACT

Diminishing tendency of petroleum resources has led to find biodiesel (synthesized from renewable resources) as the best alternative and potential energy for current petrol-derived diesel. The aim of this investigation is to find ethanol as an alternative to methanol as a transesterification regent to produce biodiesel from linseed oil by using novel transesterification double step process (TDSP). The oil was transesterificated by using ethanol as regent and acid and basic homogeneous catalysts which added in two steps. The procedure was approximately performed during 4h, the alcohol/oil/catalyst molar ratio was 20:1:0.35, and the range of temperature was between 60-80 ˚C. The obtained yield for biodiesel was 96%. Ethyl ester was analyzed by standard physico-chemical techniques in addition of FT-IR spectroscopy. The quality of the synthesized biodiesel was tested according to ASTM. Some critical parameters like oxidation stability, cetane number, iodine value and cold flow properties which were correlated with the ethyl esters composition had been studied.

Keywords: Ethyl ester, linseed, biodiesel, transesterification double step process (TDSP)

INTRODUCTION

Increased environmental concerns, about the negative implications brought by excessive usage of fossil fuels and depletion of raw material (petroleum feedstock), the speed for finding alternative energy as their substitutions are driving industry to come up with viable alternative fuels that burn more cleanly (Lim and Teong 2010. Muniyappa et al., 1996). Any types of feedstock which contains free fatty acids and/or triglycerides such as vegetable oils, waste cooking oil, animal fats, and waste greases can be converted into biodiesel (Janaun and Ellis 2010). In the last few years, biodiesel has emerged as one of the most potential renewable energy and complementary resource to replace current petrol-derived diesel and has drawn considerable amount of attention as an alternative fuel. It is a clean, non-toxic, renewable, sustainable and biodegradable fuel and has low emission profiles as compared to petroleum diesel (Lam et al., 2010. Xue et al., 2011. Hasheminejad et al., 2011. Ramos et al., 2009). Usage of biodiesel makes a balance between agriculture, economic development and the environment (Ramos et al., 2009). Fatty acid methyl ester (FAME) is the first generation of biodiesel and it is produced by the transesterification of vegetable oil with methanol (Meher et al., 2006. Liu et al 2011). Methanol produces the best results in the transesterification of oils and fats. Compared with other alcohols, methanol requires shorter reaction times and smaller catalyst amounts and alcohol/oil molar ratios (Guzatto et al., 2012). Methanol is primarily produced from fossil matter. Due to its high toxicity, methanol may cause cancer and blindness if overexposed (Marchetti et al., 2007). In contrast, ethanol emerges as a great alternative to methanol for the following advantages: mainly produced from biomass; easily metabolized by humans and generates stable fatty acid esters.

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Linum usitatissimum commonly known as linseed, flaxseed, lint bells or winterlien-belongs to the family Linaceae. This annual herb can grow up 60cm in height in most temperate and tropical regions and the seed contain 30-40% oil, including palmitic acid (4-6%), stearic acid (5-6%), oleic acid (15-17%) linoleic acid (14-16%) and linolenic acid (50-58%) (Nag, 2008). The aim of this study is to represent a modified transesterification double step process (TDSP) for obtaining FAEEs based on the combination of homogeneous acid and basic catalysts and then study of the quality of synthesized biodiesel which has been performed for the first time in Iran.

METHODS

Chemicals

Linseed prepared from the north of Iran, Normal hexane (99% purity, Merck), ethanol (99% purity, Merck), potassium hydroxide (99% purity, Merck), sulfuric acid (98% purity, Merck), and granulated silica gel (Merck).

Experimental Procedure

Oil Extraction

Linseed oil can be extracted using hexane as a solvent. Initially the linseed was grounded into small particles and placed into extraction chamber of soxhelt apparatus. The flask contained hexane was heated to reflux and moved up into the chamber contained sample. When the chamber got full of warm solvent it emptied automatically. After more than 5 hours the flask contained solvent and oil, that solvent was removed with rotary evaporator yielded the extracted oil. Solvent was recycled and oil was used as a starting material to produce biodiesel. The yield of oil extraction was 30.23%.

Synthesis of Ethyl Ester

Initially, 100 ml of Linseed oil was preheated in a simple reactor equipped with a reflux device and stabilized temperature (65 ˚C), then Potassium hydroxide (2.0 g) which have been dissolved in 120 ml (in 65˚C) of ethanol was added to the oil vessel, and the mixture was vigorously and constantly agitated. The alcohol/oil/catalyst molar ratio was 20:1:0.35. The system was under this condition for 30 min. In the second step, 4 ml of sulfuric acid (18.77mol/L) was added drop wise to the reaction mixture, followed by addition of 60 ml of ethanol and soft heating until 80 ˚C. After the heat was stabilized, the reaction resume on this condition for 2 h 30 min. The reaction mixture was then removed from the reflux system and was filtered to remove the solid residue (K2SO4). . The ethyl esters (superior layer) are then separated from the raw glycerol (lower layer) by decantation with some traces of non-reactedoil, monoglycerides, diglycerides and a small amount of ethanol. To remove the alcohol excess, the reaction mixture was concentrated using a rotary evaporator. The raw glycerol could be purified and used, for example, in the cosmetic industries. After separation of two phases, ethyl esters (biodiesel) was washed with water and dried under silica gel. The procedure was approximately performed during 4h. The obtained yield for biodiesel was 96%.

Physico-Chemical Properties

Physico-chemical characteristics conducted to evaluate the quality of obtained biodiesel. Cetane number (CN) is widely used as diesel fuel quality parameter related to the ignition delay time and combustion quality. Higher the cetane number is, better it is in its ignition properties. Iodine value is a measure of total unsaturation within a mixture of fatty acid. It is expressed in grams of iodine which react with 100 g of the respective sample when formally adding iodine to the double bonds. The iodine value of a vegetable oil or animal fat is almost identical to that of the corresponding ethyl esters (Ramos et al., 2009). The flash point is defined as the minimum temperature at which the liquid produces a sufficient concentration of vapor above it that it forms an ignitable mixture with air. The lower the flash point is, the greater the fire hazard is (Salimon et al., 2010). The cold flow properties determine the temperature range where biodiesel could be used without freezing inside the engine the kinematic viscosity test measure the Newtonian flow resistance imposed by the fluid (Guzatto et al., 2012). The acid number derives almost exclusively from the FA content. FA may cause engine deposits, particularly in fuel injectors, by catalyzing polymerization in hot recycling fuel loops (Mahajan et al., 2006). Physico-chemical properties of linseed oil and ethyl ester obtained in experimental are shown in table 1 and table 2 respectively.

Table 1. Physico-chemical characteristics of linseed oil

Linseed Oil	*Characteristics*
Viscosity in 40˚C	39
Flash point (˚C)	241
Saponification number	189-195
Iodine value	170-203

Table 2. Physico-chemical characteristics of ethyl ester

Tests	*Conclusions*	*Determined value in ASTM*	*Standard Numbers*
Average molecular weight	298.92 - -	-	-
Flash point ˚C	151	Min 130⁰C	D92
Pour point ˚C	-4	According to clime conditions	D97
Cloud point ˚C	2	According to clime conditions	D2500
Viscosity in ˚C (cSt)	4.8	1.9-6	D445
Iodine value	170.25	-	-
Saponification number	182.93	-	-
Cetane number	37.66	47	D613
Acid number	0.5	Max 0.8	D974

RESULTS AND DISCUSSION

Different analyses were performed to define the obtained biodiesel properties. FTIR were employed to define chemical structure determination. Additionally, a series of physicochemical properties of the produced biodiesel was determined to evaluate their quality and purity. A series of physico-chemical analyses were performed include The kinematic viscosity in 40˚C, (ASTM D445), flash point (ASTM D92), cloud point (ASTM

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D2500), pour point (ASTM D97), acid number (ASTM D974), cetane number (ASTM D613), iodine value and saponification value.

FT-IR Spectrometry

The FT-IR spectra of linseed oil and ethyl ester are shown in Fig.1. The esters have two characteristically strong absorption bands arising from carbonyl (C=O) around 1750–1730 cm$_{-1}$ and that of C–O (antisymmetric axial stretching and asymmetric axial stretching) at 1300–1000 cm–1. The stretching vibrations of CH3, CH2, and CH appear at 2980– 2950, 2950–2850 and 3050–3000 cm$_{-1}$, whereas the bending vibrations (ρCH2) of these groups appear at 1475–1350, 1350–1150 and 722cm$_{-1}$ respectively. The FT-IR spectra of both linseed oil and its biodiesel were almost similar but various differences could be observed for identification purposes. The shifting of absorption peaks of the oil sample at 1744 and 1162 cm$_{-1}$ to 1739 and 1178 cm$_{-1}$ in the biodiesel, respectively. The disappearance of peaks at 1099 and 913cm$_{-1}$ from the spectrum of oil and appearance of new bands in the biodiesel at 1035 and 917 cm$_{-1}$ indicate the conversion of oil into biodiesel (Tariq et al., 2011). Moreover, the ethyl ester and triglyceride spectra do not present any characteristic bands from the asymmetric axial deformation of the carboxylate ion, which would be located around 1550–1600 cm$_{-1}$. As shown, both spectra are quite similar and characteristic of long chain fatty acid esters molecules, such as triglycerides and ethyl biodiesel that are derived from triglycerides. These similarities indicate that both materials have the same functional groups, which suggests that no competitive reactions have occurred during the basic and acid catalysis steps (Guzatto et al., 2012).

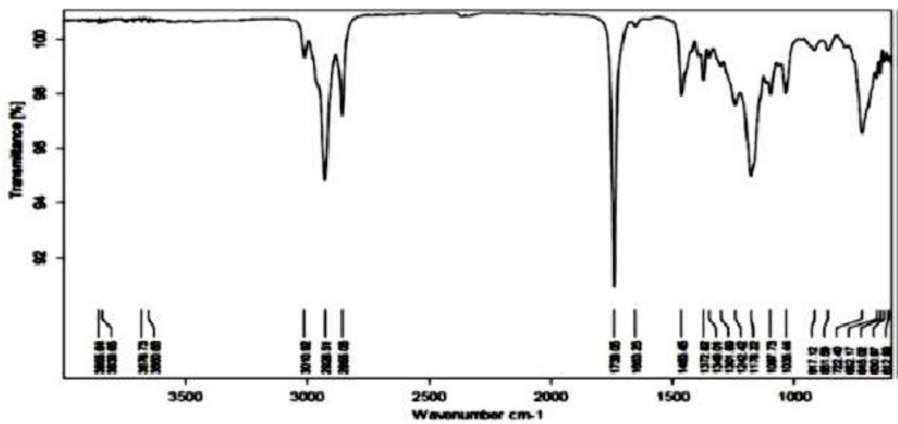

Figure 1. FT-IR spectroscopy of linseed oil

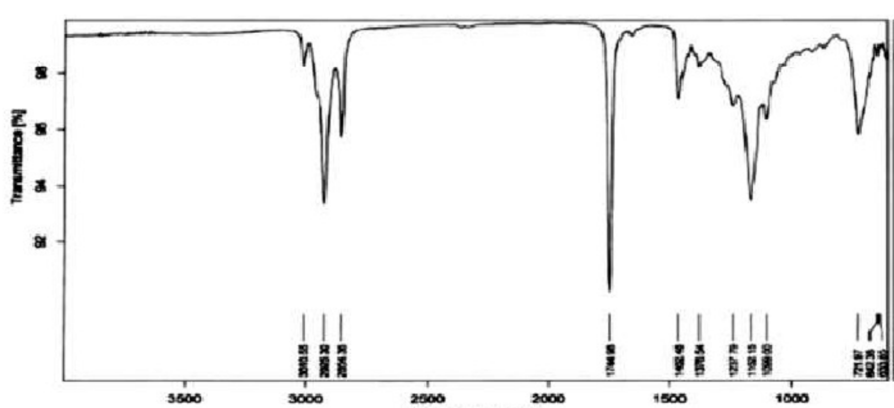

Figure 2. FT-IR spectroscopy of ethyl ester

Physico-Chemical Analysis

The obtained results of physico-chemical characteristics of linseed oil and biodiesel are shown in table 1 and 2. As it shown, the viscosity of oil is higher than the biodiesel which refers to the high molecular weight of triglycerides in plant oil. When the oil converted to biodiesel, the viscosity decrease and volatility increase, so it will be suitable to use as a fuel. Methanol is a toxic component and can cause permanent blindness by destruction of the optic nerve when contact to eyes. So ethanol is safer and more logical as an alternative to methanol. Off course the economic assessment is the main factor to produce a product and requires a skill and knowledgeable investigations. As it shown in table 2, the flash point, cold flow properties, viscosity, and acidic number of synthesized biodiesel are in the range of determination in standard methods. There has been no value for saponification number in ASTM standards but as it influence directly on cetane number, it's necessary to be calculated. In ASTM standards the determined minimum value of cetane number is 47. In synthesized biodiesel the lower cetane number and higher iodine value which related to unsaturated fatty acids such linoleic and linolenic acids. Nevertheless higher unsaturated degree, lower the cold flow properties and its one advantage to be used in climate and cold regions. Considerably the all standard tests were performed in B100 samples. So the mixture of this fuel with the gasoline will come up the problem of cetane number. Additionally with using additives of viscosity, oxidation, pour point and etc. can increase the quality of synthesized biodiesel so the B100 will be possible to use.

CONCLUSION

Currently, biodiesel is produced through TDSP from linseed oil and ethanol used for production of biodiesel. The yield of ethyl ester was 96% and the reaction time was approximately 4 hours. The results show use of ethanol also requires extremely shorter reaction times and more rapid reaction than with the acid catalysis, high conversion degrees and high purity biodiesel obtained. Also ethanol does not contain disadvantages as methanol does. Physico-chemical characteristics, FT-IR spectroscopy and the obtained yield of ethyl ester show high quality, purity and high conversion of biodiesel.

REFERENCES

[1] Lam, M. K., Lee, K. T. & Mohamed. A. R. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances, 28*, 500–518.

[2] Hasheminejad, M., Tabatabaei, M., Mansourpanah, Y., Khatami far, M. & Javani, A. (2011). Upstream and downstream strategies to economize biodiesel production. *Bioresource Technology, 102*, 461–468.

[3] Janaun, J. & Ellis. N. (2010). Perspectives on biodiesel as a sustainable fuel. *Renew. Sustain. Energy Rev., 14*, 1312–1320.

[4] Lam, M. K., Lee, K. T. & Mohamed. A. R. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances, 28*, 500–518.

[5] Lim, S. & Teong, L.K. (2010). Recent trends, opportunities and challenges of biodiesel in Malaysia: an overview. *Renew. Sustain. Energy Rev., 14*, 938–954.

[6] Liu, Y., Sotelo-Boyas, R., Murata, K., Minowa, T. & Sakanishi, K. (2011). Hydrotreatment of vegetable oils to produce bio-hydrogenated diesel and liquefied

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petroleum gas fuel over catalysts containing sulfided ni_mo and solid acids. *Energy & Fuels, 25*, 4675–4685.

[7] Mahajan, M. K. Konar, S. G. B. & Boocock. D. (2006). Determining the Acid Number of Biodiesel. *JAOCS, 83*(6).

[8] Marchetti, J. M., Miguel, V. U. & Errazu, A. F. (2007). Possible methods for biodiesel production. *Renew Sustain Energy Rev, 11*, 1300–11.

[9] Meher. L. C., Vidya Sagar, D. & Naik, S. N. (2006). Technical aspects of biodiesel production by transesterification–a review. *Renew. Sust. Energ. Rev., 10*, 248–268.

[10] Muniyappa, P.R., Brammer, S.C. & Noureddini, H. (1996). Improved conversion of plant oils and animal fats into biodiesel and co-product. *Bioresource Technology, 56*, 19-24.

[11] Nag, A. (2008). Biofuels refining and performance. New York: McGraw-Hill.

[12] Ramos, M. J., Fernández, M. C., Casas, A, Rodríguez. L. & Pérez. A. (2009). Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology, 100*, 261–268.

[13] Salimon. J., Salih. N. & Yousif. E. (2012). Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant applications. *Arabian Journal of Chemistry, 5*(2), 193-200.

[14] Tariq, M., Ali, A., Ahmad, F., Ahmad, A., Zafar, M., Khalid, N. & Ajab Khan, M. (2011). Identification, FT-IR, NMR (1H and 13C) and GC/MS studies of fatty acid methyl esters in biodiesel from rocket seed oil. *Fuel Processing Technology, 92*, 336–341.

[15] Xue, J., Grift, T. E. & Hansen, A. C. (2011). Effect of biodiesel on engine performances and emissions. *Renewable and sustainable energy reviews. 15*, 1098-1116.

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