Methanolysis And Ethanolysis Of Raw Hemp Oil: Biodiesel Production And Fuel Characterization

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Abstract

The objective of the present experimental work was to prepare hemp biodiesel (hemp methyl and ethyl ester) as a diesel fuel substitute. This was carried out experimentally and its characters were analyzed consequently. The comparison showed that hemp methyl ester is relatively equivalent to diesel fuel than hemp ethyl ester. The yield of hemp methyl ester after transesterification was 90.62% in 45 minutes where KOH (2g) was used as catalyst. The preheating temperature was 55℃, and a molar ratio of 6: 1 (methanol to oil) at 60℃ was found effective. On the other hand production of hemp ethyl ester by transesterification was 72.67% in 75 minutes using 4g of KOH as catalyst. The preheating temperature was 55℃ and the molar ratio of 5:1 (ethanol to oil) at 60℃ was used in this case. In the present investigation, an attempt was taken to use raw hemp oil as low cost sustainable potential feedstock for biodiesel production. The effects of various process parameters such as amount of catalyst, molar ratio, preheating temperature, reaction temperature etc. were examined. The fuel properties of biodiesel such as density, kinematic viscosity, flash and fire point, cloud and pour point were determined and were compared with biodiesel different standards like ASTM D6751 and EN 14214.

Keywords: Hemp biodiesel; Transesterification; Fuel properties; Renewable fuel[1]

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1. Introduction

In spite of the favorable effect on the environment, the economic aspects of biodiesel are likely to be a barrier for its market demand due to the fact that most of the biodiesels produced from edible oils. Only few researches have been done for production of biodiesel from edible oil. Cost of edible oil as biodiesel resource includes about 60-70% of raw material cost [1].One way of reducing the biodiesel production costs is to use the less expensive feedstock such as non-edible oils, animal fats and oils, recycled or waste oil and byproducts of the refining vegetable oils [2]. Biodiesel is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in presence of a catalyst to yield mono-alkyl esters and glycerin. Biodiesel consists of long-chain fatty acid esters produced by transesterification reaction of vegetable oils with short chain alcohols [3-5]. It is compatible with conventional diesel fuel and has already been served as a commercial fuel in Europe [6]. Many efforts have been made to optimize the parameters for biodiesel production [7-8]. Ethanol is only partially miscible with triglycerides at ambient temperature. An emulsion is usually formed during the reaction when vigorous agitation is applied. The emulsion is caused by formation of the intermediate monoglycerides and diglycerides which have both polar hydroxyl groups and non-polar hydrocarbon chains. The emulsion is formed when the concentrations of these intermediates reach a critical level. The emulsion formed during ethanolysis is stable and severely complicates the separation and purification of the esters [9]. The formation of stable emulsion during

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ethaolysis is hard to achieve. Methanol and ethanol are not miscible with triglycerides at room temperature. During the reaction emulsions are usually formed. In case of methonolysis, these emulsions break down quickly and easily to form a glycerol rich layer and methyl ester rich layer. In ethanolysis emulsions are more stable and severely complicate the separation and purification of esters [10]. Hemp oil that is non-refined varies from off yellow to dark green. Hempseed contains radium, thorium and rubidium and fatty oil like arachis oil. It also has high essential fatty acids. It is an herbaceous annual plant that grows from 1-5metres. It can grow in any climatic and soil condition. At present hemp oil has been found as an alternative feedstock for the production of a biodiesel fuel. Properties of hemp oil and biodiesel, prepared from hemp oil by transesterification, were within the limits of ASTM and EN standards.

2. Materials

2.1. Materials

The hemp oil used in this present study was supplied by Agrawal oil mill Udaipur (Rajasthan). All chemicals were procured from THAMES chemicals, near choura bazar, Ludhiana (Punjab)

2.2. Apparatus

The apparatus used for transesterification include water bath, reaction flask with condenser and digital rpm for controlling the mechanical stirring. The volume of the glass reactor was 500 ml. A temperature indicator was used to measure the reaction temperature.

3. Methods

3.1. Transesterification

Transesterification of hemp oil was carried out under different experimental conditions by using base catalysis.

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3.1.1. Methanolysis of hemp oil

In100g of crude hemp oil, a mixture of 2g (0.2wt %) of catalyst KOH dissolved in the required amount of methanol was added. The temperature was maintained at 60℃. Three different molar ratios of methanol and oil (4:1, 6:1, and 8:1) were used to get different yield of methyl ester of hemp. Finally, Samples were removed after 24 hr. The upper layer indicates ester and lower layer indicates glycerol. Only ester layer was washed by hot water and the obtained ester was dried by silica gel. It was found that single stage process with a period of 45min was required to achieve 90.62% of ester.

3.1.2. Ethanolysis of hemp oil

A fixed amount of ethanol (52.02g) was added into hemp oil (100g) along with KOH catalyst (4g), with a 75min time of the reaction and 60℃ temperature. The product of reaction was allowed to settle overnight. During settlement, two distinct liquid phases were formed after 12 days which are as follows- crude ester phase at the top and glycerol phase at the bottom. The crude ester phase separated from the bottom glycerol phase was then washed by hot water for three times until the washed water became clear. The excess methanol and water in ester were then removed by evaporation. After that, weight of the ester was taken.

3.1.3. Fuel properties

The physiochemical properties of the biodiesel obtained from hemp oil shown in Table 1.The fuel characteristics of the obtained esters synthesized were evaluated according to ASTM D6751 and EN 14214 standard methods.

Fuel property	Brown hemp oil	Brown hemp methyl ester	Brown hemp ethyl ester	Diesel
Fatty acid composition (%)				
Palmitic acid $C_{16:0}$	14	-		-
Stearic acid $C_{18:0}$	6	-		-
Oleic acid $C_{18:1}$	45.3	-		-
Linoleic acid $C_{18:2}$	23.4	-		-
Density (gm/cc3)	0.888	0.858	0.860	0.830
Viscosity(cSt) @ 40^oc	42.72	1.13	1.59	2.6
Flash point (^0C)	125	47	60	60
Fire point (^0C)	135	55	70	65
Cloud point (^0C)	2	-4	8	-12
Pour point (^0C)	-10	-17	3	-16
Calorific value (MJ/Kg)	43.52	42.92	43.58	43
FFA content (%)	0.175	-	-	-

Table 1 Chemical and physical properties of brown hemp oil, methyl, ester of hemp oil and diesel

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4. Result and discussion

4.1. Methyl Transesterification

A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester. Many researchers have optimized transesterification process to get biodiesel from different non-edible oils [11-13]. In single stage process the ratio of methanol to oil was 0.408 to 0.816 (w/w) and 0.01 to 0.03. % (w/w) alkali catalyst KOH was pre-mixed in methanol. The mixture was poured into water bath shaker and stirred for about 45 min at 60^oC. The rate of stirring at start was more vigorous (650-700 rpm) and it was reduced to 450-500 rpm after the mixture temperature attained 60^oC. The yield of hemp methyl ester achieved was 90.62 % in 45 min (using 2g KOH as catalyst and molar ratio of methanol to oil 6:1 at 60℃). The maximum yield of methyl ester was 93.89% in 45 min (using 2g KOH as catalyst and molar ratio of 4:1 at 60℃). The observed value was summarized in Table 2.

Preheating Temperature ^{0}C	Reaction Temperature ^{0}C	Reaction Time Min	Catalyst Con. %	Methanol Quantity Gm	Molar Ratio	Settling Time Hr	Ester Recovery %	Kinematc Viscosity cSt
55	60	45	3	82	8:1	24	84.76	2.76
55	60	45	2	82	8:1	24	Ester not formed	-
55	60	45	1	82	8:1	24	Ester not formed	-
55	60	45	3	61	6:1	24	79.10	2.35
55	60	45	2	61	6:1	24	90.62	**1.13**
55	60	45	1	61	6:1	24	93.32	4.25
55	60	45	3	41	4:1	24	87.12	1.76
55	60	45	2	41	4:1	24	**93.89**	2.38
55	60	45	1	41	4:1	24	89.26	2.15

Table 2 Methyl ester yield and kinematic viscosity with operating parameter

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4.2. Ethyl Transesterification

In single stage process the methanol oil ratio 0.408, 0.52, to 0.816 w/w and alkali catalyst (KOH) 0.01 to 0.04. % w/w is pre-mixed in a flask and added rapidly in to oil. The mixture was put into a water bath shaker and heated for 0.45-1.15 hrs at 60^{o}C. The rate of stirring at start was 650-700 rpm and it was reduced to 450-500 rpm after the mixture temperature attained 60^{o}C. The experiments have been performed by using different molar ratio (4:1, 5:1, 6:1, and 8:1). It was observed that the molar ratio of 5:1 gives better result. The optimizing parameters were preheating temperature (55,60 and 65), molar ratio(4:1, 5:1, 6:1 and 8:1), reaction time (45min, 60min, and 75min), reaction temperature (constant temperature = 60) and catalyst quantity (1gm,2gm,3gm, and 4gm).When preheating temperature55°C,molar ratio 5:1, catalyst quantity 4gm, reaction temperature 75minutes and constant reaction time 60min was used, it showed biodiesel separation after 12 days. The yield of biodiesel was 72.67% and glycerol obtained was 32.87%. The observed value was summarized in Table 3.

Preheating Temperature ^{0}C	Reaction Temperature ^{0}C	Reaction Time Min	Catalyst Con. %	Molar Ratio	Ester Recovery %	Kinematc Viscosity cSt
55	60	75	4	5:1		
55	60	75	3	5:1		
55	60	75	2	5:1		
55	60	75	1	5:1		
55	60	75	4	5:1	No ester formation	
55	60	75	3	5:1		
55	60	75	2	5:1		
55	60	75	1	5:1		
55	60	75	4	5:1	-	-
55	60	75	3	5:1	-	-
55	60	75	2	5:1	72.67 (12 days)	1.59
55	60	75	1	5:1	-	-

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Table3 Ethyl ester yield and kinematic viscosity with operating parameter

4.3.Biodiesel yield

The effect of different methanol to oil molar ratios on biodiesel yields was investigated. Generally, the biodiesel yields decreased with decreasing methanol to molar ratios. From Table 3 it can be observed that the lowest biodiesel yield of 72.67% was obtained when the ethanol to oil molar ratio was 5:1. The methanol to oil molar ratio of 4:1 gave the highest biodiesel yield of 93.89% as listed in Table 2. As shown in table 3, the biodiesel yield was higher when the mixing time of 75 min was provided.

4.4. Optimization analysis of transesterification process

In order to standardize the process parameters, three molar ratios (4:1, 6:1, 8:1), preheating time (55 min), three catalyst (KOH) concentrations (1%,2% and 3%) and reaction time (45min) was taken with constant reaction temperature. 9 ester samples were prepared to study the effect of three molar ratios, three catalyst concentrations, reaction time on ester recovery and subsequent measure of their kinematic viscosity. Further increase in catalyst concentration does not increase the conversion.

4.4.1. The effect of different oil to methanol/ethanol molar ratio on biodiesel production

In this experiment, different oils to methanol molar ratio were used which are 4:1, 5:1, 6:1 and 8:1. The reactions were carried out using different amount of KOH (1g, 2g, 3g, and 4g) at room temperature. The yield of ethyl ester was 72.67% for 5:1 of oil to methanol molar ratio. From the results, it can be seen that 5:1 oil to ethanol molar ratio gives the higher ester yield compared with 4:1, 6:1, and 8:1 oil to methanol molar ratio. Oil to methanol molar ratio of 4:1, 6:1, and 8:1 did not show yield of ethyl ester of hemp oil. Therefore, it is needed to increase the concentration of reactant such as alcohol amount, so that the reactions would be more favorable to generate FAME yield. Many of research workers found that the optimum oil to methanol molar ratio would be 6:1. With that molar ratio, one can get a higher ester yield if other reaction conditions are optimum. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility [14].

4.4.2. The effect of different alcohol types on biodiesel production

Different types of alcohol yielded different percentage of biodiesel production. Methanol and ethanol were used in this experiment. The reactions were carried out by using 4g of KOH, 5:1 oil to alcohol molar ratio and settling time 288 hrs (12 days) at room temperature. The results showed that methanol gave best yield. Formation of ethyl ester is difficult compared to formation of methyl esters. In case of methanolysis, formation of emulsions quickly and easily breaks down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters.

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4.4.3. The effect of reaction time on biodiesel production

Reaction time was also a factor that can influence the yield of biodiesel. In this experiment, mixing times were chosen as 45 min for methyl ester and 45min, 60 min, and 75 min for ethyl ester. The reactions were carried out by using 5:1 oil to ethanol molar ratio and 4g of KOH at room temperature. From the results, 75 min of mixing time was found to yield ethyl ester of hemp oil. For transesterification of triglyceride to ester, it takes about 45 min to 75 min to complete the conversion. With longer the reaction time, the more the hydrolysis of ester would occur.

4.5. Separation of biodiesel from by-products

The product of the reaction was exposed to open air to evaporate excess methanol. The product was then allowed to settle down overnight. Two distinct liquid phases: crude ester phase at the top and glycerol phase at the bottom were produced in a successful transesterification reaction.

4.6. Purification of biodiesel by washing

The top ester phase was separated from the bottom glycerol phase by transferring it to a clean 250 ml conical flask. The biodiesel was then purified by washing with distilled water to remove all the residual by-products like excess alcohol, excess catalyst, soap and glycerin. The volume of distilled water added was approximately 30% of the biodiesel volume. The flask was shaken gently for 1 min and placed on the table to allow separation of biodiesel and water layer. After separation, the biodiesel was transferred to a clean conical flask. The washing process was repeated for several times until the washed water became clear. The clean biodiesel was dried in an incubator for 48 hrs.

4.7. Fuel characterization

Properties were checked to find out whether the methyl or ethyl esters of hemp oil meets the properties of biodiesel fuel. Density and viscosity affects the atomization of a fuel upon injection into the combustion chamber. With higher viscosity such problems increases rapidly. The calorific value is related to fuel consumption and heat generation during combustion in engines. The results showed that, tranesterification improved the important properties and the comparison stated that the hemp methyl ester resembles diesel fuel in a more convenient way than hemp ethyl ester.

4.7.1. Relative density

The relative densities of hemp oil, hemp methyl ester and hemp ethyl ester were 6.99, 3.37, and 3.61 percent respectively which were little more than that of diesel fuel.

4.7.2. Kinematic viscosity

The kinematic viscosity of diesel, hemp oil, hemp methyl ester and hemp ethyl ester were found as 2.6, 42.72, 1.13, and 1.59 centistokes at 40^0C. The hemp methyl ester and hemp ethyl ester were observed to have viscosity less than that of diesel.

4.7.3. Flash and fire point

The hemp methyl ester was found to have lower flash and fire pint than those of diesel. The flash and fire point of hemp oil were found to be higher than those of diesel. The flash and fire point of hemp ethyl ester were somewhat similar to diesel.

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4.7.4. Cloud and pour point

The results indicate that pour point of hemp methyl ester is higher than that of diesel whereas cloud point of hemp methyl ester is lower than that of diesel. The result also showed that the cloud and pour point of hemp oil is lower than those of diesel. The cloud and pour point of hemp ethyl ester is lower than diesel fuel.

4.7.5. Calorific value

The calorific value of diesel, hemp oil, hemp methyl ester, and hemp ethyl ester were found as 43, 43.52, and 42.92, and 43.58 MJ/Kg respectively.

4. Conclusions

- The quality of biodiesel is in agreement with the ASTM D6571 and EN 14214 standards.
- The properties of a biodiesel fuel are influenced by the structure and distribution of fatty acid esters which vary depending on the source of raw hemp oil.
- The yield of hemp methyl ester by transesterification was 90.62% in 45 min of reaction time using 2g KOH as catalyst at 55℃. The standardized preheating temperature and molar ratio were 60℃ and 6:1 respectively.
- The yield of hemp ethyl ester by transesterification was 72.67% in 75 min using 4g, KOH as catalyst, 55℃, preheating temperature and a molar ratio of ethanol to oil of 5:1 at 60℃.
- This study supports the production of biodiesel from hemp oil as a viable alternative to the diesel fuel.

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