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Optimization of Base catalysed Transesterification and Characterization of *Brassica napus* (Canola seed) for the production of biodiesel

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Abstract: Biodiesel from vegetable oil proves to be a potential alternative for fossil fuel. In this study canola seed oil is extracted from canola seed through Soxhlet extraction procedure with n-hexane as solvent. A single stage transesterification was employed since Free Fatty Acid content was less than 2%, using KOH and methanol. The physio-chemical properties of canola seed oil is compared with other vegetable oils and found to be in ASTM limits. Optimization studies were analysed to understand the yield of biodiesel on reaction time, catalyst concentration and molar ratio. Between reaction temperatures of 55°C - 65°C, the maximum yield of biodiesel was found to be 88% with a reaction time of 80 minutes, catalyst concentration of 2.4% to the weight of oiland molar ratio of 1:5.
Keyword: Biodiesel, Transesterification, Methanol, Potassium hydroxide, Molar ratio.

Introduction

Climatic barriers, increased global warming problems and rapid depletion of fossil fuels urged the researchers to identify the various alternatives for petrol, diesel like vegetable oils, animal fat, oleaginous micro-organisms and many more. Biodiesels derived from non-edible vegetable oils find a prominent place for its use in internal combustion engines due to its comparable physio-Chemical properties like calorific value, Cetane number, Kinematic viscosity, flash point and fire point to petro-diesel. Non-toxicity, bio-degradability, renewability, enhanced lubricating effect, lesser emissions are the few advantages of biodiesel over conventional fossil fuels. Biodiesels are generally produced by transesterification of mono-alkyl esters along with methanol and potassium hydroxide as catalyst, which produces fatty acid methyl esters for its use in internal combustion engines as a straight biodiesel (or) blended with diesel fuel. The biodiesel blends are favourable to use in internal combustion engines without complicated design modifications and leads to cleaner combustion with the reduced operating temperature which produces lesser amount of oxides of nitrogen.

Many researchers have investigated the use of biodiesel in an internal combustion engine, which reduce the peak flame temperature and thereby reduction in various emissions was noticed. Hem Joshi etal. analysed the transesterification of canola oil at the molar ratio of 1:1 using both ethanol and methanol. A central composite design was applied on a model to study the concentration of catalyst, molar ratio and the reaction temperature which lead to the yield of biodiesel. It was noticed that the yield of biodiesel as 98%, the molar ratio of 20:1,1.1 weight percentage of catalyst at 25^0C. The resultant biodiesel exhibited better lubricating property and improved low temperature operations[11].Kariminia et al. presented characterization and transesterification of Iranian bitter almond oil for its use in Internal Combustion Engine as biodiesel. Single stage transesterification was implied with KOH as catalyst since the acid values of almond oil is very low, the pre-treatment process was eradicated. The molar ratio, catalyst concentration and reaction temperature for production of biodiesel was optimized as 3-11 mole/mole, 0.1% – 1.7% w/w ratio and 30^0-70^0C respectively. The physio-chemical properties of biodiesel were compared with ASTM standards and found to be in limits[16].

Kinetic study and reactive flow analysis for waste cooking oil was conducted by Isam Janajreh etal. with residence time, reactance quality, proportions, mixing state, amount of catalyst and temperature as major parameters. They constructed a robust semi-continuous reactor to initiate the transesterification and the kinetic study was carried out at optimal conversion metrics [13].Demirbas.A conducted a transesterification process with KOH and supercritical methanol for obtaining biodiesel. He identified that presence of water in waste cooking oil affects the catalyst effectiveness. Since supercritical methanol neutralizes the waster it offers the favourable condition in eliminating the pre-treatment process[4].Zang et al. experimented extraction of salmon oil by two different steps, hydrolysate production and grinding. Double stage transesterification process was employed, in the first stage acid value was reduced from 12 to 3 mg/ [KOH] g $(oil)^{-1}$ which is followed by catalysed transesterification with KOH. He further stated that, with methanol molar ratio of 9.2%, the total yield of biodiesel is 99% [12].

In the present study canola seed oil was extracted through Soxhlet extraction apparatus, a single stage transesterification was carried out to convert canola oil into biodiesel. A molar ratio and catalyst concentration of 1:5 and 2.5% w/w respectively was used in transesterification with constant agitation of 450 rpm through this process 88% of biodiesel yield was obtained.

Materials

The cultivation of canola seed was found in few places in the states of Rajasthan, Uttar Pradesh, Madhya Pradesh, Haryana and Gujarat. In Punjab and Himachal Pradesh the canola plant is found to be cultivated in the name of Gabhi Sarson with an average yield of 1025Kg/Hectare.5Kg of canola seed (*Brassica Napus* variety) was purchased from local vendor of Rajasthan. From the literature survey it is found to have an oil content of 40% by dry weight. The canola seeds were crushed using mortar and pistil for breakage of cell wall membranes and subjected to oil extraction procedure. Soxhlet apparatus containing condenser, reaction chamber, round bottom flask and heating mantle with temperature controller is employed for extraction of canola oil.n-hexane solvent was used for oil extraction protocols, 99% pure methanol and 2.5% of KOH by weight of oil was used to perform single stage transesterification with constant magnetic stirrer speed of 480 rpm[13].

Experimental procedure

Crushed Canola seed (of 80gms) was filled in cellulose thimbles and placed inside the reaction chamber of Soxhlet apparatus. In a single cycle 250ml of n-hexane solvent is poured in round bottom flask and the temperature of mantle was gradually increased. At temperature 70^0C the n-hexane solvent present in the round bottom flask reaches its boiling point and vaporizes. The hexane vapour reaches the condensing probe through by-pass side arm and gets condensed to liquid phase. The liquefied n-hexane at elevated temperature 50 ± 2^0C flows directly into the reaction chamber and occupies the cellulose thimbles filled with crushed canola seed in the extraction tube. Chemical reaction takes place between the cell wall membrane of canola seed and n-hexane, as a result of chemical reaction n-hexane carries the lipid content of crushed canola seed and flows back to the round bottom flask through the reflux side arm after reaching the reflux level. This cycle is repeated for 15 times for a period of 140 minutes to extract 40% of lipid content in the canola seed. By this procedure 1.76 litres of canola seed oil was extracted [3, 8].

Transesterification method

Transesterification process is initiated by pre-heating the extracted canola oil up to 110^0C for the removal of moisture content. Since the free fatty acid value was identified as less than 2%, base catalysed transesterification was employed to convert canola seed oil into its biodiesel.100ml of pre-treated canola seed oil was placed in a three neck round bottom flask fitted with temperature measuring units. The flask was placed on a heating element fitted with a magnetic stirrer whose operating range between 400 to 600 rpm. 2.5 grams of KOH was added to the flask which is maintained between 55^0 C and 65^0C at constant speed of 480 rpm for 60 to 75 minutes. After the process, reaction flask was allowed to cool and the settling period of 6 hours was maintained for the isolation of glycerol through gravity separation method. Batch process was followed in the above similar procedure for further transesterification of pre-treated canola seed oil. By this procedure the yield of biodiesel was found to be 88% (1.76 litres) of biodiesel was obtained [1, 15,16, 23].

Characterization of Canola biodiesel

The comparison in physio-chemical property of canola seed oil, canola biodiesel, Rubber seed biodiesel and Karanja biodiesel is given in Table (1). It can be noticed that the densities of canola biodiesel is 875 Kg/m^3, which is comparable with densities of rubber seed biodiesel as 892 Kg/m^3 and Karanja biodiesel as 797 Kg/m^3. The Calorific value of canola biodiesel was found to be better that other biodiesels. The Cetane index of canola biodiesel was noticed to be 59 which is lesser than the Rubber seed biodiesel and greater than Karanja biodiesel. The acid value of Canola biodiesel was brought to 0.018 mg/KOH g^{-1} from 0.078 mg/KOH g^{-1} through transesterification process which is very less when compared to Rubber seed biodiesel as 0.56 and Karanja biodiesel is 0.45 [11, 14].

Table 1. Comparison of Physio-chemical properties of Canola seed oil, biodiesel and other biodiesel

Properties / Biodiesel	Canola seed oil	Canola Biodiesel	Rubber Seed Oil Biodiesel	Karanja Biodiesel
Density(Kg/m^3)	910	875	892	797
Viscosity(Cst)	32.3	4.40	3.9	7
Calorific Value(MJ/kg)	36.9	33	36.60	16.54
Cetane Number	69	59	66	42.9
Flash point(^{0}C)	315	162	130	97.8
Pour point(^{0}C)	-	-13	-8	-
Cloud point(^{0}C)	-15	-4	-10	-7
Acid value (mg/ KOH/g)	0.078	0.018	0.56	0.45
Saponification value	174	168	193.5	180
Iodine value	115	88	101	91

The saponification value of Canola biodiesel was found to be 168,whereas Rubber seed biodiesel and Karanja biodiesel possess a higher saponification value of 193.5 and 180 respectively [6].

Results and Discussion

Effect of reaction time on biodiesel yield

The Figure (1) shows the variation in yield of biodiesel with reaction time at the reaction temperatures of 55°C, 60°C and 65°C.The pre-treatment of canola oil up to 110°C removes excess moisture content which is favourable for transesterification reaction.

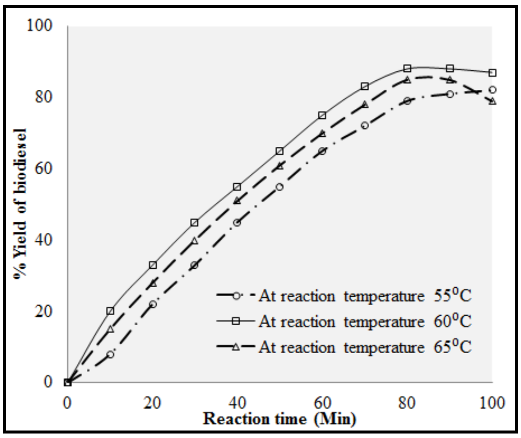

Figure 1. Comparison of biodiesel yield with reaction time at 55^{o}C, 60^{o}C and 65^{o}C reaction temperature

At 30 minutes of reaction time; 55°C of reaction temperature, yield of biodiesel found to be 45% and it was noticed that biodiesel yield continuously increases up to 80 minutes beyond which yield of biodiesel is stagnant. When temperature increased from 55°C to 60°C yield of biodiesel sharply increases up to 88% with reaction time of 80 minutes. Further increase in temperature up to 65°C yielded biodiesel up to 78% and noticed to reduce with further reaction time which may be due to vaporization of methanol whose boiling point is closer to 64.7°C. The optimal yield of biodiesel was noticed at 60°C with the reaction time of 80 minutes as 88% [2, 5-9].

Effect of catalyst concentration on biodiesel yield

Figure (2) shows effect of KOH catalyst concentration on the yield of biodiesel at reaction temperature of 55°C, 60°C and 65°C. From this it can be noticed that the maximum yield of biodiesel was lying between 75% and 88% at all reaction temperatures with the catalyst concentration of 2.4 to 2.6 % weight of catalyst to oil. At 55°C the yield of biodiesel was found to be 75% with the catalyst concentration of 2.6% weight of catalyst to oil. Further increase in catalyst concentration above 3% weight lead to sludge formation results in negative yield of biodiesel as shown in Figure (2).

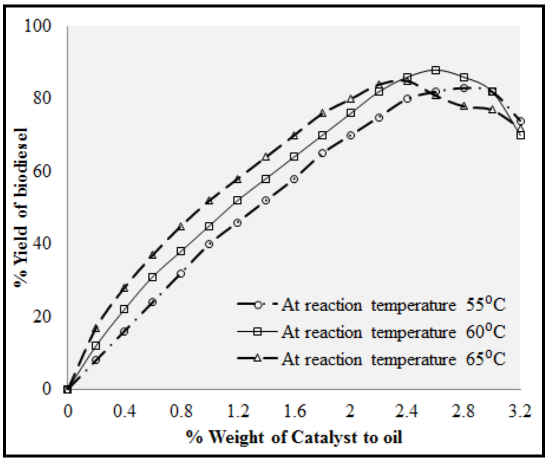

Figure 2. Comparison of biodiesel yield with catalyst concentration at 55°C, 60°C and 65°C reaction temperature

The yield of biodiesel is found to be higher (88%) with the catalyst concentration of 2.5% weight of catalyst to oil, with a reaction temperature of 60C. Further increase in temperature up to 65°C resulted with a biodiesel yield of 78% with the catalyst concentration of 2.2% beyond which biodiesel yield was drastically reduced, which may be due to unbalanced chemical equilibrium and loss of methanol [17-22].

Effect of molar ratio on biodiesel yield

The Figure (3) shows the effect of molar ratio on the biodiesel yield at the various reaction temperature. Theoretically the molecular weight of canola oil and methanol was found to be 885 g/mole and 32.04 g/mole respectively. The optimal molar ratio to be used in transesterification with KOH as catalyst was arrived at 1:5 at temperature between 55°C and 65°C. At 55°C the maximum yield of biodiesel was found to be 81% at molar ratio 1:5. With increase in temperature up to 60°C yield of biodiesel was found to improve up to 88% at molar ratio 1:5 beyond which methanol was found to have no reaction with canola oil.

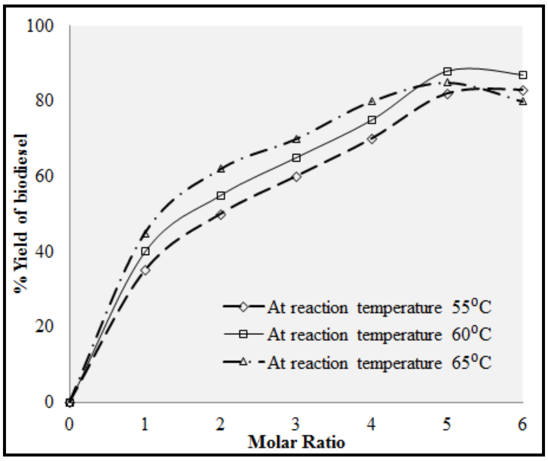

Figure 3. Comparison of biodiesel yield with molar ratio at 55°C, 60°C and 65°C reaction temperature

At 65°C the yield of biodiesel also shows steady increases with increase in molar ratio up to 1:5 but shows negative improvement after 80% which may be due to evaporation loss of methanol. This could be compensated by addition of methanol beyond 60°C which may be difficult to recover [10, 24].

Conclusion

Biodiesel obtained from canola seed oil was found to be a promising source with the following conclusions.

- Soxhlet oil extraction procedure for extracting oil from canola seeds was very much efficient with extraction efficiency of 97%. n-hexane which was used as solvent for extraction was also recovered up to 90 – 95%.
- The acid value and FFA content of canola biodiesel was found to be 0.018 mg/KOH g^{-1} and less than 2% respectively which eliminates the acid catalyse esterification.
- The base catalyse transesterification was carried out using methanol and KOH as a catalyst which yielded 88% biodiesel useable in Internal Combustion Engines.
- The yield of biodiesel was optimized with reaction temperatures 55°C, 60°C, 65°C based on reaction time, catalyst concentration and molar ratio.
- The results indicated that optimal yield of biodiesel was obtained at reaction temperature 60°C and reaction time 80 minutes, 2.5% of catalyst concentration and molar ratio of 1:5.
- The physio-chemical properties of canola seed oil was compared with other vegetable oils and found to be in ASTM 6751 standards.

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