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Extraction and Optimization of biodiesel yield from wax esters of Apis melifera (Honey Bee)

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Abstract: Wax esters from Apis melifera (honey bee) is studied in this research article for extraction of Biodiesel. The study shows that the long chain mono-alkyl ester from the beeswax is transformed into small chain methyl esters by a two stage trans-esterification reaction. Primary stage constitutes of acid catalysed esterification in which Wax Esters, Methanol and Concentrated Hydrochloric acid is used to reduce the free fatty acids. Base catalysed esterification is followed with treated wax ester, Methanol and catalyst at the ratio of 4:1:0.02. An optimization study was conducted with changing the catalyst (Sodium Hydroxide and Potassium Hydroxide), reaction temperature and molar ratio. It is found that at molar ratio 1:0.25, reaction temperature 60^{o}C, Sodium Hydroxide concentration of 0.02% by weight, yielded 85% of Biodiesel.
Keywords: Wax Esters, Trans-esterification, Biodiesel, Animal fat.

1. Introduction

Nowadays, the engineering world is encountering dual crisis, one on depletion of fossil fuel and the other on hazardous environmental pollutant. It is very important for today's world to identify an alternative to fossil fuel to meet the future demands for energy. Researchers identify four major sources of energy which would replace the fossil fuels to the considerable level namely vegetable oils, used vegetables oils, animal fats and oleaginous micro-organisms.Biodiesel is found to have gained qualitative attractions by many researchers due to their comparable physio chemical properties with petro diesel, reduced environmental effects and their renewability [1,2].

The mono alkyl long chain esters contribute as biodiesel for its use in diesel engines as a fuel. It is estimated that 65% to 75% of alternative fuels lie in the category of used and straight vegetable oil whereas the remaining quantity is derived from animal fat and micro-organisms .oleaginous micro-organisms yield a better quantity of oils and fatty acids with few species of bacteria, fungi and algae. Animal fat relatively finds a better place in the production of biodiesel because of its availability and economic advantage incomparison with other sources. Secretion of many insects as a bi-product leads to accumulation of fatty acids in its hive which are solid at room temperature as waxes. Chemically treating, these waxes converts them self into fatty acids with longer hydro carbon chains so it is mandatory to convert these longer hydrocarbons chains into smaller groups so that it remains as liquid at room temperature. Honey bee wax is one of the major contributors as bio diesel to be used in internal combustion engines [3,4].

In India Apis melifera is one of the most abundantly found species of honey bee which secretes wax at prominent quantity as a bi-product of honey. Honey bee wax is composed of many heterogeneous complex substances like long chain hydro carbons includes Alkanes, Alkynes,Esters and Fatty acids.Tulloch analysed and compared the composition of bee wax and other waxes secreted by insects. he expressed the wax of insects has structural and productive material and found that it contains unhydrolysed wax and hydroxyl acids at

various compositions he concluded that bumble bee wax contains both saturated and unsaturated hydro carbons along with the mono and di unsaturated esters [15].Manzano has discussed the production of biodiesel from various insects depending upon its fat content. He noticed that the lipid content was varied between 25% to 30% for many insect species with the Arophalus sp. containing 56.8% of lipid content as the highest. He has analysed the lipid content of many insect at various stages of development like larvae, perpupa, pupae, nymph and adult across the orders of coleoptera, hymenoptera, orthoptera and Lepidoptera [10].Michel. A. Jackson used supercritical carbon-di-oxide in the Methanolysis process for isolating long chain aliphatic alcohol from bee's wax he has described that beeswax consists of 40% long chain esters which can be transformed into fatty acid methyl esters by the trans-esterification process using supercritical carbon-di-oxide. He also demonstrated the separation of waxes and triglycerides from corn bran wax [11,12].

In this paper, trans-esterification process is reported in two stages. Acid catalysed esterification being the primary stage in which the solid beeswax was heated to critical temperature and Methanolysis was carried out. This process is followed by base catalysedesterification by sodium hydroxide and methanol to convert mono- alkyl ester into fatty acid methyl ester.

2. Experimental methods

6Kg of honey bee hive was collected from Javadhu hills, Thiruvannamalai district which was mainly formed by Apis melifera (honey bee). The hive was cleaned thoroughly for removing the excess honey and soaked in boiling water at 80^{o}C for 4 hours for separating the hive debris and wax .The entire setup is brought to the room temperature after which solid wax occupying the top layer was removed carefully. The process is repeated for 3-4 times to remove the unwanted impurities from the beeswax.The two stage trans-esterification process was employed to transform the beeswax into a bio diesel usable in internal combustion engines. The primary stage comprises of acid catalysed esterification with the ratio of 1:2:0.04 of wax, methanol and concentrated hydrochloric acid for reducing the free fatty acid content from 14.5%to >2%. The process is followed by base catalysed esterification in which 1:0.25:0.02 of treated oil, methanol and sodium hydroxide.

100gm of honey beeswax was placed in a flat bottomed beaker and heated up to 60^{o}C 200ml of methanol and 4ml of Concentrated Hydrochloric acid was mixed thoroughly and poured in the flat bottomed beaker and stirred constantly for 120 minutes to achieve the homogenous phaseseparation and allowed to cool to get the content of beeswax in liquid form.by this process 65ml of treated beeswax oil was mixed with methanol and 2.5 gm. sodium hydroxide at the molar ratio of 1:0.25 at 60^{o}C.By this process 85% of beeswax biodiesel was obtained an optimization study was also carried out by varying the reaction time and temperature and the yield of biodiesel were estimated [5,6,14].

3. Results and discussion

The yield of biodiesel was optimised based on temperature and nature of catalyst the primary optimization study was carried out at 55^{o}C,60^{o}C and 65^{o}Cfor both acid and base catalysed esterification in the secondary optimization study was used to optimize effect of catalyst on the trans-esterification rate by employing sodium hydroxide and potassium hydroxide for the yield of biodiesel.

3.1 Acid catalysed esterification

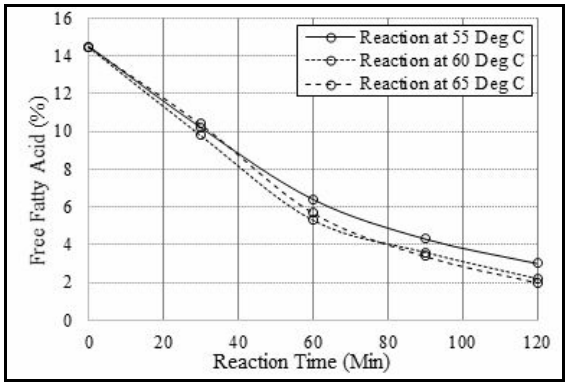

Figure 1. Acid catalysed esterification at 55^{o}C, 60^{o}C and 65^{o}C

Five sets of 100ml flat bottom beaker equipped with heating element, thermometer and a magnetic stirrer was used for this acid catalysed esterification of free fatty acid. The reaction setup is maintained between 55 to 65^{o}C and 200 rpm throughout the entire process. The figure 1 shows the reduction of free fatty acid content with reaction time and at various reaction temperatures in acid catalysed esterification. The reaction temperature was varied between 55 and 65^{o}C for the entire experimentation. The free fatty acid content of beeswax oil was estimated to be 14.5% which is to be reduced to a greater value for converting it into a Biodiesel. At55^{o}C, the beeswax oil was mixed with concentrated hydrochloric acid and methanol which continuously reduced the free fatty acid content from 14.5% to 3% with a reaction time of 20 minutes. With an increase in temperature up to 60^{o}C the conversion rate was noticed to be efficiently increased and there by the free fatty acid content was brought down to >2.2% as shown in figure 1 further increase in the temperature to 65^{0}C showed minimal effect in the conversion rate of free fatty acids.

3.2 Base Catalysed Esterification

Figure 2A and 2B shows the variation in Biodiesel formation with respect to reaction time by using Potassium Hydroxide and Sodium Hydroxide respectively. Figure2A depicts the formation of Biodiesel with variation in the reaction temperature between 55 to 65^{0}C and 150 rpm using KOH as the catalyst at 55^{o}C,30 minutes reaction time the conversion efficiency of biodiesel was around 39% and gradually increased up to 76% for a period of 60 minutes beyond which further improvement in the conversion efficiency was not noticed. With an increase in reaction temperature upto 60^{o}C and KOH as a catalyst the conversion efficiency was found to be 80% whereas with an increase in the temperature up to 65^{o}C the base catalysed esterification showed marginal negative improvement with a conversion efficiency of 79% which may be due to delayed dissociation of potassium ion and hydroxide ion to initiate the catalyst reaction.

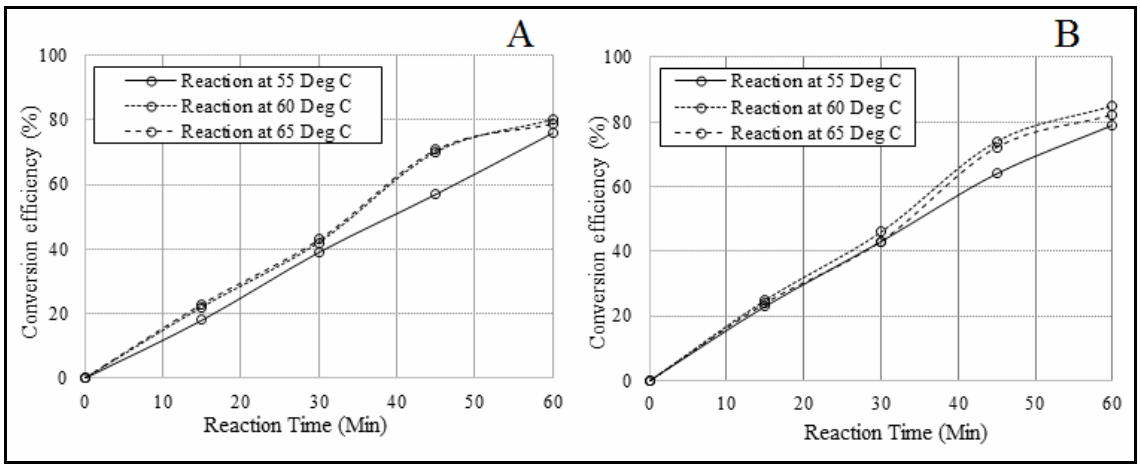

Figure 2. Comparison of Base catalysed esterification efficiency with Potassium Hydroxide (A) and Sodium Hydroxide (B) as catalyst

Figure2B showsthe base catalysed esterification with Sodium Hydroxide as a catalyst under the similar reaction environment. At 55^{o}C the conversion efficiency was found to be 79% with a reaction time of 60 minutes with an increase in temperature up to 60^{o}C the biodiesel conversion efficiency was found to increase upto 85% with a reaction time of 60 minutes beyond which no further improvement was noticed. Further increasing the reaction temperature up to 65^{o}C showed a negative improvement in the yield of Biodiesel at this temperature the conversion efficiency was found to be 82% with reaction time of 60 minutes. With the comparison of potassium hydroxide and sodium hydroxide as catalyst sodium hydroxide was found to perform better with minimal amount of energy loss.

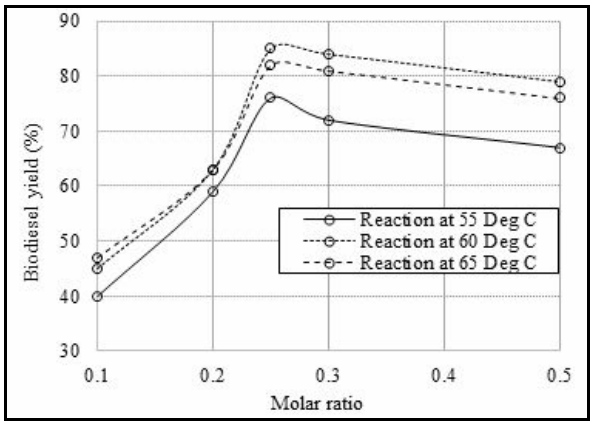

Figure 3. Yield of biodiesel as with respect to molar ratio and reaction temperature

The Figure 3.shows the effect of molar ratio on the yield of Biodiesel at 55 ^{o}C,60^{o}C and 65^{o}C at 55^{o}C, the Biodiesel yield was noticed to be the maximum of 76% at a molar ratio of 1:0.25 with a reduction in molar ratio between 0.1 to 0.2 evidenced a lower yield of Biodiesel between 40 to 58%. On the on the other hand when the molar ratio was increased between 0.3 to 0.5, the yield of Biodiesel was found to decrease up to 67% which may be due to excess methanol and unstable chemical equilibrium [13]. When the reaction temperature was increased up to 60^{o}C a similar trend in yield of Biodiesel was noticed with 85% efficiency at 1:0.25 molar ratio further increase in temperature up to 65^{o}C showed a reduction in the yield of Biodiesel from 85% to 76% as shown in the Figure 3.

4. Conclusion

In this present experimental investigation the two stage trans-esterification procedure proved to be an effective method to produce beeswax bio diesel. Acid catalysed esterification with concentrated hydrochloric acid and methanol reduces the free fatty acid content from 14.5% to less than 2% at 60^{o}C and 200 rpm. The base catalysed esterification with 0.02% sodium hydroxide and 25% by volume of methanol at 60^{o}C yielded 85% biodiesel. An optimization study indicates the maximum yield ot reaction temperature of 60^{o}C, reaction time of 120minutes and 60 minutes for acid catalysed esterification and base catalysed esterification respectively, constant stirring between 150 and 200, with sodium hydroxide as a catalyst.

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