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BIODIESEL SYNTHESIS FROM KARANJA USING SONOCHEMICAL REACTOR

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ABSTRACT

With depleting peteroleum resources, there is urgent need to find for alternative sources of energy. Biodiesel obtained from renewable sources such as Karanja oil can be better alternative to meet the growing demand and environmental concerns. Karanja is found abundantly in all parts of India. Other aspects need to address on reducing the cost of processing of biodiesel synthesis from Karanja. Since non-renewable consists of higher amount free fatty acids and it needs to be treated by process of pretreatment followed by biodiesel synthesis. In present work sonochemical methods base on cavitation technique was used for reducing the processing conditions for biodiesel synthesis. It has been observed that temperature requirement is reduced from 60 to 40^{0}C compare to conventional method and conversion of biodiesel was 98%. Obtained biodiesel properties are closely match with ASTM standards.

Keywords: *Biodiesel, Karanja, Pretreatment, Sonochemical, Transesterification*

INTRODUCTION

With increasing number of automobiles has leads to increase in demand of fuels. The increasing cost of petroleum is another concern for developing countries as it will increase their import bill. The world is also presently confronted with the twin crisis of fossil fuel depletion and environmental degradation. Fossil fuels have limited life and increasing cost of these fuels has led to the search of alternative renewable fuels for ensuring energy security and environmental protection. Increasing environmental concern, diminishing petroleum reserves and agriculture base economy of our country are the driving forces to promote biodiesel as an alternate fuel [1].

For developing countries fuels of bio-origin can provide a feasible solution to this crisis. Certain edible oils such as cottonseed, palm, sunflower, rapeseed, and safflower can be used in diesel engines. For longer life of the engines these oils cannot be used straightway. These oils are not cost effective to be used as an alternate fuel in diesel engines at present. Since India is net importer of vegetable oils, edible oils cannot be used for production of biodiesel. India has the potential to be a leading world producer of biodiesel, as biodiesel can be harvested and sourced from non-edible oils like Jatropha Curcus, PongamiaPinnata, Neem (Azadirachtaindica), Mahua, castor, linseed, Kusum (Schlecheratrijuga), etc [2].

Long-term engine test results showed that durability problems were encountered with vegetable oils because of deposit formation, carbon buildup and lubricating oil contamination. Thus, it was concluded that vegetable oils must either be chemically altered or blended with diesel fuel to prevent premature engine failure. Blending, cracking/pyrolysis, emulsification or transesterification of vegetable oils may overcome these problems. Heating and blending of vegetable oils may reduce the viscosity and improve volatility of vegetable oils but its molecular structure remains unchanged. Hence, polyunsaturated character remains. Blending of vegetable oils with diesel, however, reduces the viscosity drastically and the fuel handling system of the engine can handle vegetable oil-diesel blends without any problems [3].

On the basis of experimental investigations, it is found that converting vegetable oils into simple esters is an effective way to overcome all the problems associated with the vegetable oils. Most of the conventional production methods for biodiesel use basic or acidic catalysis. A reaction time of 45min to 1h and reaction temperature of 55-65° C are required for completion of reaction and formation of respective esters. Biodiesel consists of alkyl esters of fatty acids produced by the transesterification of vegetable oils. The use of biodiesel in diesel engines requires no hardware modification. In addition, biodiesel is a superior fuel than diesel because of lower Sulphur content, higher flash point. Biodiesel has a higher cetane number than petroleum diesel, no aromatics and contains up to 10% oxygen by weight. Biodiesel fueled engine emits fewer pollutants. The characteristics of biodiesel reduce the emissions of carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) in the exhaust gas as compared with petroleum diesel. Biodiesel can be used in its pure form or as a blend of diesel. It can also be used as a diesel fuel additive to improve its properties [4-6].

Present work investigated synthesis of biodiesel from non-edible sources such Karanja which is abundantly available in all parts of India. Intensified techniques will be employed for enhancing the rate of synthesis process with an objective of reducing the operation cost of biodiesel synthesis. Sonochemical technique base on cavitation phenomena found to be more suitable for intensifying the rate of biodiesel synthesis. Operational parameters for biodiesel synthesis such temperature, molar ratio and catalyst concentration were considered and properties for biodiesel were evaluated using ASTM standards.

Methodology

Pretreatment of Karanja oil: Alkali catalysis process requires unhydrous conditions, so instead of direct use of metal alkali alkoxides we have to reduce the FFA

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content from oil. The suitable method used to reduce FFA is Acid Esterification i.e. homogeneous alkali catalysis (Conc. H_2SO_4). This technique uses a strong acid such as sulfuric acid to catalyze the esterification of the FFAs and the transesterification of the triglycerides. In separation the methanol-acid layer is removed and low FFA oil is washed with Hot distilled water. This removes the fraction of acid or methanol from oil. This oil is then kept in vacuum evaporator.

Biodiesel Synthesis: Reaction Oil with low FFA <5% is allowed for transesterification reaction. Sodium hydroxide NaOH is first mixed with methanol so that sodium alkoxide is formed as shown by reaction (eq.1) from figure 3.3. Triglyceride in the feedstock reacts with sodium methoxide to produce biodiesel -FAME- and Glycerin. This mixture is allowed for separation for 24 h. As biodiesel is lighter than glycerol it forms two-layer upper layer of biodiesel and lower layer of glycerol.

Post-treatment: Glycerol should be removed by gravity separation and biodiesel stock is washed with acid wash (1% H_3PO_4) to neutralize the alkali fraction present in biodiesel stock. This mass is then washed with hot distilled water, which removes the traces of acid present in the mixture. All the unwanted water is removed by gravity separation. The traces of moisture removed by vacuum evaporator. Which is then used for HPLC analysis. The properties of biodiesel verified to maintain ASTM standard quality.

RESULTS AND DISCUSSION

Pretreatment of Oil: Conversion of free fatty acid was monitored using measuring the acid value of oil. Temperature, molar ratio and catalyst concentration parameters were optimized. The change in acid value with respective time base on these parameters is shown in Figures 1, 2 and 3 respectively. These figures clearly indicate that acid value is decreasing with time, initial increase in temperature, molar ratio and catalyst concentration, with further increase (optimal value) these parameters does not have the significant impact on reduction in acid value.

1. The refined Karanja oil has shown excellent qualities as a raw material. The experiments showed that the correct tuning in the process variables can promote higher conversions into methyl esters.
2. The ratio ethanol / oil was the most influential variable in transesterification methods.
3. The best conversion and phase separation conditions were obtained with the use of NaOH.
4. Comparison between the conventional and ultrasound methods show that the reaction time have been considerably reduced with the use of ultrasound.
5. The remarkable results obtained with the reaction time when ultrasounds were employed can be explained by intense mass transfer afforded by the unique conditions generated by cavitation noise.
6. Thus, the use of ultrasounds presents itself as a potential technological route of

production of biodiesel, capable of meeting high demands in short periods of time. Adjustments related to the type of ultrasonic reactor (or transducer) and in the process of vegetable oils sonolysis can lead to an excellent alternative for biodiesel production.

CONCLUSIONS

- The refined Karanja oil has shown excellent qualities as a raw material. The experiments showed that the correct tuning in the process variables can promote higher conversions into methyl esters.
- The ratio ethanol / oil was the most influential variable in transesterification methods.
- The best conversion and phase separation conditions were obtained with the use of NaOH.
- Comparison between the conventional and ultrasound methods show that the reaction time have been considerably reduced with the use of ultrasound.
- The remarkable results obtained with the reaction time when ultrasounds were employed can be explained by intense mass transfer afforded by the unique conditions generated by cavitation noise.
- Thus, the use of ultrasounds presents itself as a potential technological route of production of biodiesel, capable of meeting high demands in short periods of time. Adjustments related to the type of ultrasonic reactor (or transducer) and in the process of vegetable oils sonolysis can lead to an excellent alternative for biodiesel production.

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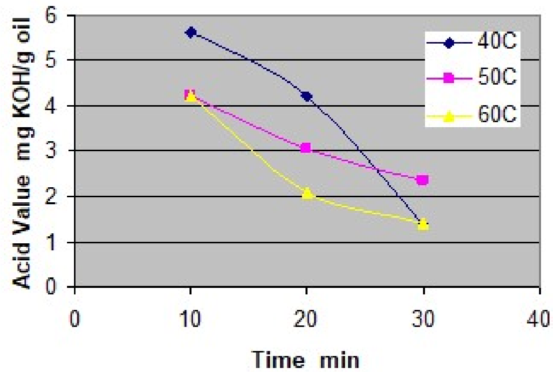

Figure 1: Effect of temperature on esterification for 1:6 molar ratio, 1% weight of catalyst concentrations using sonochemical method

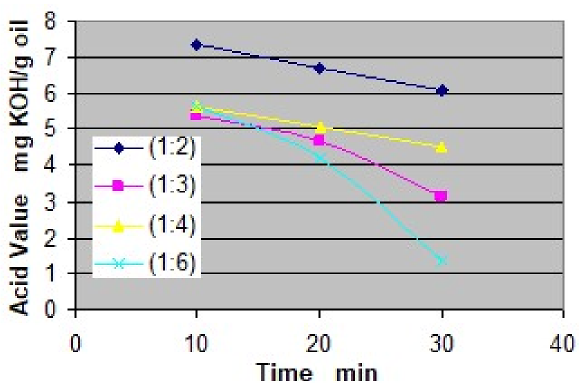

Figure 2 Effect of molar ratio on esterification for temperature 40^{0}C, 1% weight of catalyst concentrations using sonochemical method

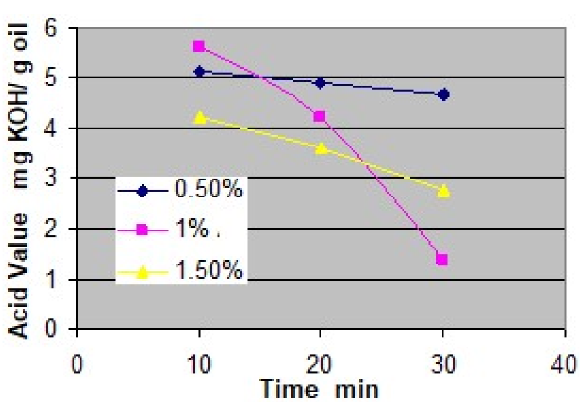

Figure 3 Effect of catalyst concentration on esterification for 1:6 molar ratio, temperature 40^{0}C using sonochemical method

Synthesis of Biodiesel

Similar to pretreatment of oil, effect of operational parameters on biodiesel synthesis were optimized and optimized results of study have been desipated in table 1.

Table 1: Optimized parameters for biodiesel synthesis

Parameters	**Value**
Temperature	40^{0}C
Molar ratio (oil to methanol)	1:6 (Oil /Methanol)
Catalyst concentration	1 % NaOH wt/wt of oil
Conversion	98%

Properties of Pure Biodiesel (B100): Properties of biodiesel were evaluated using the procedure stated by ASTM D6758 and results of same is shown in Table 2. These values clearly stated that obtained biodiesel was meet the standard.

Table 2: Properties of Biodiesel

Property	**Unit**	**Value**	**ASTM**	**BIS**
Acid Value	mg of KOH / g of Oil	0.814	0.8	< 0.8
Viscosity at ^{0}C	cSt	4.527	1.9-6.0	5.431
Density at 32 ^{0}C	g/ml	0.852	0.86-0.9	0.889
Flash point	^{0}C	240	>100	116