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BIODIESEL DEVELOPMENT FROM HIGH FREE FATTY ACID PUNNAKKA OIL

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ABSTRACT

Punnakka oil, non-edible oil available in India, was esterified to produce biodiesel. The procedure involves a two stage process, acid esterification and alkaline esterification. The oil contains high free fatty acid (FFA) content of 19.8%. The acid value of the oil was reduced by acid esterification. The product from this stage was subjected to alkaline esterification to produce biodiesel. The effects of important parameters like methanol to oil ratio, reaction temperature, catalyst concentration and reaction time were studied and optimum conditions were established. A conversion efficiency of 92.5% was obtained with the optimized reaction conditions. The viscosity and other measured properties are within the range specified by biodiesel standards and are close to the properties of petroleum diesel.

Keywords: punnakka oil, biodiesel development, high free fatty acid oil, transesterification.

1. INTRODUCTION

The research on alternate fuels is at a high profile in the world for quite some time now. The increasing energy demands and depleting fossil reserves are the main cause for this. Also the increasing global warming and other environmental hazards force to reduce the energy extraction from fossil fuel [1]. Out of the alternative fuel used as substitution for fossil fuel, biodiesel is an important one. The attractive fact in the case of biodiesel is that it can be produced from vegetable oils with simple chemical reactions [2]. At the same time the production of biodiesel from vegetable oils, especially edible oils, has started to pose threats to the food security in some countries. This has shifted the attention to biodiesel development from non edible oils. But the non edible oils usually contain more free fatty acids than edible oil thus creating difficulties in the biodiesel production process.

One of the important methods for biodiesel production is transesterification which is a reversible reaction. It produces mono alkyl esters of long chain fatty acids, which is known as biodiesel. For oils with free fatty acid (FFA) content less than 3%, transesterification using a base catalyst is found to be the easier way for biodiesel production [3]. When FFA content is high, as usually seen in non edible oils, it reacts with the alkaline catalyst to form soap. This reduces the conversion efficiency to a large extent [3]. Hence for oils with high FFA content other methods like two stage esterification are required to be designed. The two stage esterification comprises of a first stage acid esterification and a second stage base esterification. The acid esterification stage needs comparatively large amounts of methanol for completion of the reaction [3]. This methanol quantity depends on the FFA content of the oil.

The present paper develops optimum conditions of reactions to produce biodiesel from punnakka oil. Punnakka oil (calophyllum inophyllum) consists of a high amount of FFA in it. Hence it requires careful two stage esterification to produce biodiesel from it. Also the effect of different process parameters are studied by conducting experiments with varying combinations of important parameters.

2. PROPERTIES OF PUNNAKKA OIL

The tree called punna belongs to the family clusiaceae and its botanical name is calophyllum inophyllum L. It is a medium to large size tree with shining leaves and golden seeds. The seed oil is being used as fuel oil for lamps and has got medicinal applications also. Some common names of the tree in other languages are Alexandrian Laurel (English), Surpan (Hindi), Punnagavirshaka (Sanskrit) and Punnai (Tamil) [4]. This tree is found in many countries especially in coastal areas. The kernels of the seeds have high oil content (75%) [5]. usually the seeds are crushed and kernels are separated and sun dried. Oil is taken from the dried kernels.

The fatty acid profile of punnakka oil is shown in Table-1 [6]. The majority of the fatty acid constituents belong to C18 chains i.e.; stearic, oleic, lonoleic acids. It contains about 39% saturated and remaining unsaturated fatty acids. The properties like cloud point, cetane number, stability are increased by the saturated fatty acid esters while the presence of unsaturated fatty acid esters reduce these properties [7].

The acid value of the punnakka oil is found to be 39.6 mgKOH/g oil i.e.; the FFA content is 19.8%. The transesterification procedure can not be successful when the FFA content is more than 3%. Hence to produce biodiesel, the FFA must be converted to esters using acid catalytic esterification before attempting alkaline catalytic esterification.

Table-1. Fatty acid profile of punnakka oil.

Fatty acid	Acronym	Molecular weight	Weight (%)
Palmitic	16:0	256.43	17.9
Hydnocarpic	16:1	254.47	2.5
Stearic	18:0	284.43	18.5
Oleic	18:1	282.47	42.7
Linoleic	18:2	280.45	13.7
Linolenic	18:3	278.49	2.1
Lignocerate	24:0	384.65	2.6

3. METHODS

The punnakka oil contains high amount of free fatty acids. The acid value of the oil is 39.6mg KOH/g of oil. This high percentage of FFA content makes difficulties in the alkaline transesterification process due to soap formation. Therefore a two stage esterification procedure is adopted here. The first stage, namely acid esterification, consists of the use of conc.sulphuric acid as the catalyst. This reaction converts the free fatty acids in the oil to esters thus reducing the FFA. The FFA content of the oil should be less than 3% so as to facilitate alkaline esterification. The acid esterification procedure involves heating of oil, reaction with methanol and conc. sulphuric acid as catalyst. The second stage is alkaline esterification which converts the product from first stage in to biodiesel. KOH is used as catalyst in this stage. The catalyst is dissolved in methanol and mixed with the product from first stage along with continuous heating and stirring.

The set up used in both the cases consists of a flat bottom flask to carry out the reaction, a magnetic stirrer with heating coil for continuous heating and stirring. The mixture after reaction is transferred to a separating funnel for settling.

In the first stage, one liter of crude punnakka oil is taken in the flask and heated to temperature between 50 to 55^{o}C. Methanol is added to the preheated oil and conc. sulphuric acid is added as catalyst. The quantity of methanol is to be in excess of the stochiometric ratio since the reaction is reversible. Excess methanol is required to drive the forward reaction to complete [3]. The mixture is heated and stirred continuously for the required time. Reaction temperature is also an important parameter affecting the speed of reaction and efficiency of conversion. The mixture after the reaction is completed is transferred to a separating funnel and allowed to settle. The excess methanol, acid and other impurities will form a separate layer in the top. This is removed and the bottom layer is used for the second stage i.e.; alkaline esterification.

The product from the acid esterification stage is measured and taken in the flask. It is heated to temperature between 50 to 55^{o}C. The required quantity of KOH as catalyst is dissolved in methanol and added to the preheated first stage product. The reaction is carried out with continuous heating and stirring for the specified time. The mixture after reaction is transferred to the separating funnel and allowed to settle. The biodiesel forms the top layer on settling and the glycerin and any impurities form the bottom layer. The bottom layer is drained out and the biodiesel is taken and washed to remove any excess methanol present.

4. EFFECT OF PARAMETERS

The important parameters that influence the process output quantity and quality are methanol to oil ratio, catalyst concentration, reaction temperature, reaction time and settling time. Experiments are conducted with different sets of parameter values and optimum conditions are established for maximum efficiency of the process.

4.1. Acid esterification

The purpose of this stage is to reduce the FFA content of the crude oil to less than 3%. Experiments are conducted with four sets of methanol to oil ratio (0.35, 0.50, 0.65 and 0.75 v/v), three sets of reaction temperatures (40^{o}C, 50^{o}C and 60^{o}C) and four sets of reaction time (30 minutes, 60 minutes, 90 minutes and 120 minutes). The acid catalyst concentration is taken as 0.75% v/v of oil in all cases. The FFA content of the product is determined in each case using standard chemical titration procedure [8].

4.1.1. Effect of methanol to oil ratio

The molar ratio of methanol required as per stochiometric ratio is 3:1. But since the reaction is reversible large quantity of methanol is required to drive the reaction to complete. When methanol at the ratio of 0.35 and 0.5 v/v were used the reaction was not complete which is indicated by the black layer forming at the bottom instead of at the top. Methanol at the ratio of 0.65 v/v is found to be sufficient to complete the reaction. The FFA content is reduced to below 2% at this condition. Further increase in methanol reduces FFA content more but the reduction is not significant. Also this will increase the cost of the production. Hence the ratio of 0.65 v/vis taken as the optimum ratio. The results are shown in Figure-1.

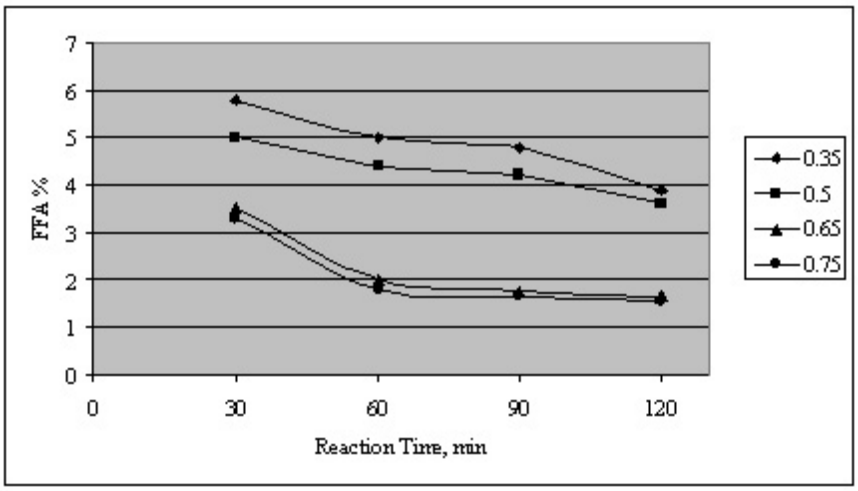

Figure-1. Effect of methanol-to-oil ratio and the reaction time on reduction of FFA of punnakka oil (catalyst concentration of 0.75% v/v of oil and reaction temperature of 60°C).

4.1.2. Effect of reaction temperature

Heating of the oil increases the speed of the reaction. Preheating of oil is done to temperatures between 50 - 55°C. Reaction temperatures of 40°C, 50°C and 60°C are used and FFA content of products in each case is measured. The methanol to oil ratio of 0.65 v/v, found out as optimum earlier, is used in all cases. The FFA content is reduced to lower values as the reaction temperature is increased. This is matching with the findings by earlier researchers [9, 10]. FFA content of less than 2% occurs at 60°C as shown in Figure-2. Further increase in temperature may cause more reduction in FFA content but is not preferred since there is chance of methanol loss due to vaporization at high temperatures [9].

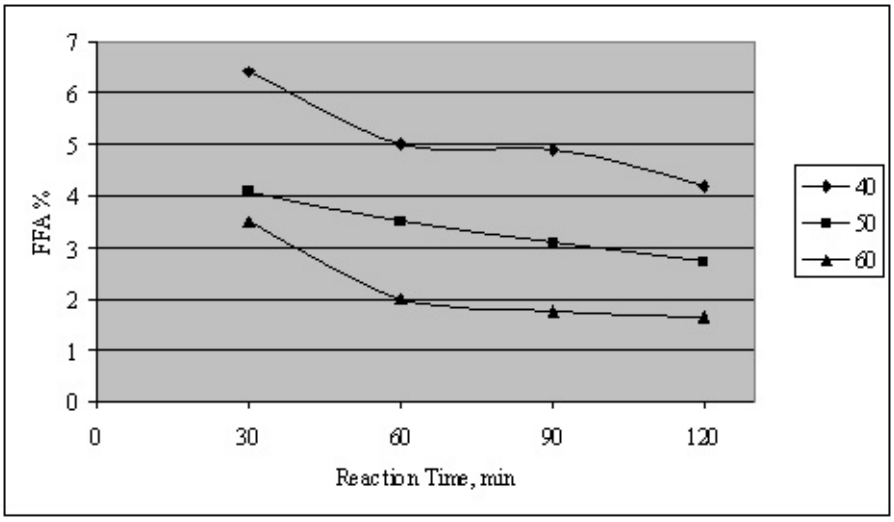

Figure-2. Effect of reaction temperature and reaction time on the reduction of FFA of punnakka oil (methanol-to-oil ratio of 0.65 v/v and catalyst concentration of 0.75% v/v of oil).

4.1.3. Effect of reaction time and settling time

In general the FFA content reduces more or the reaction becomes more complete by conducting the reaction for more time. The experiments show that reaction for 60 minutes is sufficient to complete the reaction with required reduction in FFA content of the oil. Further increase in reaction time causes slight increase in FFA content reduction but is not much beneficial as more reaction time needs more heat energy input. The mixture after completion of reaction is to be allowed to settle when the excess methanol, acid and other impurities separate as top layer. It is seen that the layer separation starts after 30 minutes settling time. But allowing the mixture to settle for 90 minutes is found as required time for complete separation. More settling time does not benefit significantly.

4.1.4. Optimum parameter values

Increasing the different parameter values causes more reduction in the FFA content of the oil. But optimum conditions are established based on the observations with varying conditions which leads to sufficient reduction in the FFA content ie; to less than 3%. The preferred optimum conditions are methanol to oil ratio of 0.65 v/v, acid catalyst concentration of 0.75% v/v of oil, reaction temperature of 60°C, reaction time of 60 minutes and settling time of 90 minutes.

4.2. Alkaline esterification

The product from the first stage consisting oil with FFA less than 3% is subjected to transesterification using KOH, a base catalyst. The oil is taken in standard flask and heated to temperature between 50 - 55°C. Methanol in the required quantity is taken and measured quantity of KOH is dissolved in it. The catalyst is dissolved in methanol prior to addition to the oil to avoid problems of moisture absorption by the catalyst [1]. The potassium methoxide prepared is added to the preheated oil. The mixture is continuously stirred at constant speed keeping temperature constant at 60°C and is not allowed to go above 60°C to avoid methanol loss. The mixture after heating and stirring for required time is transferred to a separating funnel and kept for settling. On settling, the biodiesel forms as the top layer and glycerin and any impurities remain as the bottom layer. The bottom layer is removed and biodiesel is collected. It is washed to remove the presence of any excess methanol and soap. The biodiesel is further dried to remove any moisture present in it.

The oil used in the different set of experiments in the second stage is produced by conducting the first stage with the optimum conditions of different parameters already established. Reaction temperature of 60°C is used in all experiments. The conversion efficiency resulting from different experiments are measured and the variation with respect to different parameters is studied to establish the optimum conditions. Conversion efficiency refers to the percentage of yield of biodiesel from the oil by transesterification [7].

4.2.1. Effect of methanol to oil ratio

Methanol for transesterification is taken based on the quantity of product oil resulting from the first stage. Even though the stochiometric ratio is 3:1, excess methanol is required to drive the forward reaction to complete. Experiments are conducted with three different methanol to oil ratio (0.1, 0.2 and 0.3 v/v) at different reaction temperatures and catalyst concentrations. The plot of conversion efficiency to methanol oil ratio is given in Figure-3. It is seen that the conversion efficiency is low when methanol to oil ratio of 0.1 is used. The efficiency is found optimum with methanol to oil ratio 0.2 v/v. Further increase in methanol quantity does not produce significant increase in the conversion efficiency. Hence 0.2 is selected as an optimum value for the methanol to oil ratio.

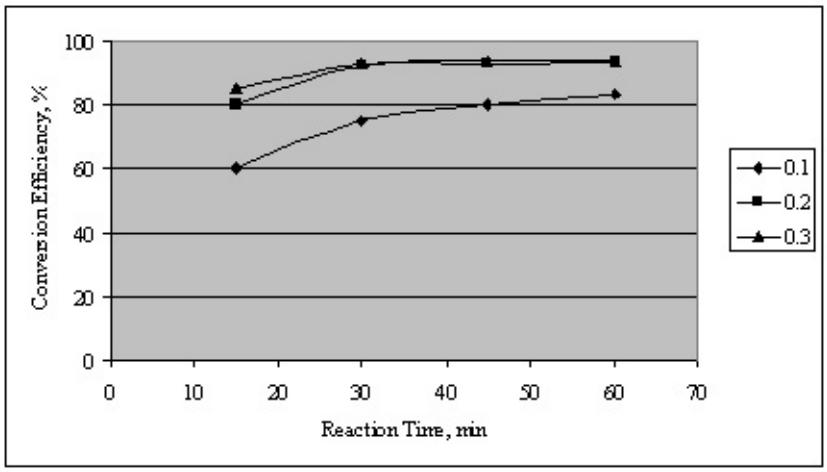

Figure-3. Effect of methanol-to-oil ratio and reaction time on conversion efficiency (catalyst concentration of 1% w/v of oil and reaction temperature of 60°C).

4.2.2. Effect of catalyst concentration

The presence of catalyst is very essential to carry out the transesterification successfully. It is earlier reported that without the presence of catalyst, with even 120 minutes of reaction time of Cynara cardunculus L. oil with methanol, the transesterification does not take place [10]. KOH is used as catalyst in this case. Experiments are conducted with four different catalyst concentrations (0.5, 0.75, 1.0 and 1.5% w/v of oil) to find out the optimum concentration amount. The conversion efficiency increases as the catalyst concentration is increased. Maximum efficiency occurs at catalyst concentration of 1.0, as shown in Figure-4. Further increase in catalyst concentration reduces the conversion efficiency due to the gel formation which increases viscosity [7].

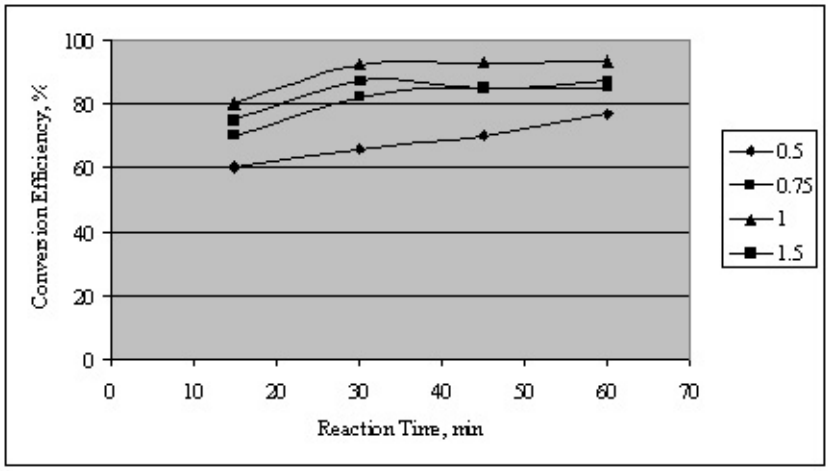

Figure-4. Effect of catalyst concentration and reaction time on conversion efficiency (methanol-to-oil ratio of 0.2 v/v and reaction temperature of 60°C).

4.2.3. Effect of reaction time and settling time

The conversion to biodiesel starts after 15 minutes of reaction itself. But the conversion efficiency is very low at this stage. The conversion efficiency increases as the reaction time is increased. Optimum conversion efficiency is reached after 30 minutes of reaction time. Further increase in reaction time does not result significant increase in conversion efficiency. Also more reaction time needs more energy input due to extended heating of the mixture. The mixture after reaction is transferred to a separating funnel and allowed to settle. The separate layer formation starts after 15 minutes itself. But the separation is completed after 60 minutes of settling and further increase in settling time does not make more positive results.

4.2.4. Optimum conditions for alkaline esterification

The conditions of transesterification for maximum conversion efficiency are established from the different sets of experiments. The maximum conversion efficiency is obtained with a methanol to oil ratio of 0.2 v/v, alkaline catalyst concentration of 1.0% v/w of oil, reaction temperature of 60°C, reaction time of 30 minutes and settling time of 60 minutes. In literature, for similar oil like polanga oil, the two stages (in fact they describe a three stage process) are carried out with lesser methanol to oil ratios but with long reaction times [12].

5. PROPERTIES OF PUNNAKKA BIODIESEL

The important properties of the punnakka biodiesel like specific gravity, calorific value, flash point, and FFA content are determined. The standards used for measurement of properties and the property values are listed in Table-2. The standards specified for biodiesel by ASTM 6751-02 and the standard values for petroleum diesel are also shown in Table-2. The values are comparable with the standards set for biodiesel and also with those for petroleum diesel. The important part of the punnakka biodiesel structure is by C18 chains. Approximate percentages of carbon, hydrogen and oxygen composition are 76.6% carbon, 12.5% hydrogen and 10.9% oxygen. The transesterification process reduces the viscosity of the punnakka oil from 64.2 mm^2/s to 5.6 mm^2/s, which is in the limits specified for biodiesel. The calorific value of the punnakka biodiesel is 37, 500 kJ/kg and the flash point is 146°C.

Table-2. Properties of punnakka biodiesel in comparison with biodiesel standards and properties of petroleum diesel.

Property	Testing procedure	Biodiesel standard ASTM 6751-02	Punnakka biodiesel	Petroleum diesel
Specific gravity	ASTM D4052	0.87-0.9	0.875	0.840
Calorific value MJ/kg	ASTM D240	-	37.5	42.5
Viscosity mm^2/s at 40°C	ASTM D445	1.9-6.0	5.6	2.87
Flash point (°C)	ASTM D93	min. 130	146	76
Acid value mg KOH/g oil	ASTM D974	0.8	0.5	-

6. CONCLUSIONS

The present analysis developed a two stage esterification procedure to produce biodiesel from punnakka oil. The oil contains FFA of 19.8% with C18 chains forming the main constituent. The first stage consists of esterification using conc.sulphuric acid as the catalyst. This converts the FFAs in the oil to methyl esters and thus reduces the FFA content of the oil. The product from this stage is subjected to transesterification in the second stage using KOH as catalyst resulting in to punnakka biodiesel. The biodiesel has properties in agreement with the biodiesel standards and closely matching with those of petroleum diesel. The observations of the analysis are as follows:

The acid esterification reduced the FFA content from 19.8% to 2%. The optimum conditions for the reaction are, methanol to oil ratio of 0.65 v/v, catalyst concentration of 0.75% v/v of oil, reaction temperature of 60^{o}C, reaction time of 60 min and settling time of 90 min. Then the product from this stage is transesterified using alkaline catalyst to produce biodiesel. The optimum conditions of this stage are methanol to oil ratio of o.2 v/v, catalyst concentration of 1.0% w/v of oil, reaction temperature of 60^{o}C, reaction time of 30 min and settling time of 60 min. Conversion efficiency of 92.5% is achieved with these optimum conditions of reaction.

The increasing values of the different parameters show an increasing trend in the reduction of FFA content in the first stage and conversion efficiency in the second stage. In the case of methanol to oil ratio and reaction temperature the optimum conditions are selected at a value beyond which the improvement in the respective properties of the stages is not significant. For catalyst concentration in second stage the optimum condition is selected above which the conversion efficiency is reduced. The results are direct indicatives of the suitability of the low cost punnakka oil for biodiesel production.

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