Optimized Biodiesel Production and Emulsification of Pongamia Seed Oil Using Taguchi Method

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Abstract - In the present investigation, two stage transesterification process of raw Pongamia oil with concentrated sulphuric acid, methanol and sodium hydroxide produced *Pongamia pinnata* seed biodiesel. The process parameters including the reaction time, reaction temperature, acidic concentration, base concentration and methanol to oil molar ratio were varied within the specified range to obtain maximum biodiesel yield. Methanol to oil molar ratio 7:1, reaction time 60 minutes, reaction temperature 70^{o}C and catalyst concentration of 0.25% yielded 96% of biodiesel. Design of experiments based on four factor three level (L9) orthogonal array of Taguchi approach reduced the number of iterations from 81 to 9 in identifying the stable emulsified formulation of biodiesel, diesel and water with surfactant. Sample number 8 viz., D75-PBD20-W5-S6 emulsified fuel blend was found to be stable for more than fourteen days. Based on this Taguchi method, number of experiments and duration was significantly reduced in identifying the stable emulsified fuel blend which can be tested further in CI engine.

Keywords - Pongamia oil, Biodiesel, Two stage transesterification, optimization, Taguchi method.

1. Introduction

Stringent diesel emission standards and diminution of fossil fuels has propelled the researchers to identify an alternate for the petroleum products. Increased energy demand in the transportation and industrial sector has escalated the usage of fossil fuels thereby making it a necessity to develop renewable energy resources. As per the International Energy Agency report, the energy demand in the year 2030 is anticipated to be 50% more than the existing energy consumption. Recently researches are carried out on the biofuels such as biodiesel, alcohols, hydrogen etc. which are being considered as substitute to the fossil fuel [1, 2]. Biodiesel at present the most widely accepted substitute for the diesel fueled engines due to its technical and environment advantages. Biodiesel or methyl esters produced from the animal fat, vegetable or water cooking oil (WCO) are currently being explored by many researchers for its usage. Biodiesel has favored greater acceptance over petroleum diesel due to their bio degradable properties, higher cetane number, low carbon monoxide, particulate matters, unburnt hydrocarbons, sulfur content etc. However, it could not completely replacing the petroleum diesel due to its higher NO_x emission, high viscosity, oxidation and poor fuel atomization [3].

Pongamia pinnata is a thriving leguminous tree associated to humid and sub-tropical climatic conditions with the potential for high oil production rate. It is adaptable in all kind of soil conditions varying from drought land such as strong as stony and dry sand to marshy lands. The extracted pongamia pinnata oil is yellowish brown in color possessing dreadful smell and sour taste. The presence of chemicals such as karanja, pongapin, pongaglobin and other toxic flavonoids classifies the oil as non-edible oil, thereby averting feedstock consumption to a relatively larger extent [4, 5]. Production of biodiesel from the pongamia oil is carried out by double stage transesterification process in presence of sodium hydroxide and sulfuric acid which acts as base and acid catalyst respectively. The reaction time, catalyst concentration and methanol to oil molar ratios are

optimized during transesterification. It is observed that double stage transesterification of triglycerides by methanol has proved to be the most effective process for the production of biodiesel [6]. Due to high viscosity, lower density, poor fuel atomization and higher NO_x emission rate by biodiesel, researchers carried out studies on blending and emulsifying techniques. Emulsion of water with diesel and biodiesel are the ongoing trends with respect to performance, combustion and environmental aspects [7-10].

Meher et al. [11] adopted transesterification process to produce biodiesel from pongamia oil in presence of methanol and potassium hydroxide as catalyst. The biodiesel yield was 97% by employing oil to methanol molar ratio of 12:1 at 65°C reaction temperature. The process was carried out for three hours at an agitating speed of 360 rpm. The biodiesel was further characterized by TLC and HPLC analysis to verify various FAME contents, glycerides, glycerol etc. Physiochemical properties such as viscosity, flash point, fire point, cloud point and pour point were identified to determine the quality of fuel. Gourav Dwivedi et al. [12] described the potential aspects of pongamia pinnata. Large scale production due to its non-edible properties, prospects of growing on unpleasant and relentless environmental conditions and oil extraction contents were describe in this paper. Production of biodiesel was obtained by transesterification process with sodium hydroxide as catalyst under the molar ratio of 6:1 of alcohol to oil and reaction temperature of 60°C for one hour. Brake thermal energy and brake specific fuel consumption were compared with the neat diesel. Emissions such as hydrocarbons and carbon monoxide were quite low in case of biodiesel.

Md Nurun Nabi et al. [13] presented the prospects and production of biodiesel from jatropha curcas. The biodiesel was produced by two stage transesterification process along with their physiochemical properties which was found to be within the ASTM and EN standards. FTIR and GC-MS analysis of biodiesel unveiled a maximum of 97% of FAME content. On further experimental testing on the engine, emissions such as carbon monoxide, smoke, engine noise decreased with significant increase in the formation of NO_x. Mehdi Atapour et al. [14] employed Taguchi method for design of experiment (DOE) during the production of biodiesel by alkali catalyzed transesterification. The DOE was accomplished by carrying out a double five level four factor central composite design in order to optimize the reaction condition and study the effect of biodiesel yield. Reaction temperature, catalyst concentration, molar ratio of alcohol to oil, reaction time and type of catalyst were the factors considered for the optimization. Methanol to oil ratio of 9:1, reaction temperature of 65°C with reaction time 45 minutes and sodium hydroxide concentration of 0.72% w/w as catalyst were found to be the optimum conditions for better yield. Chongkong et al. [15] have synthetized the production of biodiesel form palm fatty acid distillate (PFAD). Taguchi method was carried out for PFAD to study the impact reaction temperature, molar ratio of methanol to PFAD, quantity of catalyst and reaction time. Many researchers have experimentally analyzed the biodiesel production in similar way [18-22].

The present experimental analysis is to investigate the various aspects of biodiesel obtained from Pongamia pinnata seed. FFA contents of the vegetable oil is reduced by double stage transesterification process and the triglyceride oil is converted to methyl esters. Physiochemical properties are identified and found to be within ASTM and EN standards. Emulsion of biodiesel diesel blend with water is carried out by using Taguchi method for DOE to achieve optimized results.

2. Materials and Methods

2.1. Production of Pongamia oil

Five kgs of Pongamia pinnata seeds is purchase from a dealer in Gummidipoondi, Chennai, India. The seeds are scattered and placed under sunlight for 72 hours followed by drying and removing the moisture content present in the pongamia pinnata seeds. Traditional mechanical oil expeller method is employed to extract the oil content present in the dried pongamia seeds. Oil yield of 88% is obtained after the seeds are processed by this method.

2.2. Acid Catalysed Transesterification

Acid catalyzed transesterification is carried out after measuring the free fatty acid (FFA) content of pongamia pinnata seed by titration method. The FFA content is noticed to be up to 12% in pongamia oil. The process is carried out in 1500 ml screwed flat bottom bottles with a built in temperature indicator arrangement. The pongamia oil was initially is preheated before proceeding with the reaction.1.5% of sulfuric acid is mixed with 200ml of methanol in a flat bottomed beaker which is later poured into the preheated pongamia oil. The mixture is maintained at 450 rpm agitation speed using a magnetic stirrer at reaction temperatures of 50°C to 70°C for 70 minutes. The reaction is observed thoroughly and monitored. Free fatty acid content of the oil is found to be 0.5% which is confirmed by a ring formation thereby making it favorable to undergo base esterification. The biodiesel yield produced by acid transesterification is found to be 98%.

2.3. Base Catalysed Transesterification

Base catalyzed transesterification is carried out after the FFA level is reduced to less than 1%. Initially the treated

oil is rinsed with distilled water and is soaked at 100°C for 60 mins to remove excess of moisture content. 1000ml of pre heated pongamia oil is taken in the three necked flat bottom flask equipped with magnetic stirrer and temperature indicator device. Sodium methoxide solution is prepared by mixing 0.25% of sodium hydroxide with 450 ml of methanol. 1000 ml of pongamia oil is poured and mixed with 300 ml of sodium methoxide solution. The reaction is carried out at different reaction temperatures from 50°C to 70°C at 450 rpm agitating speed. The mixture is further transferred in to a separating funnel, allowing it to cool and separate the glycerol from fatty acid methyl esters (FAME) with a settling time of 24 hours. FAME content obtained from base catalyzed esterification is washed in distilled water. The methanol to oil molar ratio is varied between 1 and 10 to obtain optimized ratio for biodiesel yield.

2.4. Emulsification of fuel blends using Taguchi Method

Emulsified Fuel formulation is carried out on the biodiesel obtained from pongamia pinnata oil by blending it with diesel and emulsifying the biodiesel diesel blend with water by adding adequate quantity of surfactant. Span 80 is used as surfactant having 98% purity and 4.7 HLB value (Hydrophilic-lipophilic balance). Lower value of HLB is taken into consideration since it has the tendency to make a stable water in oil emulsion (W/O) whereas higher HLB is used to produce oil in water emulsion. Water in oil is preferred since the water acts as a dispersed phase and oil as continuous phase thereby enhancing the combustion and performance characteristics of the engine due to the micro explosion phenomena. Taguchi method of DOE using orthogonal arrays are formulated to study the stability of the emulsified fuels. Orthogonal table for optimizing different fuel concentration is carried out which influenced the process and extent to which it can be varied thereby reducing the number of experiments needed to be perform. Biodiesel, diesel, water and surfactant concentrations are optimized as shown in the Table 1 [16, 17]. Orthogonal array for DOE with four parameters (factors) at three level (3^4) is implemented. By using Taguchi method, the number of experiments are reduced to nine experiments from the possible 81 experiments that is to be conducted actually. Biodiesel, diesel, water and surfactants were the influential parameter taken for optimization.

Table 1. Taguchi Table for $L_9 3^4$

Parameters	Concentration levels (%)		
	L_1	L_2	L_3
Diesel	85	80	75
Biodiesel	15	20	25
Water	5	10	15
Surfactant	2	4	6

Biodiesel and diesel is blended together in a flat bottomed beaker with a magnetic stirrer and temperature indicator device. The blend is agitated at 450 rpm at reaction temperature of 30°C for 30 minutes. The biodiesel diesel blend is further emulsified with water in presence of span 80 as emulsifying agent to attain water in oil (W/O) micro emulsion. The emulsion process is carried out for 40 minutes at agitating speed of 450 rpm under ambient environment conditions. The emulsified mixture is then poured into a 30 ml bottled capped test tubes to observe the stability of the fuel. A total of nine samples is stored in the test tubes and placed under frequent monitoring for a maximum of two weeks.

3. Results and Discussion

3.1 Influence of reaction time on FFA content at different reaction time

Reduction of free fatty acid (FFA) is optimized with respect to reaction time at varied reaction temperature. The temperature is optimized at 50°C, 60°C and 70°C respectively during the process. Initially FFA content is found to be 12% which is to be reduced to greater than 1% in order to undergo base catalyzed transesterification for converting the FFA to FAMEs. At 50°C, it is noticed that FFA content reduced from 12% to 1.4% at reaction time of 60 minutes. With further increase in temperature up to 70°C, the conversion efficiency is noticed to be effective with FFA level reduced to 0.5% which is observed to be the optimal reduction which is less than 1%. As shown in Figure 3. Further increase in temperature exhibited negligible conversion efficiency of FFA.

3.2 Influence of molar ratio on biodiesel yield at different reaction time

Methyl ester content (FAME) of transesterification reaction is optimized by varying the molar ratio of methanol to oil between 1:1 to 1:10 at reaction temperature of 50°C, 60°C and 70°C. The optimal biodiesel yield is found to be 91% at 7:1 methanol to oil molar ratio with reaction temperature of 70°C. Lower yield of biodiesel production rate is noticed to be 38% at molar ratio of 1:1 with reaction temperature of 50°C. The yield of biodiesel is noticed to increase rapidly with increase in methanol to oil molar ratio of 1:7. Subsequent increase in molar ratio beyond 1:7 revealed a gloomy effects on yield of biodiesel as given in Figure 2.

3.3 Influence of reaction time on biodiesel yield at different reaction temperature

Biodiesel production rate is optimized by varying the reaction time with reaction temperature ranging from 50°C to 70°C as shown in Figure 1.

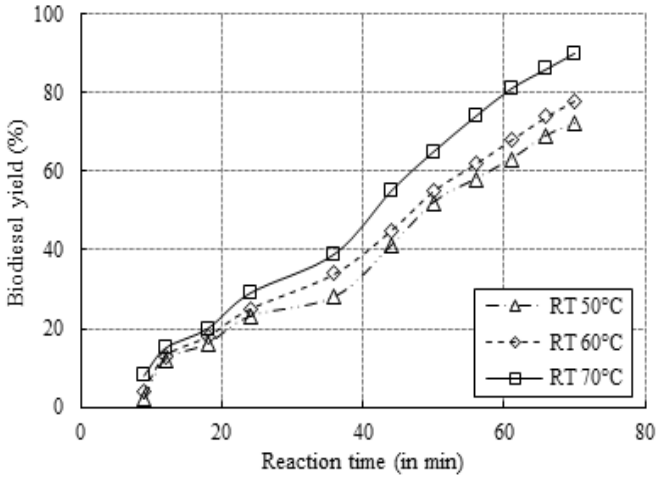

Fig. 1. Effect of reaction time on biodiesel yield.

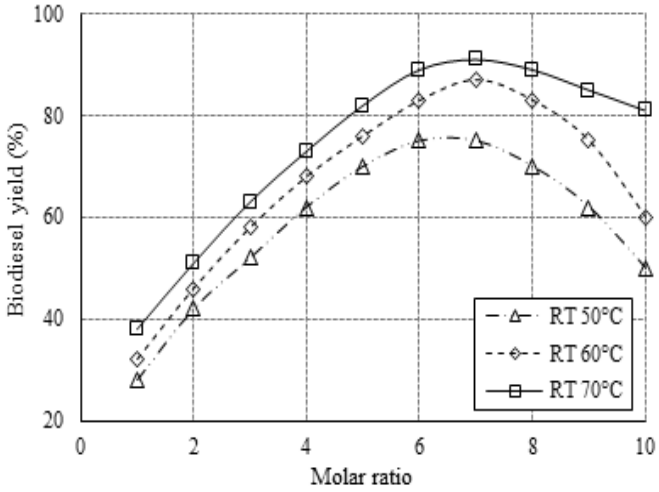

Fig. 2. Variation of biodiesel yield with molar ratio.

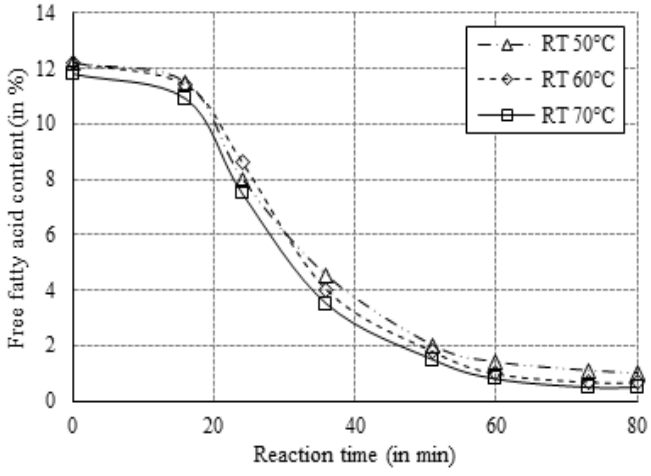

Fig. 3. Variation of FFA content with reaction time.

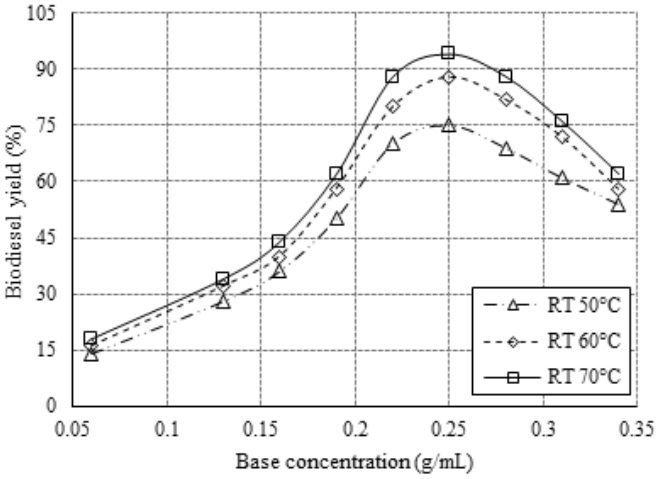

Fig. 4. Variation of biodiesel yield with base concentration.

At 50 min of reaction time and 50°C of reaction temperature, the biodiesel yield is observed to be 51% which is further increased up to 71% at 70 min. Biodiesel production rate increased sharply to 91% with increase of reaction temperature to 70°C reaction time of 70 minutes. Further increase in reaction temperature decreased the conversion efficiency of biodiesel yield which may be due to low boiling point of methanol thereby accelerating the saponification of glycerides before the completion of methanolysis. The optimum biodiesel yield is noticed to be 91% with a reaction time of 70 minutes and reaction temperature of 70°C.

3.4 Influence of base concentration on biodiesel yield at different reaction time

Variation of biodiesel with respect to base catalyst concentration and reaction temperature of 50°C, 60°C and 70°C in presence of Sodium hydroxide as base catalyst is carried out respectively as shown in Figure 4. The base catalyst concentration varied between 0.05% to 0.34% w/w of sodium hydroxide. Lower catalyst concentration of 0.05% sodium hydroxide is insignificant to catalyze the reaction completion. 0.25% of sodium hydroxide is found to be optimal the reaction with biodiesel yield of about 95% conversion efficiency at 70°C reaction temperature. Increase in temperature beyond 70°C resulted in a sharp decrease of biodiesel yield which may be due to the vaporization of methanol which has a low boiling point. Severe reduction in biodiesel yield is observed as the reaction temperature increases beyond 0.25% concentration of sodium hydroxide results in sludge formation which is mainly caused by the dissociation of sodium and hydroxide ion.

Table 2. Optimized biodiesel production at 70°C RT

Reaction time (min)	Base concentration (g/mL)	Molar ratio	Biodiesel yield (%)
10	0.06	1	12
15	0.13	2	26
24	0.16	3	34
36	0.18	4	53
44	0.22	5	62
59	0.25	6	79
70	0.27	7	93
79	0.32	8	82
83	0.34	9	76
91	0.37	10	66
95	0.42	11	59

Biodiesel production was found to be increasing until the reaction time of 70 min with base concentration 0.27g/mL and molar ratio of 7:1 where the yield was 93% which is the highest production. Until this biodiesel yield of 93% all the parameters (reaction time, base concentration & molar ratio) were at an increasing trend which has been detailed in Table 2. Beyond that reaction time, base concentration and molar ratio, biodiesel yield was found to be deteriorating.

3.5 Determination of fuel stability by Taguchi method

Table 3 shows L^9 orthogonal array for emulsified fuel formulation. The stability of fuels in terms of days is observed for a fortnight weeks for the nine sets of experiments. In the present work, the stability of fuels for longer period is also a set objective. It is observed that experiment number 8 has the longer stability period of fourteen days and experiment number 3, 4, 5 and 7 experienced phase separation within few day. Sample number 6 has the second best stability phase of six days followed by experiment number 1 which has a stability of four days. Stability findings revealed sample 8 had the higher stable condition i.e., fourteen days with the concentration of 75% diesel, 20% biodiesel, 5% water and 6% surfactant. Second highest stability was seen for sample 6 where the concentration is 80% diesel, 25% biodiesel, 5% water and 4% surfactant. Next highest stable formulated fuel was sample 1 which had the concentration as 85% diesel, 15% biodiesel, 5% water and 2% surfactant. The sample number 8 had the longest stability period which was considered to be the optimum fuel blend for the engine testing.

Table 3. L9 Orthogonal array for Emulsified fuel formulation

Expt No.	Parameter and concentration level (%)				Stability (in days)
	Diesel	Biodiesel	Water	Surf	
1	85	15	5	2	4
2	85	20	10	4	2
3	85	25	15	6	1
4	80	15	10	6	1
5	80	20	15	2	1
6	80	25	5	4	6
7	75	15	15	6	1
8	75	20	5	6	14
9	75	25	10	2	2

3.6 Optimized fuel properties

Table 4 describes the base and stabilized fuel properties. Density of biodiesel was found to be little higher than diesel fuel. Kinematic viscosity was found to be little lesser for both biodiesel and diesel-biodiesel blend comparing diesel fuel. Specific gravity had the closer value to the diesel fuel for both biodiesel and diesel-biodiesel blends. Cetane number was found little less as 46, 47 for biodiesel and diesel-biodiesel blend respectively comparing diesel as 50. Flash point was found to be higher for biodiesel which might also be good for storage purpose.

Table 4. Optimized fuel property

Property	Pongamia Biodiesel	Diesel	D75 PBD20 W5 S6
Density at 30°C (kg/m^3)	888.38	830	800
Kinematic viscosity at 40°C	4.79	4.85	4.60
Specific gravity	0.89	0.8	0.78
Calorific value (kJ/kg)	38405	44800	41281
Cetane number	46	50	47
Ash content (% by mass)	0.0085	-	-
Sulphur content	0.002	-	-
Acid value (mg/KOH)	0.42	-	-
Flash point (°C)	92	71	72
Fire point (°C)	103	82	82.1
Cloud point (°C)	10	-1	1.3
Pour point (°C)	-3	-5	-4.4

4. Conclusion

The experimental study described the various prospect of biodiesel production from Pongamia seed oil and its optimization during double stage transesterification process. The optimum FFA content during acid catalyzed transesterification is obtained at 0.5% at a reaction temperature of 70°C with a reaction time of 60 minutes

followed by base catalyzed transesterification. Effect of sodium hydroxide base catalyst is analyzed and optimized experimentally with a 0.25% concentration yielding the maximum biodiesel production of 96% at a reaction temperature of 70°C. Methanol to oil molar ratio of 7:1 is noticed to be the optimized ratio during base transesterification process at reaction temperature of 70°C. Taguchi method for DOE is carried out to optimize and reduce the number of experiments conducted for emulsifying biodiesel diesel and water in presence of the surfactant. Sample number 8 exhibited a longer duration of stability and it is noticed to be stable for 14 days which can further be used for investigation in a CI engine. The physio chemical properties of the stabilized fuel was found to be within the optimum range for using in a CI engine.

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