



Optimization using Response Surface Methodology for FAME Production From Waste Papaya seeds

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Abstract— Biodiesel is one of the alternative fuels to diesel engines that reduce the use of petroleum diesel fuel and produced from renewable biological sources. The seeds are generally discarded in order to more efficient use of Papaya. It is important investigating the use of seeds as source of oil. Mechanical extraction technique is used to extract oil. There are four ways to produce biodiesel, direct use and blending, Microemulsion, thermal cracking (pyrolysis) and transesterification. The most widely use method is trans-esterification reaction because of Trans-esterification reaction is reduce the viscosity during the production of biodiesel. The purpose of this method is to reduce the viscosity of oil using base catalyst in the presence of methanol. So, Trans-esterification reaction is use to produced Fatty acid methyl ester (FAME) from papaya seeds oil at different experimental conditions. The parameters studied are; mass ratio of ethanol to oil, reaction temperature, catalyst concentration, and reaction time using completely randomized 3^{4-1} Fractional factorial design using Minitab Software in surface response methodology (RSM). Accordingly, the optimal conditions for the production of fatty acid methyl esters from papaya seeds oil were determined as; 9:1 molar ratio of methanol to oil, 0.5 % catalyst concentration by weight of oil, 120 minutes reaction time at a temperature 60°C. Validate optimization condition with Experimental. Analyzed papaya seeds oil and FAME. Fatty acid methyl ester Properties are found and close to that of diesel fuel and also meet the specifications of ASTM standards.

Key words— Biodiesel, Feedstock: Papaya seeds, Trans-esterification, Optimization using Minitab, Analysis of oil & FAME sample, Characteristics of FAME.

I. BIODIESEL

The main important for protecting global environment and long term energy security, necessary to develop alternative fuels and those properties comparable to petroleum based fuel. Biodiesel based fuels are renewable, non-toxic and safe to store, because of their oxygen content, the combustion is more complete and less carbon monoxide emission. There is a number of nonedible tree based oil seeds available in many countries around the world and from that biodiesel can be produce [1].

There are different ways to produced biodiesel with different kinds of raw materials likes refine crude or frying oils. Also there are different types of catalyst, basic ones such as sodium or potassium hydroxides, acids such as sulfuric acid, ion exchange resins, lipases and supercritical fluids. One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetables or animal fat, making it biodegradable and nontoxic [2].

High emissions of CO₂, NO_x, SO₂, particulate matter, poly aromatic hydrocarbons and hydro-carbons are produced during the using of fossil fuel and creating environmental problems. These facts have converged in the search for renewable energy sources, such as biofuels- bioethanol and biodiesel [3].

1.1 Advantage of Biodiesel

Biodiesel is the only alternative fuel that runs in any conventional, unmodified diesel engine. Maintain the payload capacity and range of conventional diesel engines. Diesel skilled mechanics can easily attend to biodiesel engines. Exhaust emissions are lower. Biodiesel fuel is non-toxic and biodegradable.

1.2 Disadvantage of Biodiesel

Quality of biodiesel depends on the blend thus quality can be tampered. Biodiesel has excellent solvent properties. There may be problems of winter operability. Spills of biodiesel can decolorize any painted surface if left for long.

II. MATERIAL AND METHODS

2.1 Food Waste: Food Waste is an inheritable consequence of the food industry. Food industry produces large volumes of wastes, both solids and liquid because of production, preparation and consumption of food. These wastes increasing disposal and potential severe pollution problems and signify a loss of valuable biomass and nutrients. The wastes contain valuable components such as: sucrose, glucose, fructose and other Nutrients. Fruit pulp wastes after extracting juices are one of the major byproducts of food processing industries. Byproducts of food processing plant represent a major disposal

problem for the industry concerned, but they are also promising sources of biomaterials. These biomaterials can be used as substrates for bioethanol production [4].

2.2 Feedstock: Papaya seeds Carica papaya originated in Central America. It contains many biologically active compounds. Two important compounds are chymopapain and papain, which are supposed to aid in digestion. Carica papaya could be a rich source of dietary fiber which can have beneficial effects. Papaya is important for its fruit and it is only recently that it has been cultivated purpose. Seeds of papaya fruits are discarded, because of bad experiences when they are consumed by humans or animals. The papaya seed oil contained 10.3% free fatty acid [5].

The papaya seed is currently a waste product as it is often discarded after eaten the papaya fruits due to its very limited uses at the moment. Papaya seed are recently gaining importance due to its medicinal value. The seed had recently been linked to curing sickle cell diseases, poisoning related renal disorder, and as an antihelminthes. There are scarce information's on this relatively underutilized seed despite its importance [6].

2.3 Use of Papaya seeds:(1) Prevents from Parasites (2) Kills Parasitic Worms (3) Treats Liver Cirrhosis (4) Kills Harmful Bacteria (5) Prevents from Kidney Failure [7]

2.4 Oil Extraction: Papaya seeds are discarded after eaten the papaya fruits. The seeds were collected from the different households as one discards the seeds after consuming the fruit. The collected seeds were dried. Dry Papaya seeds are raw material for extract of oil using mechanically hand press expeller.

2.5 Trans-esterification Reaction:

Papaya seeds Oil is used into trans-esterification reaction and that reaction carried out in a batch system. In this experiment, Methanol use as alcohol and NaOH as a catalyst. First mix catalyst in alcohol up-to NaOH dissolve into methanol. Preheat the oil-bath to set constant temperature. Add oil into 3-neck round bottom flask and mixture of methanol plus NaOH and provide continuous stirring using magnetic stirrer. Allow the reaction mixture to react for different time interval. After completion of Reaction take out mixture from 3-neck round bottom flask and pour into separating funnel and let it to be settle. When two layers are appeared, in which upper layer is Biodiesel and lower layer is Glycerol. Collect both layers and Find the yield of biodiesel.

The trans-esterification reaction carried out at different Experimental conditions. For different alcohol to oil molar ratio 3:1, 6:1, 9:1, 12:1, temperature of reaction is 50-60°C and reaction times are 60-90-120min at catalyst amounts are 0.5, 1, and 1.5%. Various experiments perform and concluded that 2% and 4% of NaOH catalyst concentration used at that time Soap formation occurs and difficult to Separate Two phase of Biodiesel and glycerol.

2.6 Experimental Design:

A Three-level-four-factor Central composite design(CCD) used and four design factors are methanol/oil molar ratio (X_1), catalyst concentration (X_2), temperature (X_3) and reaction time (X_4) and three levels are (-1),(0) and (1). The Central values chosen for experiment design were: methanol/oil molar ratio =9:1, catalyst concentration = 1%, temperature = 55°C and reaction time = 90min. Fractional factorial method used and Formula = (Level)^{(Factor)-1}. So that, optimization study, required only 27 experiments. The maximum values of the yield were taken as the responses of the design experiment. Table 1 shows that coded levels for Molar ratio (-1) = 3:1, (0) = 9:1 and (1) = 12:1. For % catalyst concentration (-1) = 0.5, (0) = 1, (1) = 1.5. For temperature (°C) (-1) = 50, (0) = 55, (1) = 60. For time (min) (-1) = 60, (0) = 90, (1) = 120. $R^2 = 80.74$.

Table 1: Coded and Uncoded levels of independent variable used for the Trans-esterification reaction

Variable	Symbol	Level		
		-1	0	1
Alcohol to oil molar ratio	X_1	3:1	9:1	12:1
Weight % catalyst concentration	X_2	0.5	1	1.5
Temperature(°C)	X_3	50	55	60
Time(min)	X_4	60	90	120

2.7 Statistical analysis:

Statistical analysis of the model was performed to calculate the analysis of variance. Once the experiments performed, response variable was fitted model in order to correlate response variable to independent variable. General form of polynomial equation is as follows:

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^4 \sum_{j=i+1}^4 \beta_{ij} X_i X_j$$

Where i and j are linear and quadratic coefficients, b is regression coefficients and 4 is the number of factor.

$$\begin{aligned} \text{Yield} = & 90.1155 + 2.89745 * X_1 - 0.36867 * X_2 - 3.56873 * X_3 - 2.56873 * X_4 + -15.311 * X_1^2 + 3.11246 * X_2^2 \\ & + 1.62888 * X_3^2 + 6.88765 * X_1 * X_2 + 2.32176 * X_1 * X_3 + 1.53221 * X_1 * X_4 - 1.33310 * X_2 * X_3 - \\ & 2.71043 * X_2 * X_4 + 3.55801 * X_3 * X_4 \end{aligned}$$

III. RESULTS AND DISCUSSION

3.1 Trans-esterification reaction: Different experiment performed at different conditions to give best yield and that condition: 0.5% catalyst concentration, 120min reaction time, Temperature 60°C and 9:1 alcohol to oil molar ratio to obtain best yield 96.7%. Yield response Analysis at the design points and all the four variables in uncoded form are given in Table 2.

Table 2: Yield response in uncoded form

Run	Molar ratio	Concentration	Temperature	Time	Yield	
					Experimental Response	Predicted Response
1	-1	0	-1	0	72.88	77.797
2	-1	-1	-1	0	84.67	86.833
3	0	0	1	-1	86.37	87.007
4	-1	-1	1	-1	77.00	77.000
5	0	-1	1	-1	92.57	89.110
6	0	0	1	0	84.54	86.547
7	1	1	1	1	87.85	86.373
8	0	0	1	1	92.68	89.345
9	0	1	1	1	83.73	88.045
10	1	1	-1	-1	95.52	98.667
11	-1	1	-1	0	86.44	74.987
12	-1	1	-1	1	60.50	66.426
13	0	0	1	1	92.68	89.345
14	1	0	-1	1	75.67	76.163
15	1	0	-1	-1	88.14	84.993
16	-1	0	-1	1	72.00	71.947
17	0	-1	1	1	96.70	96.869
18	1	0	1	1	83.14	80.786
19	-1	-1	-1	1	87.38	83.693
20	1	-1	1	1	77.59	81.422
21	0	-1	1	0	89.03	91.361
22	-1	0	-1	-1	83.37	86.906
23	-1	-1	-1	-1	94.58	93.231
24	0	1	1	0	87.91	87.957
25	1	1	-1	1	84.91	84.417
26	0	0	1	-1	86.37	87.007
27	0	1	1	0	87.97	87.957

The graph between actual and predicted Yield (%) is given in Fig.1 shows that predicted values quite closed to actual values. So that, validating the reliability of the model developed for establishing the correlation between process variable and Yield. The effect of the variables as linear, quadratic or interaction coefficients on the response was tested for significance by ANOVA. P-value to determine whose factors are significant or not. If the p-value is lower than 0.05, then the factor is significant and that Shown in Fig 2.

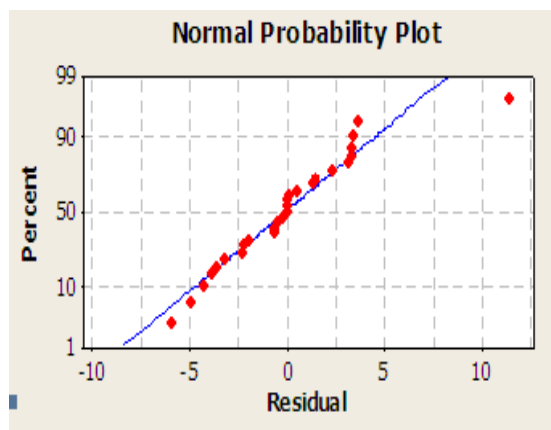


Fig 1: Predicted vs. actual Yield

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	13	1378.56	1378.56	106.043	4.19	0.007
Linear	4	431.78	170.50	42.625	1.68	0.213
molar ratio	1	120.98	47.49	47.494	1.88	0.194
concentration	1	85.21	1.23	1.235	0.05	0.829
Temp	1	67.37	82.51	82.506	3.26	0.094
Time	1	158.23	82.00	81.999	3.24	0.095
Square	3	349.70	380.56	126.854	5.01	0.016
molar ratio*molar ratio	1	234.60	349.72	349.724	13.82	0.003
conc*conc	1	110.24	48.45	48.445	1.91	0.190
time*time	1	4.86	9.52	9.519	0.38	0.550
Interaction	6	597.07	597.07	99.512	3.93	0.018
molar ratio*conc	1	188.39	194.78	194.784	7.70	0.016
molar ratio*temp	1	110.04	26.19	26.191	1.04	0.328
molar ratio*time	1	3.85	16.02	16.024	0.63	0.440
conc*temp	1	6.16	13.46	13.461	0.53	0.479
conc*time	1	109.82	44.14	44.144	1.74	0.209
temp*time	1	178.80	178.80	178.801	7.07	0.020
Residual Error	13	328.92	328.92	25.302	-	-
Lack-of-Fit	10	328.92	328.92	32.892	54819.83	0.000
Pure Error	3	0.00	0.00	0.001	-	-
Total	26	1707.48			-	-

Fig 2: ANOVA of Yield

3.2 Effect of Reaction Parameters: Figure 3 shows that four parameters affected on FAME Yield. Yield is increase with increase in molar ratio upto 9:1 and then decrease. Yield is increase with first increase upto 0.5% NaOH concentration and then decrease. Yield increase with increase time upto 60 min and then decrease. Yield is increase with increase temperature.

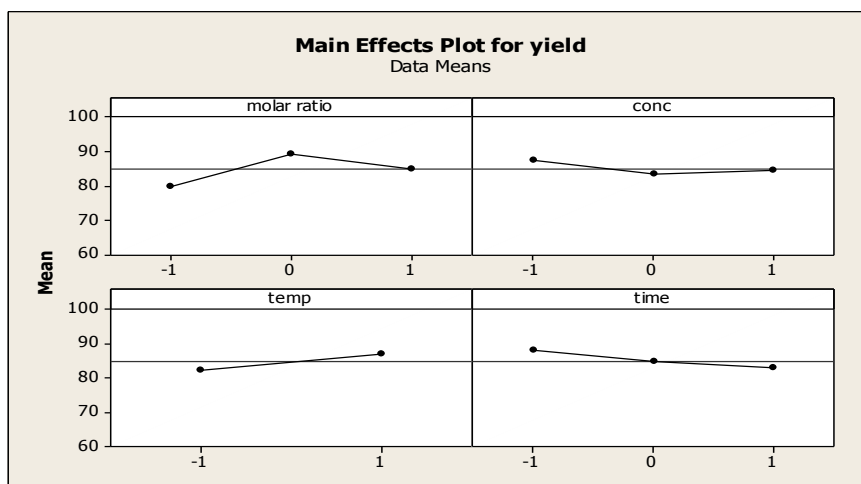


Fig 3: Effect of Reaction parameters

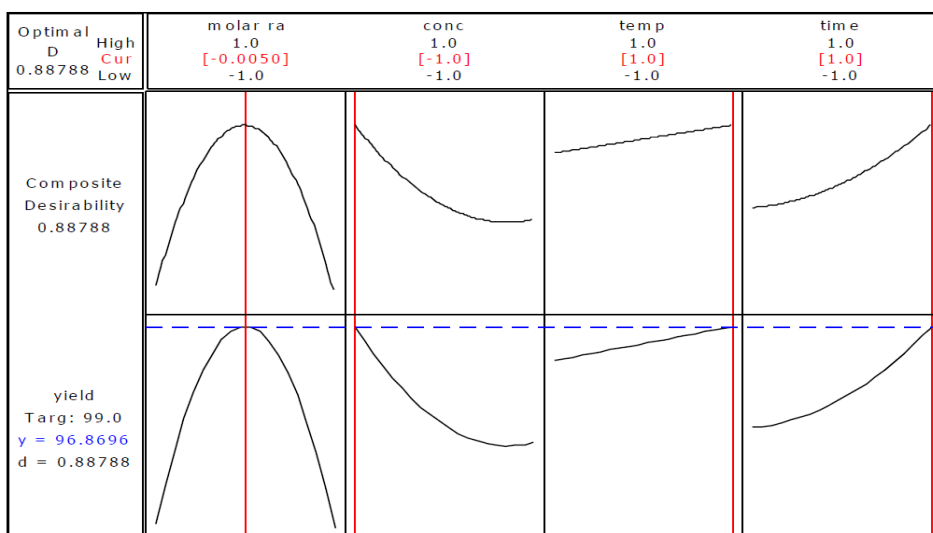


Fig 4: Maximum Yield Condition Plot

Using the optimization function in Design and was predicted that at the following conditions; 9:1methanol to oil molar ratio, 0.5% catalyst concentration and 60 °C of reaction temperature and reaction Time 120 min at that time an optimum FAME yield of 96.86% can be obtained (Fig 4.).

3.3 Analysis of papaya seeds Oil and FAME:

3.3.1 FTIR Analysis: The FTIR spectra of papaya seed oil and the optimal biodiesel fuel were measured for two purposes; the first is for the qualitative determination of some of the obtained characteristic bands, the second is for the quantitative determination by monitoring the Trans-esterification reactions. The main differences observed between the infrared spectra of papaya seed oil and the produced biodiesel fuel are a small displacement of the stretching C=O band and stretching C-H band as well as the C-H bonding band of the biodiesel to the lower energy. This is attributed to the substitution of the glycerol by the methoxy radical (Fig 5-6).

3.3.2 GC-MS Analysis: Gas chromatography is used to separate mixtures into individual components using temperature controlled capillary column and Mass spectroscopy used to identify the various components from their mass spectra and each compound has a unique mass spectrum that can be compared with mass spectral database and thus identified. Shown GC-MS Analysis in below Fig 7. Figure in which Molecular formula and Formula name and Mol % are obtain GC-MS graph of FAME from Library-NIST11s.lib.

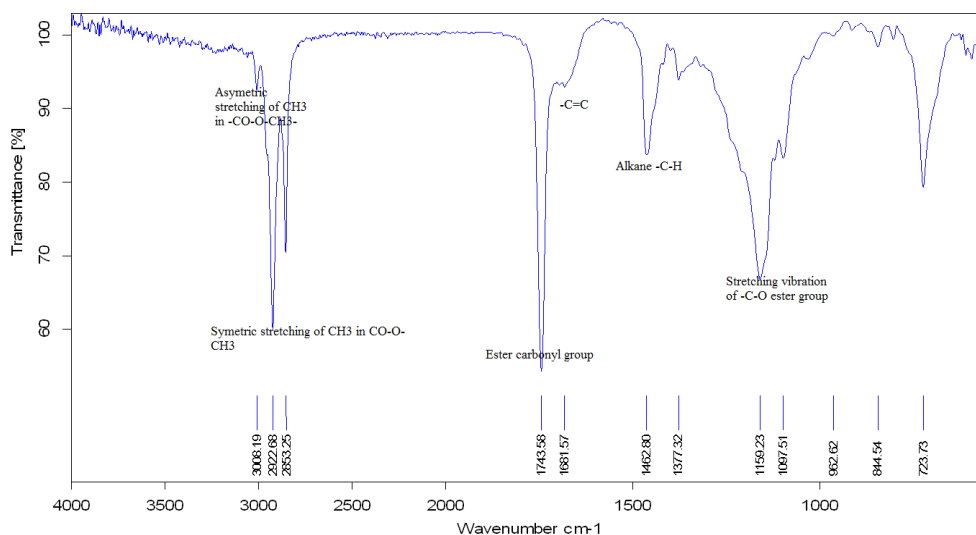


Fig 5: FTIR Analysis of Papaya seed oil

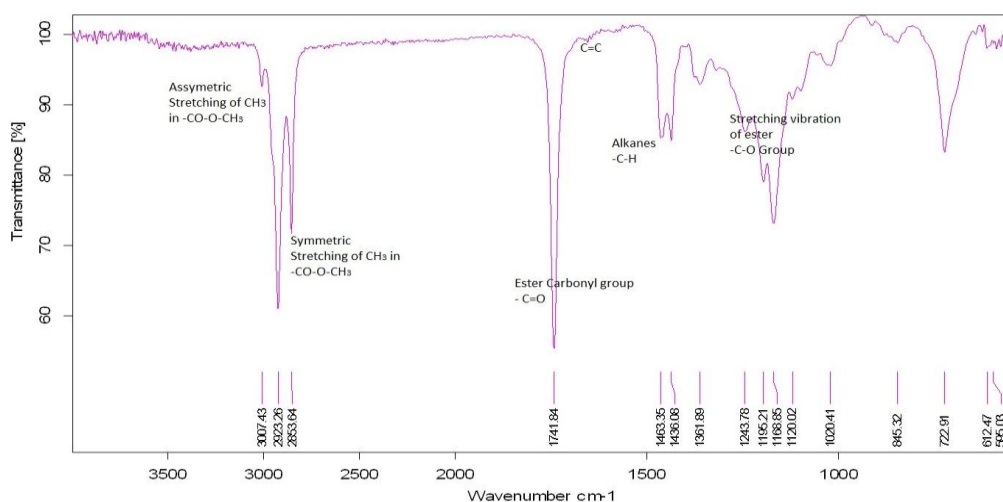


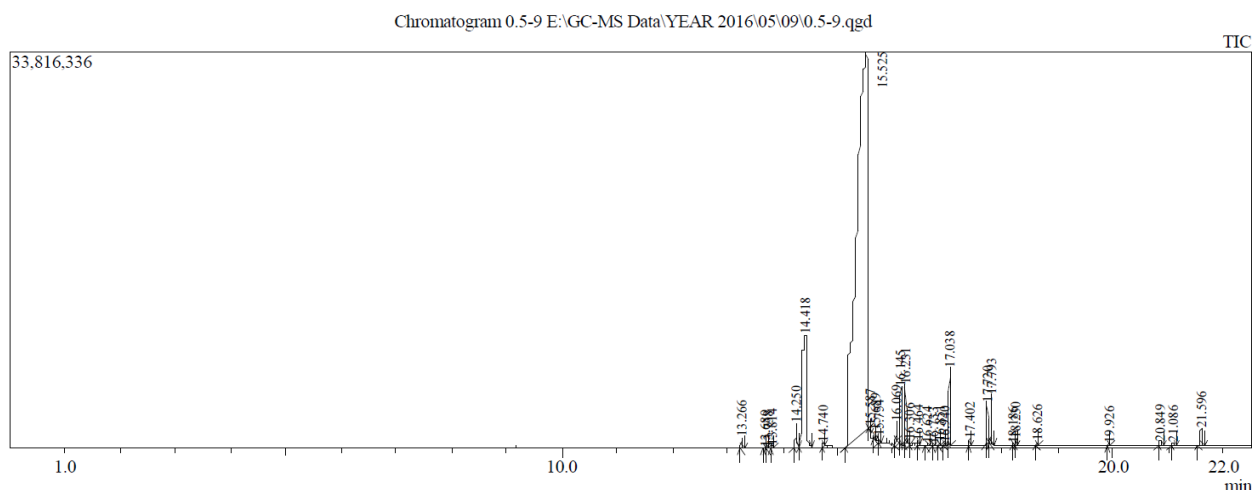
Fig 6: FTIR Analysis of FAME

3.4 Characteristics Properties of FAME:

Characteristics Properties are found using ASTM Method and Properties value related to standard so we can use as Biodiesel.

Table 2: Characteristics Properties of FAME

Sr No.	Properties	Value	Unit	Test Name
1	Acid value	0.03	mg KOH/g	ASTM D664
2	Kinetic viscosity	3.5	mm ² /s	ASTM D445
3	Flash point	389	K	ASTM D93
4	Density	0.8	gm/ml	ASTM D4052



CONCLUSION

Biodiesel is a mono-alkyl esters of fatty acids derived from vegetable oil or animal fat. Biodiesel is much less polluting than petroleum diesel, resulting in much lower emissions of every pollutant like carbon dioxide, sulfur oxide, particulates, carbon monoxide, air toxics and unburned hydrocarbons. Papaya seeds is discarded after eat papaya. Mechanical method is relatively low yield obtain compared to chemical method but purity of oil is high compared to chemical method to extract oil. Response surface methodology was successfully applied for transesterification of methanol. The regression showed that the model was well fitted to the experimental data. The ANOVA understood that Which Factors are great significant affected on Biodiesel Yield. Optimize Conditions are: 0.5% catalyst concentration, 120 min reaction time, Temperature 60°C and 9:1 alcohol to oil molar ratio to obtain best yield 96.86 %. Validated with Experiment and that give Yield 96.70 %. Characteristics Properties are relevant to standard Biodiesel B100. Finally we concluded that Biodiesel of papaya seeds are Suitable for replacement of petrodiesel without any change of diesel engine.

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