

Bioprocess Optimization for Biodiesel Production from *Pongamia Pinnata*

Vidhvath Viswanathan, Vinodh Mohan, Viswa Purusothaman, Subhasish Das⁺

School of Chemical & Biotechnology, SASTRA University, Thanjavur, Tamilnadu

Abstract. In this work reaction parameters namely 1) temperature, 2) time, 3) NaOH concentration and 4) methanol/oil ratio in biodiesel production by two step acid/base catalysed trans-esterification of a non-edible vegetable oil from *Pongamia pinnata* has been optimized by 2⁴ central composite design in order to increase diesel yield and reduce reaction time and temperature. Biodiesel yield and composition was confirmed with HPTLC and GC-MS analysis. The optimal conditions were found to be: 1.44 hours reaction time, 65 °C reaction temperature, 0.80 wt % NaOH and 7.4:1 methanol to oil ratio. The optimum yield was observed to be 98.84% with the optimal conditions of experiment

Keywords: *Pongamia pinnata*, two step acid/base reaction, central composite design

1. Introduction

It is a very hard time for the modern civilization that we are on the verge of expiry of natural petroleum resources. Although importance of finding alternative biofuel was realized by scientific community in 70's but commercial production of alternative biofuel with available raw material and so far scientific knowledge are not sufficient to meet our enormous requirement. Biodiesel is "a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats." It has higher flash point (423 K) than petro-diesel (337K) and biodegradable, emits almost no-toxic fumes while burning. Although biodiesel can be produced from a variety of vegetable oils, the biggest challenges remain that the vegetable oil should not be edible oil, should be cheap and its supply should be unlimited to the manufacturers. Hence in this study we have tried to explore the possibility of using a non-edible vegetable oil from *Pongamia pinnata* for biodiesel production with lesser energy input and faster rate. *Pongamia* tree has been reported to grow easily without much care, because it is nitrogen-fixing, can survive draught and is fast-growing (5 m per 5-7 years). 30-40% oil can be extracted from dried ripe seeds [1]. *Pongamia* (Karanja) oil contains palmitic, oleic, stearic and linoleic acid mostly along with small amount of other long chain fatty acids [1] and has a high acid number of 2.5 [2] and calculated average molecular weight 892.7 [3]. Although some works on biodiesel production from *Pongamia* oil has been reported [3]-[5], no literature is available reporting a try to minimize reaction temperature and time by optimizing reaction parameters. In the present study reaction parameters involved in biodiesel production from *Pongamia* oil by 2-step acid/base catalyzed transesterification has been optimized using central composite design in order to increase biodiesel production.

2. Material and Methods

2.1. Chemicals

Pongamia oil (Suresh Forestry, Bangalore), Methanol (99.8%, Loba Chemie), sodium hydroxide, and hydrochloric acid (Merck) were used for biodiesel production. Solid sodium methoxide flakes were also tried

⁺ Corresponding author. Tel.: +55-21-80805712; .
E-mail address subhasishdas@scbt.sastra.edu.

for biodiesel production replacing NaOH. n-Hexane and reference standards such as methyl palmitate were purchased for HPTLC analyses.

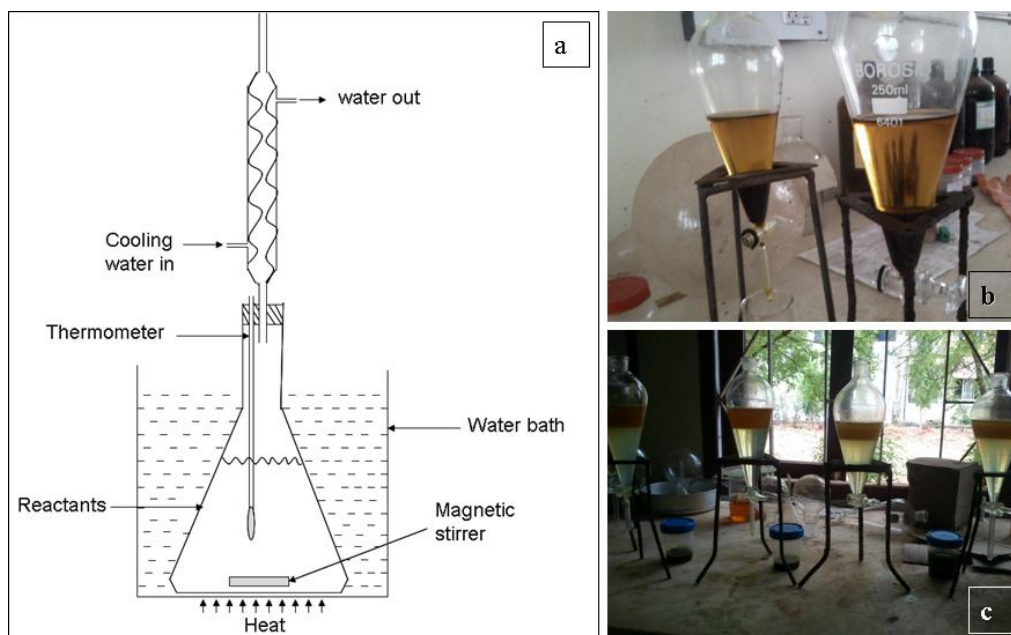


Fig. 1: (a) Schematic diagram of trans-esterification reaction (b) Separation of crude biodiesel and glycerol after alkali treatment, (c) Removal of impurities from biodiesel by water wash.

2.2. Two step acid base transesterification reaction

Pongamia oil was preheated and acid pre-treated, followed by base-catalyzed transesterification [6], [7]. Reaction time, temperature and MeOH, NaOH, oil ratio were varied. Reflux condenser was used to prevent loss of methanol (Fig 1a). After reaction was over contents were transferred to separating funnel and left overnight resulting two distinct layers (Fig. 1b). The bottom crude glycerol layer was collected. Upper biodiesel layer was further washed with 1% HCL, followed by wash with hot water repeatedly to remove excess methanol (Fig. 1c). Initially one-step transesterification of Pongamia oil [4], [5] was also tried and was compared for biodiesel production and down steam processing efficacy to that of 2-stage transesterification.

2.3. Purity analysis

Purity and composition of biodiesel samples were analyzed by (1) HPTLC (at 203nm) using Silica Gel 60 F₂₅₄ stationary phase and hexane: ethyl acetate: acetic acid (9:1:0.1) mobile phase; (2) GC-MS (PerkinElmer Clarus 500) equipped with Elite-5MS capillary column (column length: 30m and column id: 250 μ m) with 1ml/min flow of helium, injector temperature 280 $^{\circ}$ C, column temp 50 $^{\circ}$ C increasing at 8 $^{\circ}$ C/min to a final of 150 $^{\circ}$ C after 5min. The MS was operated in electron ionization mode (70eV).

2.4. Response surface optimization

In order to optimize four reaction parameters namely reaction temperature ($^{\circ}$ C), reaction time (h), methanol/oil molar ratio and NaOH concentration (wt %), a 2^4 full factorial central composite design was made. Coded values of parameters were set on the basis of literature and initial trial batches with following equation: coded value, $A_i = \frac{a_i - a_i^*}{\Delta a_i}$, where a_i = real value of parameter, a_i^* = central value of parameter (70 $^{\circ}$ C, 2h, 8 mol/mol, 0.6% respectively), Δa_i = step change value (10 $^{\circ}$ C, 0.5h, 2 mol/mol, 0.1% respectively). To explain final experimental responses in terms of coded values a second order quadratic model was chosen: $\hat{y} = \beta_0 + \sum \beta_i A_i + \sum \beta_{ii} A_i^2 + \sum \sum \beta_{ij} A_i A_j$, where \hat{y} = coded response (yield); β_0 = intercept coefficient, β_i = linear terms, β_{ii} = squared terms and β_{ij} = interaction terms, and A_i and A_j as the coded parameters. A total of 30 experiments ($2^4 + 2 \times 4 + 6$) were designed and accordingly experiments were performed.

Table 1: Biodiesel and glycerol yield and percentage of methyl palmitate (MP) in biodiesel in 30 experiments of central composite design

Expt. No.	Temp (°C)	Time (h)	MeOH/oil (mol/mol)	NaOH (wt %)	Biodiesel (ml)	% MP in biodiesel	Glycerol (ml)
1	60	1.5	6	0.5	96	36.23	23
2	80	1.5	6	0.5	95	41.45	22
3	60	2.5	6	0.5	95	42.59	19
4	80	2.5	6	0.5	91	40.2	19
5	60	1.5	10	0.5	89	40.95	31
6	80	1.5	10	0.5	90	41.92	30
7	60	2.5	10	0.5	92	41.98	29
8	80	2.5	10	0.5	92	41.51	32
9	60	1.5	6	0.7	95	42.46	22
10	80	1.5	6	0.7	93	42.66	26
11	60	2.5	6	0.7	91	42.07	22
12	80	2.5	6	0.7	91	43.2	23
13	60	1.5	10	0.7	93	43.26	37
14	80	1.5	10	0.7	91	35.98	30
15	60	2.5	10	0.7	89	37.37	30
16	80	2.5	10	0.7	89	37.08	37
17	50	2	8	0.6	93	39.32	30
18	90	2	8	0.6	90	38.08	29
19	70	1	8	0.6	93	35.42	25
20	70	3	8	0.6	91	37.94	29
21	70	2	4	0.6	90	38.37	15
22	70	2	12	0.6	86	42.11	42
23	70	2	8	0.4	99	45.04	22
24	70	2	8	0.8	99	42.25	26
25	70	2	8	0.6	97	42.82	23
26	70	2	8	0.6	97	41.46	29
27	70	2	8	0.6	98	Not studied	28
28	70	2	8	0.6	96	Not studied	29
29	70	2	8	0.6	96	Not studied	28
30	70	2	8	0.6	97	Not studied	27

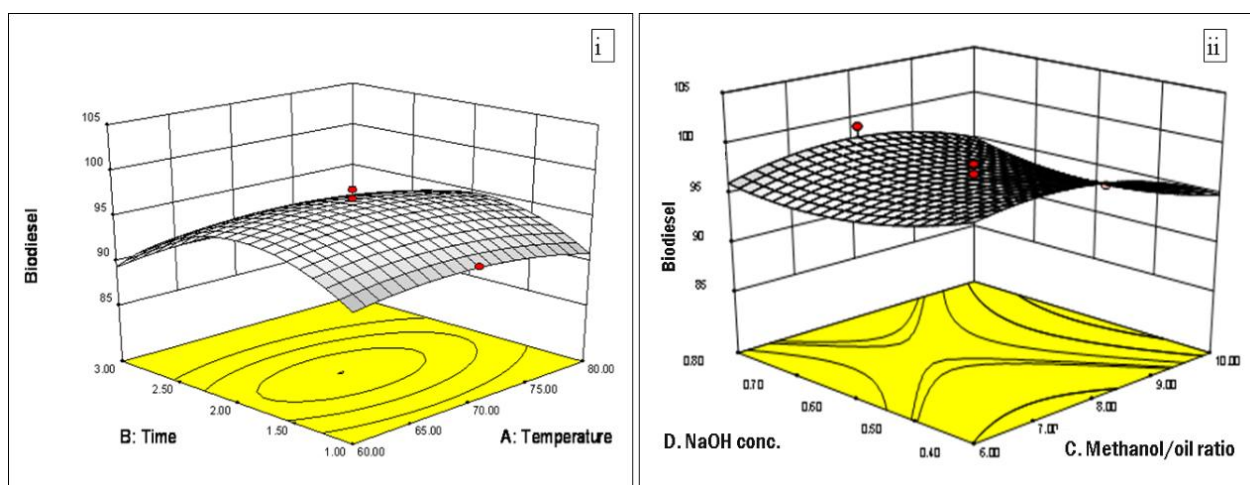


Fig. 2. Effect of (i) temperature, Time, (ii) methanol: oil ratio and % NaOH in 3D contour plot

3. Results and Discussion

Our initial experiments showed that use of one step base catalysed transesterification [4], [5] and use of sodium methoxide instead of sodium hydroxide catalyst was not efficient and resulted in saponification making it difficult to separate biodiesel, because of high acid number of Pongamia oil. Hence two-step acid-

base catalysed transesterification reactions were found to be most satisfying in terms of down-stream processing. It was also noticed that agitation of more than 400rpm did not increase yield, but lowering of speed decreased yield. Hence 400 rpm agitation was used throughout the experiments. Yield of biodiesel and glycerol of the above mentioned experiments are given in Table 1 along with percentage fraction of methyl palmitate (MP).

Table 2: Statistical analysis of Response Surface Quadratic Model

Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Model	308.80	14	22.06	16.01	< 0.0001	significant
A-Temperature	8.17	1	8.17	5.93	0.0279	
B-Time	10.67	1	10.67	7.74	0.0139	
C-Methanol/oil ratio	37.50	1	37.50	27.22	0.0001	
D-NaOH Conc	2.67	1	2.67	1.94	0.1845	
AB	0.000	1	0.000	0.000	1.0000	
AC	2.25	1	2.25	1.63	0.2207	
AD	0.000	1	0.000	0.000	1.0000	
BC	6.25	1	6.25	4.54	0.0502	
BD	9.00	1	9.00	6.53	0.0219	
CD	2.25	1	2.25	1.63	0.2207	
A ²	56.68	1	56.68	41.14	< 0.0001	
B ²	47.25	1	47.25	34.29	< 0.0001	
C ²	146.68	1	146.68	106.46	< 0.0001	
D ²	5.25	1	5.25	3.81	0.0699	
Residual	20.67	15	1.38			
Lack of Fit	17.83	10	1.78	3.15	0.1088	not significant
Pure Error	2.83	5	0.57			
Cor Total	329.47	29				

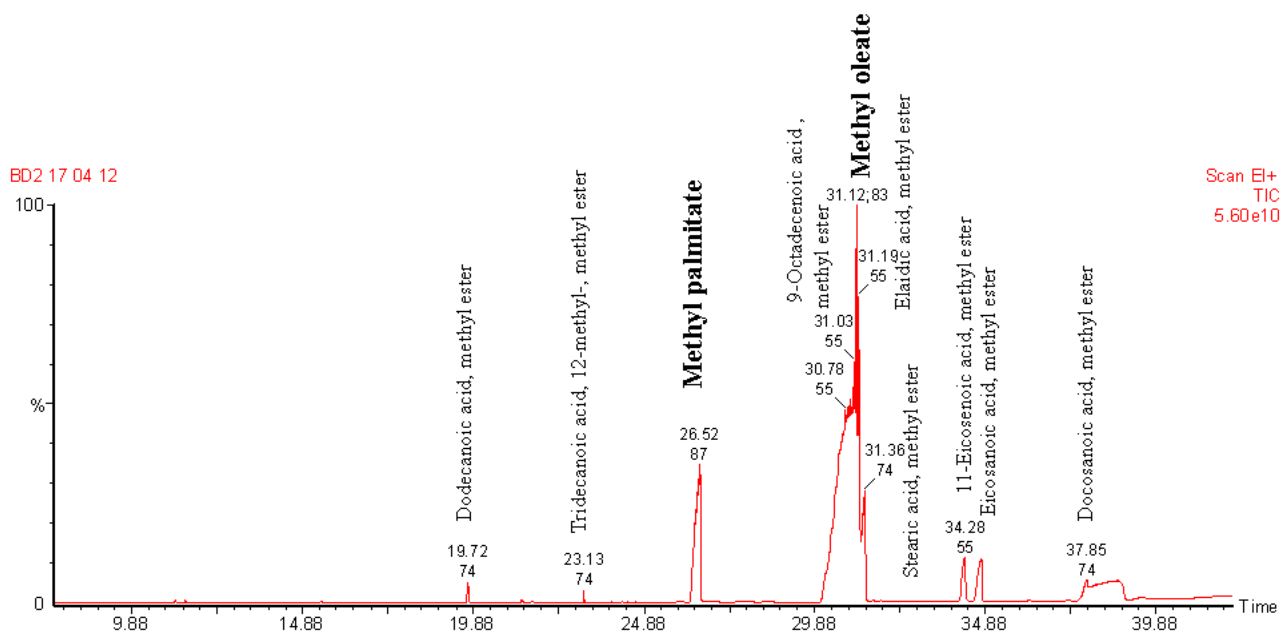


Fig. 3: GC-MS chromatogram of biodiesel from final batch

Biodiesel yield was 99% with reaction temperature 70 °C, time 2h, methanol/oil ratio 0.8 (Table 1). HPTLC analysis showed that approximately 39.34±3.92% MP was present in all biodiesel samples (Table 1). Effects of temperature (A), time (B), methanol: oil ratio (C) and % NaOH (D) on final biodiesel yield has been shown in 3D contour plots in Fig. 2. Although effects of temperature and time upon yield showed a rotatable response surface relation [Fig 2(i)], the effects of other two parameters upon yield did not [Fig 2(ii)]. Therefore we would proceed to statistical analysis (Table 2) of the response surface model, which

showed the P-value of the model was significant and as desired for a good model the lack of fit was not significant. Although A, B and C had good linear effects (as well as the square terms A^2 , B^2 , C^2 having even stronger effects) on biodiesel yield, D (and D^2) affected yield to a lesser extent. There was no interaction between A, B and also between A, D terms on affecting response.

The optimum condition was determined to be 1.44 hours reaction time, 65.02 °C reaction temperature, 0.80 wt % NaOH and 7.40:1 methanol to oil ratio. Using this set of conditions 98.84% biodiesel yield was obtained, which was higher than previously reported yield from *Pongamia* oil [3], [4]. GC-MS analysis of the purified biodiesel revealed the composition to be 40.3% methyl palmitate and 7.13% methyl oleate along with other methyl esters of long chain fatty acids (Fig 3), which was similar to previous report [4].

4. Acknowledgement

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5. References

- [1] P.T. Scott, L. Pregelj, N. Cheng, J. S. Halder, M.A. Djordjevic, P.M. Gresshoff. *Pongamia pinnata*: an untrapped resource for biofuels industry of the future. *Bioenerg. Res.* 2008, **1**:2-11.
- [2] S. Birajdar, S. Ramesh, V. Chimkod, C.S. Patil. Phytochemical and physiochemical screening of *Pongamia pinnata* seeds. *Int. J. Biotechnol. Applications.* 2011, **3(1)**:52-54.
- [3] Y.C. Sharma, B. Singh. Development of biodiesel from karanja, a tree found in rural India. *Fuel.* 2008, **87**: 1740–1742.
- [4] L.C. Meher, S.N. Naik. Methanolysis of *Pongamia pinnata* (karanja oil) oil for production of biodiesel. 2004, *J. Sci. Ind. Res.* 2004, **63**:913-918.
- [5] Vivek, A.K. Gupta. Biodiesel production from Karanja oil. *J. Sci. Ind. Res.* 2004, **63**:39-47.
- [6] H. J. Berchmans, S. Hirata. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Biores. Technol.* 2008, **99**: 1716–1721.
- [7] J. Ye, S. Tu, Y. Sha. Investigation to biodiesel production by the two-step homogeneous base-catalyzed transesterification. *Biores. Technol.* 2010, **101**: 7368–7374.