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Optimization and Characterization Studies on Bio Oil Production From Mahua Oil Cake By Pyrolysis Using Response Surface Methodology

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ABSTRACT

In this work Mahua oil cake was used to extract the bio oil using fixed bed fast pyrolysis experiments. The effects of three parameters on the pyrolysis efficiency were tested to identify the optimal bio oil production. The parameters are temperature, nitrogen gas flow rate and feed stock particle size. The Response Surface Methodology (RSM), with a Box Behnken Design (BBD), was used for modelling and optimizes the process parameters. The results showed that the second-order polynomial equation explains adequately the non-linear nature of the modelled response. An R² value of 0.9318 indicates a sufficient adjustment of the model with the experimental data. The optimal conditions found to be at the temperature of 550°C, N₂ flow rate of 0.3 lpm and particle size of 4 mm. The yield of bio-oil was obtained 25.90 wt %. In addition the bio oil was characterized by elemental the gas chromatography - mass spectrometry (GC- MS) were analyzed.

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1. Introduction

As a renewable energy sources, biomass is the largest global contributor of primary energy supply, can be converted to bio oil by pyrolysis. Bio oil is the one of the pyrolysis products, known as pyrolysis oil [1.] The new non conventional sources might reduce the demand on fossil fuels in addition, it can be renewed in a short time to time and it is frequently more environmentally friendly, especially on air emissions [2]. Among the categories, agricultural residues represent important potential for raising the bio energy industry [3]. The main benefit of using agricultural residue is that they have slight or no promote value and ready for production in large quantities. These residues generated through straight harvest of crops at the growing site or as a byproduct of dispensation at a processing facility [4]. A number of researchers have explored the energy of agricultural residues for energy and the results are encouraging [5-8].

In most of the earlier reported batch and continuous mode studies, consequence of individual parameters has been reported while maintaining other process parameters constant at undetermined levels. This approach does not depict the combined effect of all process parameters. It is time consuming and requires a number of experiments to determine optimum levels, which may be unreliable. These restrictions of a classical method can be eliminated by optimizing all the parameters together by statistical experimental design such as response surface methodology (RSM). The most important aspect in this optimization study is to gain the maximum amount of bio oil by pyrolysis process. This paper reports the

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combined effect of three process parameters such as temperature, flow rate of N_2 and particle size of mahua oil cake, on the yield of bio-oil produced from mahua oil cake based on box Behnken design in RSM. Also gas chromatography/ mass spectrometry (GC- MS) techniques were used to characterize the bio-oil obtained under optimum conditions.

2. Experimental Investigation

a. Pyrolysis procedure

The experiments are carried by a fast pyrolysis method in 2 kg Fixed bed reactor. The reactor inner diameter is 220 mm and a length of 450 mm. Nitrogen gas (sweep gas) flow is connected on top of the reactor. The electric furnace is used to heat the reactor and temperature measured using a K-type thermocouple. A sample of mahua oil cake (feed stock) and photographic view of the experimental setup is shown in figure 1 and 2 respectively. The temperatures chosen are 500°C, 550°C and 600°C and the heating rate is 10°C/min. The sweep gas flow rates of N2 are conducted at 0.2 lpm, 0.3 lpm and 0.4 lpm. The particle sizes of samples are varied in size range of 2 mm, 4 mm and 6 mm. The parameters were optimized using response surface methodology (RSM) with a Box- Behnken (BBD). RSM is carried by 15 experiments based on the three factors. The pyrolysis gas is condensed in a condenser in the form of bio oil and char was collected in the bottom of the reactor. The bio oil and char is weighted. Uncondensed gas quantity is measured by material balance. The product yield is calculated as follows:

Liquid yield, wt % =
$$\frac{\text{Liquid yield output (g)}}{\text{mahua oil cake input (g)}} X 100$$
 (1)

Char yield, wt % =
$$\frac{\text{Char yield output (g)}}{\text{mahua oil cake input (g)}} X 100$$
 (2)

Non condensable gas yield, wt % = 100 wt % - (Liquid yield, wt % + Char yield, wt %) (3)

b. Design of Experiments

In this research work, the three levels, Box-Behnken design is found to be appropriate for designing the experimental conditions. The process parameters coded are temperature (A), particle size of the empty fruit bunch (B) and flow rate of N_2 (C). Table 1 shows, the level of each parameter are assigned in low, center and high levels as -1, 0 and +1 respectively. In this work, experiments are designed based on three levels and three factors with 15 runs. The performance of the regression analysis is estimated using second order polynomial.

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

Where Y is the predicted response, β_i , β_j and β_{ij} are coefficients estimated from the regression and they represent the linear, quadratic and cross products of X_1, X_2 and X_3 on response and k is the number of studied factors.



Fig 1. Mahua oil cake



Fig 2. photo graphic view of fast pyrolysis plant.

Table 1. Experimental conditions proposed by BBD for

| EFB. | | | | | | | | |
|----------------|-------------|-----|-----|-----|--|--|--|--|
| Variable | Real values | | | | | | | |
| | Code | -1 | 0 | 1 | | | | |
| Temperature °C | А | 500 | 550 | 600 | | | | |
| Size mm | В | 2 | 4 | 6 | | | | |
| Flow rate lpm | С | 0.2 | 0.3 | 0.4 | | | | |

Table 2. BBD matrix for the experimental design and predicted responses for the oil yield.

| Dun andan | Coded Values of Variables | | | Ac | tual level of | Evnovimentel | Duadiatad | |
|------------|---------------------------|----|----|---------|---------------|------------------|--------------|-----------|
| Kull order | | | | Temp °C | Size mm | Flow rate lt/min | Experimental | Predicted |
| 1 | -1 | -1 | 0 | 500 | 2 | 0.3 | 13.70 | 13.26 |
| 2 | 1 | -1 | 0 | 600 | 2 | 0.3 | 13.80 | 13.46 |
| 3 | -1 | 1 | 0 | 500 | 6 | 0.3 | 18.50 | 18.83 |
| 4 | 1 | 1 | 0 | 600 | 6 | 0.3 | 22.90 | 23.33 |
| 5 | -1 | 0 | -1 | 500 | 4 | 0.2 | 18.50 | 18.56 |
| 6 | 1 | 0 | -1 | 600 | 4 | 0.2 | 22.30 | 22.26 |
| 7 | -1 | 0 | 1 | 500 | 4 | 0.4 | 21.10 | 21.13 |
| 8 | 1 | 0 | 1 | 600 | 4 | 0.4 | 22.20 | 22.13 |
| 9 | 0 | -1 | -1 | 550 | 2 | 0.2 | 13.20 | 13.57 |
| 10 | 0 | 1 | -1 | 550 | 6 | 0.2 | 22.00 | 21.60 |
| 11 | 0 | -1 | 1 | 550 | 2 | 0.4 | 14.70 | 15.10 |
| 12 | 0 | 1 | 1 | 550 | 6 | 0.4 | 22.90 | 22.52 |
| 13 | 0 | 0 | 0 | 550 | 4 | 0.3 | 25.90 | 25.76 |
| 14 | 0 | 0 | 0 | 550 | 4 | 0.3 | 25.80 | 25.76 |
| 15 | 0 | 0 | 0 | 550 | 4 | 0.3 | 25.60 | 25.76 |

| Source | Sum of Squares | Degree of freedom | Mean Square | F Value | p-value Prob > F | Remarks | | | |
|--|-------------------|-------------------|----------------|---------|------------------|-----------------|--|--|--|
| Model | 287.0202 | 9 | 31.89 | 125.64 | < 0.0001 | Significant | | | |
| A-Temperature | 11.045 | 1 | 11.05 | 43.51 | 0.0012 | Significant | | | |
| B-Size | 119.3513 | 1 | 119.35 | 470.20 | < 0.0001 | Significant | | | |
| C-Flow rate | 3.00125 | 1 | 3.00 | 11.82 | 0.0185 | Significant | | | |
| AB | 4.6225 | 1 | 4.62 | 18.21 | 0.0080 | not significant | | | |
| AC | 1.8225 | 1 | 1.82 | 7.18 | 0.0438 | not significant | | | |
| BC | 0.09 | 1 | 0.090 | 0.35 | 0.5775 | Significant | | | |
| A^2 | 30.16641 | 1 | 30.17 | 118.84 | 0.0001 | Significant | | | |
| B^2 | 119.2626 | 1 | 119.26 | 469.85 | < 0.0001 | Significant | | | |
| C^2 | 13.09641 | 1 | 13.10 | 51.59 | 0.0008 | Significant | | | |
| Residual | 1.269167 | 5 | 0.25 | | | Significant | | | |
| Lack of Fit | 1.2225 | 3 | 0.41 | 17.46 | 0.0546 | not significant | | | |
| Pure Error | 0.046667 | 2 | 0.023 | | | | | | |
| Cor Total | 288.2893 | 14 | | | | | | | |
| Standard Deviation $= 0.50$ Maan $= 20.21$ D2 $= 0.0056$ Adjusted D2 $= 0.0077$ C.V. $\theta'_{i} = 2.40$ Dradiated D2 $= 0.0218$ Adjusted | | | | | | | | | |

Table 3. ANOVA for Response Surface Quadratic model.

Standard Deviation = 0.50, Mean = 20.21, R2 = 0.9956, Adjusted R2 = 0.9877, C.V. % = 2.4 Precision = 30.397 Predicted R2 = 0.9318, Adequate

3. Result and Discussion

a. Optimization by response surface modeling

The results of the ANOVA are tabulated in Table 3. The model is significant with an F value of 125.64. The probability of large F-value is only 0.01%, which could occur due to noise. If the values of "Prob > F" less than 0.0500, then the model is significant. The model terms identified as significant here are A, B, C, AB, AC, A^2 , B^2 and C^2 . If the values are greater than 0.1000, then the model was not significant. Lack of fit is not significant based on the pure error and F value 17.46.

There is a 5.46 % possibility that a narge Lack of Fit Fvalue could occur due to noise. Non significant shown in lack of fit was good. The Predicted R^2 of 0.9318 was in rational agreement with the Adjusted R^2 of 0.9877, the difference is less than 0.2. A ratio greater than 4 was attractive. The ratio of 30.397 shows an enough signal. The experimental results are analyzed using RSM. The results of the theoretically predicted outputs are given in Table 2. The mathematical expression of the relationship to the response with the variables is

Oil yield = $+25.77 +1.17 \text{ A} +3.86 \text{ B} +0.61 \text{C} +1.07 \text{ AB} -0.67 \text{AC} -0.15 \text{BC} -2.86 \text{ A}^2 -5.68 \text{B}^2 -1.88 \text{C}^2$ (5)

Response for given levels of every factor is identified by the above equation. The +1 is coded for in high level factor and -1 for coded in low level factors. Thus the coded equation is used to identify, compare the factor coefficients and relative impact factor.

Where A, B and C are the temperature (°C), particle size (mm) and N_2 flow rate (lpm), respectively. Equation 5 can be used to predict the bio oil yield within the limits of the experimental factors. Figure.3, ensures that the predicted response values are closer to actual response values. The response surfaces and contour graphs are produced for distinctive interaction of any two autonomous variables, while holding the estimation of the other variable as constant. Such three dimensional graphs give exact geometrical representation and give helpful data about the behaviour of the system within the experimental design. The response surface curves for the oil yield are shown in Figure. 4 to 6



Figure 3. Actual versus predicted responses of bio oil yield.



Figure 4. The combined effect of temperature and size for the yield of bio oil at constant 0.3 lpm of flow rate.



Figure 5. The combined effect of temperature and flow rate for the yield of bio oil at constant 4 mm in size.



Figure. 6 The combined effect size and flow rate for the yield of bio oil at constant temperature.

The three dimensional response surfaces which show the most important two variables temperature and particle size on bio-oil conversion at an N2 flow rate 0.3 lpm is shown in Figure.4. The maximum bio-oil conversion was obtained at 25.90 wt %, at constant 0.3 lpm of flow rate, 550° C of temperature and 4 mm of particle size. Figure 5 shows the three dimensional response surfaces of the combined effects of temperature and the N2 flow rate at constant particle size 4 mm. The maximum bio-oil production 25.90 wt % was obtained at temperature 550 °C and N₂ flow rate 0.3 lpm. Figure 6 shows the response surface graph for the optimum yield of bio oil. The figure depicts the interaction between the N₂ flow rate and particle size in three dimensional response surface plots. The maximum conversion of 25.90 wt % was obtained at constant temperature 550°C.

b. Optimized values by RSM for MOC bio oil

The optimum values, to obtain the bio oil yield, as inferred from the Figure.4 to 6. Under these conditions, the bio oil yield value predicted by the RSM design is 25.76 wt %. To verify the accuracy of optimization by RSM design. From the figure 7 the desirability value is 0.992 on condition of temperature 550°C, size 4 mm and flow rate 0.3 lpm is selected as optimum value and the experimental value of oil yield value is found to be 25.90 wt %. It is observed that the RSM predicted value of bio oil is 99 % accurate to the experimental value.



Figure 7. Bio oil Optimisation plot for mahua oil cake.

| Table 4. Pro | perties of | f mahua | oil c | ake p | vrolvsis | oil |
|--------------|------------|---------|-------|-------|-----------|-----|
| | | | | | , , ~ _ ~ | ~ |

| Test Property | Values | Procedure |
|------------------------------------|--------|---------------------|
| Net Calorific value kJ/kg | 28180 | IS: 1448 Part 6 & 7 |
| Kinematic viscosity @ 40° C in cSt | 2.71 | IS: 1448 Part 25 |
| Flash point in ° C | 52 | ASTM D 92 |
| Fire point in ° C | 64 | ASTM D 92 |
| Cetane number | 25 | ASTM D 974 |

c. Bio oil characteristics for mahua oil cake

The GC-MS analysis of the oil sample obtained from the Mahua oil cake was carried out to know the exact composition of the oil (Figure 12) and seventy two compounds were detected which are summarized in the Table.2. In the seventy two components five components are major and other is minor. On the basis of the MS database, these peaks can be identified. With 9-octadecenoic acid (Z), methyl ester being present in highest amount (27.45%), many derivatives of 9-octadecenoic acid (Z), methyl ester were also detected. On the basis of the MS database, these peaks can be identified (Phenol, Naphthalene, 1,6,7-trimethyl-, 9-octadecenoic acid (Z), a methyl ester, 9,12-octadecadienoic acid, (Z, Z) - methyl ester Methyl stearate).



Figure 8. GC-MS test results for bio oil – MOC.

|] | Table 5. Cor | nponents o | btained in | bio oil –MOC |
|---|--------------|------------|------------|--------------|
| | | | | |

| S.No | Name | Formula | RT | Area in% | Synonyms | MW |
|------|--|---------------------------------|---------|----------|--------------------------------|--------|
| 1 | Phenol | C ₆ H ₆ O | 4.731 | 2.08 | Carbolic | 94.11 |
| 2 | Naphthalene, 1,6,7- trimethyl- | $C_{13}H_{14}$ | 13.371 | 2.12 | 2,3, 5-Trimethylnaphthalene | 170.25 |
| 3 | 9-octadecenoic acid (Z), methyl ester | $C_{19}H_{36}O_2$ | 18.913 | 27.45 | Oleic acid methyl ester | 296.48 |
| 4 | 9,12-octadecadienoic acid (Z,Z)- methyl ester | $C_{19}H_{34}O_2$ | 718.876 | 12.18 | Methyl octadeca-9,12-dienoate | 294.47 |
| 5 | Methyl stearate | $C_{19}H_{38}O_2$ | 119.173 | 6.00 | Octadecanoic acid methyl ester | 298.50 |

4. Conclusion

The optimum process condition is produce bio-oil from the Mahua oil cake was determined using the box Behnken design in RSM. Mathematical model equations were built using sets of experimental data and ANOVA. The temperature, particle size and N2 flow rate was found as the significant factor in the optimization of bio-oil production. The interaction between the temperatures and particle size, particle size and N2 Flow rate are not significant factors. The optimum point achieved at temperature of 550 °C with a particle size 4 mm and a nitrogen flow rate of 0.3 lpm. From GC-MS analysis, it can be concluded that, the bio-oil composition is dominated by oxygenated species

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