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Evaluation of influential factors in microwave assisted pyrolysis of sugarcane bagasse for biochar production

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ABSTRACT

Microwave assisted pyrolysis (MAP) is an efficient technology for the production of biochar. However, its large-scale application is limited due to lack of process optimization resulting in lower yield. Identification of significantly influencing parameters is essential for efficient optimization. Thus, in present study, screening of factors like the feedstock amount, feedstock size, moisture content, catalyst dosage, microwave power and exposure time using half fractional factorial screening design was done to identify the most influencing factor affecting sugarcane bagasse biochar yield. The formulated linear model was found to be significant with a regression coefficient (R^2) of 0.9365. Half normal plot and the Pareto chart analysis showed that MAP to be mostly influenced by feedstock amount, microwave irradiation time, feedstock size and microwave power. Maximum biochar yield of 44.46% was obtained with 10 g feedstock (0.015 cm) at 720 W after 20 min, which would be optimized further to improvise the process efficiency.

1. Introduction

India is the leading country in producing sugarcane accounting for 29.66 mega metric tonnes compared to other countries like Brazil, Thailand and China (Khichi and Arshad, 2021). After the processing of sugarcane in industries for the ethanol production or extraction of sucrose enriched product from the stalks, the left over bagasse will be treated as solid waste. Sugarcane bagasse (SB) is one of the abundant agricultural waste that is being generated and has the potential for transformation into energy and fine chemicals (Akinfalabi et al., 2020). Around 280 kg of wet bagasse is produced from every one tonne of sugarcane and is being used in many sugar mills to power the milling process, however substantial amount of bagasse is left stockpiled and burnt on site (Fu et al., 2017). The heaped biomass is of low monetary product and increases the risk of unprompted combustion that possess severe threats for the industry and surrounding places. The alternative way is to convert these residues into valuable product that could act as chemical/ energy of higher economic value and it is feasible option to reduce the environment deterioration and fossil fuel consumption.

The conversion of agricultural residues into solid product biochar after the devolatilization of biomass has been realized as better energy recovery opportunity and this was attained through thermochemical/ biochemical techniques (Ok et al., 2015; Ibrahim et al., 2019; Behera et al., 2020a). Pyrolysis is one of the imperative thermochemical techniques used widely for production of energy products in terms of solid biochar, liquid bio oil, and gases (Zhang et al., 2020). Of these numerous pyrolysis technologies, Microwave assisted pyrolysis (MAP) involves microwave dielectric heating that penetrates into the biomass and the energy is dissipated throughout the volume of the material resulting in product formation with less

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temperature and time (Dong et al., 2018; Yang et al., 2021). MAP is more effective than conventional pyrolysis owing to rapid, localized and uniform heating with higher rate of reaction which are promoted under the frequency of microwave (Selvam and Paramasivan, 2021).

Lin and Chen (2015) has reported that biochar is the main product under microwave pyrolysis of sugarcane bagasse and the time required to reach steady state temperature is lower compared to conventional pyrolysis. Production of engineered biochar from sugarcane bagasse using MAP is being utilized in various applications like performance as carbon electrode, magnetic biochar for effluent remediation etc. (Noraini et al., 2016; Tang et al., 2020). Presently, various authors have focused on optimizing the process conditions of MAP to derive higher yield of biochar with better characteristics (Hossain et al., 2017; Tripathi et al., 2020). The optimum yield of biochar is dependent on the properties of feedstock, type of reactor, pyrolysis conditions and microwave absorbers/ catalyst (Li et al., 2016). Sahoo and Remya (2020) has reported that interactive effect of microwave time and power has positive influence on the yield of rice husk biochar, whereas, Zhu et al. (2015) has stated that effect of particle size showed less significant response on surface functionality of biochar. The effect of microwave absorber is also significant as microwave power and time during MAP (Abd et al., 2018). Based on the previous literatures reported, it could be comprehended that process optimization of influential factors will lead to obtain higher yield and better quality that could be utilized in various applications. Several multifactor optimization studies by Hossain et al. (2017), Tripathi et al. (2020) has already been conducted for microwave based pyrolysis for different feedstock. All the above mentioned studies have considered a specific range of each factor and directly expressed the significant variables during MAP. However, this multifactor optimization study has been performed in a sequential manner, wherein the influencing parameters like feedstock amount, size, moisture content, and microwave power, and the range of these variables were carefully selected based on the preliminary trials and detailed literature for the screening design. Often direct implementation of the CCRD increases the number of runs which is highly time-consuming. Thus, the screening design provides a strategic way to understand the individual effect of factors and screen out the necessary variables before proceeding for process optimization.

To the best of author's knowledge, the optimal response of the operating factors on the yield of biochar from sugarcane bagasse and its property derived through MAP has not been reported yet. In this study, the half fractional factorial design has been employed to analyse the individual response of influential factors on the yield of biochar. Statistical significance of the model, and the diagnostic plots were analysed in detail to highlight the accuracy of the response, as well as to study the quantitative influence of variables over the biochar yield. Such study will aid in reducing the time and costs involved in subsequent process optimization considering only the most critical factors to maximize the yield, thereby producing better quality of biochar for sustainable environmental applications.

2. Materials and methods

2.1. Feedstock preparation

Sugarcane bagasse was collected from the National Institute of Technology (NIT) Rourkela campus. The collected sugarcane bagasse sample has been rinsed with tap water and dried in hot air oven at 80 °C for overnight. The samples were then subjected to size reduction through laboratory grinder for making 0.015 cm and manual cutting for 1.5 cm respectively. The biomass with a size of 1.5 cm was measured using a geometric scale, while the powdered sample was sieved using mesh of size 150 μm. The sample sizes denote the average size of 0.015 cm and 1.5 cm respectively which was then used for the further study. The samples had an initial moisture content of 4.2%. Samples were then sprayed with distilled water and was kept static under ambient conditions for moisture conditioning until it reached the requisite moisture content of 8% and 16%, which was confirmed through gravimetric analysis using American Society of Testing Material (ASTM) D1762-84 protocol (ASTM, 2013). The samples were then packed in air tight containers and stored inside a desiccator until further use. Catalyst used in the present study is a commercial biochar (powdered form) sold under the tag name "Satavic Biochar" [Satavic Farms, Kolkata, India] having a moisture of 4.83 ± 0.15%. Proximate analysis of the catalyst showed a volatile content of 17.5%, ash content of 4.1% and fixed carbon of 78.2%. The catalyst has elemental carbon content of 33.61%, oxygen content of 48.93%. pH and electrical conductivity of catalyst utilized were 6.1 and 240 μS cm^{-1} respectively.

2.2. Experimental methodology for fractional factorial design

The yield of biochar in a microwave oven is often influenced by a series of process variables like the feedstock quantity, the size of feedstock, the moisture content, catalyst dosage, microwave power as well the exposure time. These factors were selected to simulate an experimental design using the Design Expert® software (Version 13, US Stat Ease). The factors and its ranges has been selected based on the preliminary experiments and literature studies. The microwave power and time were selected based on the preliminary trials on the basis of biochar formation. The dosage of microwave absorber is selected based on studies by Mohamed et al. (2016), Nhuchhen et al. (2018) and Sahoo and Remya (2020), where the dosage ranges of 10% to 30% has been used. The level for moisture content and particle size of the sample is selected based on studies by Azni et al. (2019), Dineshkumar et al. (2020) and Li et al. (2018) respectively. The maximum biomass quantity has been selected as 10 g based on the previous study by Rex et al. (2020) who has pyrolysed plastic waste

Table 1
Range of variables selected for screening the influential factors in microwave pyrolysis of sugarcane bagasse.

Parameters	Feedstock amount (g)	Feedstock size (cm)	Moisture content (%)	Catalyst dosage (%)	Microwave Power (W)	Reaction time (min)
Lower value	2	0.015	8	10	360	5
Higher value	10	1.5	16	30	720	20

using microwave power of 180 W, 360 W, 540 W and 720 W which is similar to microwave power levels used in this study. The least biomass quantity of 2 g has been fixed in the present study in order to find out the minimum quantity of biomass that can efficiently adsorb the microwave irradiation leading to biochar formation. The factors and its levels has been given in Table 1. The influencing variables were combined based on the randomized design statistically generated using the Design Expert® software to generate a set of 32 experimental runs *via* the Resolution 5, half fractional factorial design, which is one of the most common screening technique. The number of runs are calculated using Eq. (1) as outlined in Wong et al. (2015)

$$No\ of\ runs = \frac{1}{2}[2^k] \tag{1}$$

where k represents the number of factors/ variables considered in the study.

The microwave assisted pyrolysis was conducted using domestic microwave oven (Electrolux C25K151 BG-CG) with rated output power of 180–900 W, having a frequency of 2450 MHz. The cavity dimensions of the microwave reactor were of 190 mm (H) * 310 mm (L) * 300 mm (W). A vent has been provisioned at the side to let the exhaust volatiles out. Biomass samples were kept in a borosilicate glass container inside the microwave cavity as per the amount and the combination of parameters as mentioned in Table 1. The infrared pyrometer is used to measure the process temperature. Once the process is over, the solid residues will be weighed and yield will be calculated on the basis of conversion efficiency of biochar formation as per the Eq. (2) as provided below.

$$Biochar\ yield\,(\%) = \frac{Mass\ of\ biochar\ (g) - Mass\ of\ catalyst(g)}{Mass\ of\ biomass(g)} * 100 \tag{2}$$

The data obtained from the experiments were fed into the software for identifying the most influential factors affecting the biochar yield.

2.3. Statistical analysis

2.3.1. Identification of the most influential factors

The most influential factors affecting the biochar yield was determined using the Shapiro–Wilk test by analysing the half normal plot (Şenol, 2020). The factors (indicated by square labels) situated at a distant point from the half normal line are considered significant. The parameters lying near or almost on the half normal probability line are considered to have no significant influence. The positive or negative impact of factors can be determined from the colour of the square labels in case of each variable. Orange coloured square box indicates positive interaction while the blue coloured box shows negative influence over the response.

The effect of the parameters was further confirmed by the Pareto chart. The most influential factors were identified by their position between the t-value line and the Bonferroni limit. The degree of influence is usually represented by the height of the bar graphs from left to right on the chart. Colour code similar to that of the half normal plot indicates the positive/ negative interactions between the factors and that of the response (Semhaoui et al., 2018).

2.3.2. Model adequacy and fit statistics

The factors identified were fitted into the linear model (suggested by the software) to analyse the adequacy for predicting the biochar yield. The significant factors were identified with a higher Fischer test value (F-value). Considering a 95% confidence interval, the factors with a p-value less than 0.05 were considered significant. The overall model adequacy was analysed based on the F value and the p-value of the factors, along with the lack of fit analysis. Further, the model adequacy was determined based on the regression coefficient (R^2), which closer to 1 represents the model to be adequate with a good correlation between the experimental data and that of the model predicted data. Further, the variants of R^2 involving the predicted R^2 and the adjusted R^2 were evaluated to study the influence of any deletion of terms or model runs over the model validity. The actual versus predicted curve was analysed to study the correlation between the experimental data and the predicted values. Further, the covariance and adequate precession values were examined to confirm the adequacy of the model.

2.3.3. Residual error analysis

It is essential to validate the model through residual error analysis by analysing the distribution of externally studentized residual values. The normal probability plot of externally studentized residuals; residual versus run plot and residuals versus predicted plot were studied to analyse the distribution of errors with respect to the model.

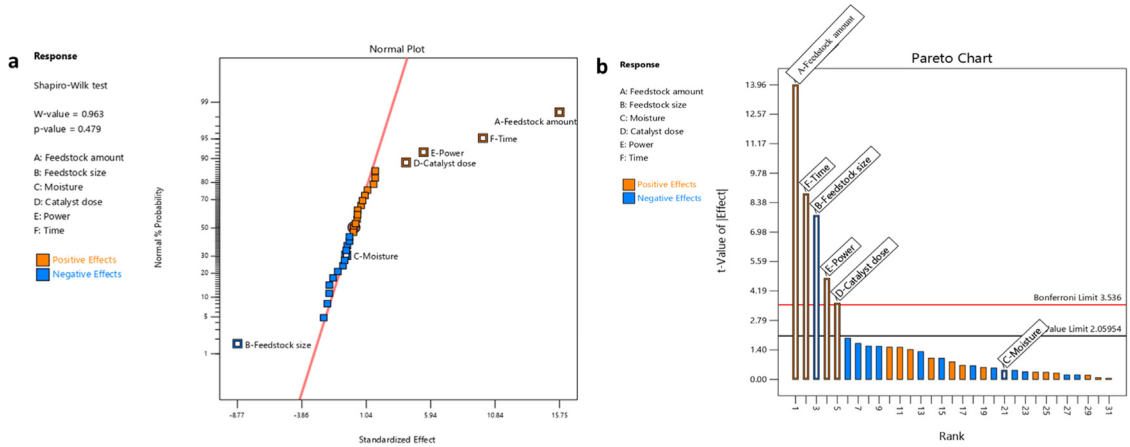

Fig. 1. (a). Shapiro–Wilk test and (b). Pareto chart for the evaluation of influencing variables on biochar yield obtained from sugarcane bagasse through microwave pyrolysis.

2.4. Analysing the effect of factors on response

The output or the response variable is often influenced by the operational parameters during the experimental condition. The effect of different parameters on the response or the biochar yield was evaluated based on the regression equation in terms of the coded values. The factors with a positive coefficient were found to have positive influence over the biochar yield, on the other hand, the factors with negative coefficient had negative influence on the biochar yield. The effect of factors on the response was also studied via the evaluation of the interaction plots of individual parameter over the biochar yield.

2.5. Numerical optimization

To cross-validate the model the numerical optimization was carried out with the aid of the desirability function. A desirability function closer to 1 is often selected with a feasible combination of parameters to achieve the desired yield. In the present study, the goals were to maximize the biochar yield by keeping all the factors within the range provided earlier. All factors were given equal weightage (+++), the desirability solutions were obtained starting with 100 random points, 50 design points and duplicate solution filter at epsilon to avoid any kind of repetitive solutions. Out of the 100 probable solutions (only 10 solutions represented), the solution with the highest desirability was selected and further validated in triplicates under the laboratory conditions to study the degree of variation in terms of the standard error.

2.6. Characterization of biomass and optimized biochar

The proximate composition of biomass and biochar were identified through standard ASTM protocol (ASTM, 2013). The H/C and O/C ratio of biochar were identified according to study by Klasson (2017). The calorific values were identified through Parr 6100 bomb calorimeter. The morphological porous structure was observed through the scanning electron microscope (SEM) [JSM-6480 LV, JEOL] with theoretical resolution of 1 nm and acceleration of 15 kV. The cross sections of samples were analysed in longitudinal and transverse directions. The JEOL JSM-6480LV scanning electron microscope was equipped with an INCAPentaFET-x3 X-ray microanalysis system with high-angle ultra-thin window detector and a 30 mm^2 Si(Li) crystal to analyse the surface elemental content.

3. Results and discussion

3.1. Identification of the most influential factor on biochar yield

The half normal probability plot was used to identify the significantly influencing parameters over the biochar yield. Based on the distance from the near zero line (red coloured line) in Fig. 1a, feedstock amount (A) was found to be important, followed by the time (F), feedstock size (B), and microwave power (E) and catalyst dosage (D). Pareto chart (Fig. 1b) is used to identify the essential factors depicted in descending order based on the height of bars from left to right and their relative effect over the biochar yield. Pareto chart has two important indicators red coloured line (*i.e.*) the Bonferroni limit and the blue coloured line called the t-value, any parameters between these two limits are considered statistically acceptable (Wilkinson, 2006). Parameters above the Bonferonni limits are considered most essential, compared

Table 2
Fractional screening design for the determination of influential factors of microwave pyrolysis of sugarcane bagasse.

Run	A:Feedstock amount (g)	B:Feedstock size (cm)	C:Moisture (%)	D:Catalyst dosage (%)	E:Power (Watt)	F:Time (min)	Temperature (°C)	Biochar yield (Exp) (%)	Biochar yield (Pred) (%)
1	2	1.5	8	30	720	20	92	13.69 ± 4.52	17.32
2	10	0.015	8	10	720	5	119	25.39 ±3.02	27.85
3	10	0.015	8	30	360	5	93	25.64 ±3.79	26.52
4	10	1.5	16	10	360	20	161	18.30 ± 0.70	21.68
5	10	0.015	16	30	720	5	130	31.46 ±4.65	31.42
6	10	0.015	16	30	360	20	118	38.05 ±4.31	35.94
7	2	1.5	16	30	360	20	81	8.62 ±1.89	10.00
8	10	0.015	16	10	720	20	183	44.46 ±3.11	37.27
9	2	0.015	16	30	720	20	124	23.80 ± 3.07	25.59
10	10	1.5	16	30	720	20	177	29.98 ±1.81	32.57
11	10	1.5	16	30	360	5	145	13.87 ±2.39	15.83
12	2	0.015	8	10	360	5	83	5.46 ±1.66	5.28
13	2	0.015	8	30	360	20	112	22.55 ±3.53	20.69
14	10	1.5	8	10	360	5	93	10.80 ± 0.84	12.26
15	2	1.5	16	30	720	5	82	8.81 ±4.76	5.48
16	10	1.5	8	10	720	20	148	30.85 ±4.56	29.00
17	10	0.015	8	10	360	20	120	31.07 ±4.85	32.37
18	2	1.5	16	10	720	20	103	9.45 ±3.32	11.33
19	10	0.015	8	30	720	20	148	38.00 ±0.42	43.26
20	2	1.5	8	30	360	5	62	2.76 ±0.14	0.57
21	2	0.015	8	10	720	20	150	18.61 ±2.71	22.02
22	2	1.5	16	10	360	5	83	2.02 ±0.27	5.41
23	10	1.5	16	10	720	5	90	13.35 ±1.60	17.16
24	10	1.5	8	30	360	20	143	27.37 ±4.19	27.67
25	2	0.015	16	10	360	20	129	13.82 ±3.31	14.70
26	10	0.015	16	10	360	5	115	18.48 ±4.08	20.53
27	2	0.015	16	30	360	5	65	7.31 ±1.98	8.85
28	2	0.015	8	30	720	5	96	11.74 ±4.44	16.17
29	2	1.5	8	10	720	5	86	3.29 ±0.95	1.91
30	10	1.5	8	30	720	5	168	26.00 ± 2.61	23.15
31	2	1.5	8	10	360	20	95	7.81 ±0.17	6.43
32	2	0.015	16	10	720	5	96	11.39 ±3.45	10.18

Table 3
ANOVA and statistical table for selected factorial model in predicting the influential factors of microwave pyrolysis of sugarcane bagasse.

Source	Sum of Squares	Df	Mean Square	*F*-value	*p*-value	
Model	3752.31	6	625.39	61.49	< 0.0001	Significant
A-Feedstock amount	1983.56	1	1983.56	195.02	< 0.0001	
B-Feedstock size	614.78	1	614.78	60.44	< 0.0001	
C-Moisture	1.93	1	1.93	0.18	0.6668	
D-Catalyst dose	132.44	1	132.44	13.02	0.0013	
E-Power	232.96	1	232.96	22.90	< 0.0001	
F-Time	786.66	1	786.66	77.34	< 0.0001	
Residual	254.28	25	10.17			
Cor Total	4006.59	31				
Lack of Fit						Insignificant

R^2: 0.9365; Adjusted R^2: 0.9213; Predicted R^2: 0.8960 Std. Dev.: 3.19; Mean: 18.57; C.V (%): 17.18

to the parameters above the *t*-value line. Similar to the conclusions obtained from the half-normal probability plot, feedstock amount was found to be important, followed by the time, feedstock size, and microwave power were considered to be significantly influencing the microwave based biochar yield. In the present study, all the parameters except the moisture content were found to be above the Bonferonni limit, showing significant influence over the response.

3.2. Statistical analysis to estimate the model adequacy

Table 2 shows the design matrix using the combination of different variables. The maximum and the minimum biochar yield of 44.46% and 2.02% was obtained in run 8 and 22 respectively. The ANOVA (Table 3) showed the model to be significant with a *p*-value of <0.0001, and *F* value of 61.49, considering 95% confidence interval. Also, the regression coefficient (R^2) of 0.9365 showed the suitability of the model. An insignificant lack of fit implies that the experimental data accurately correlates with the predicted values with respect to the pure error. Out of the six selected variables, five factors such as feedstock amount, feedstock size; catalyst dosage; microwave power and time were found to be

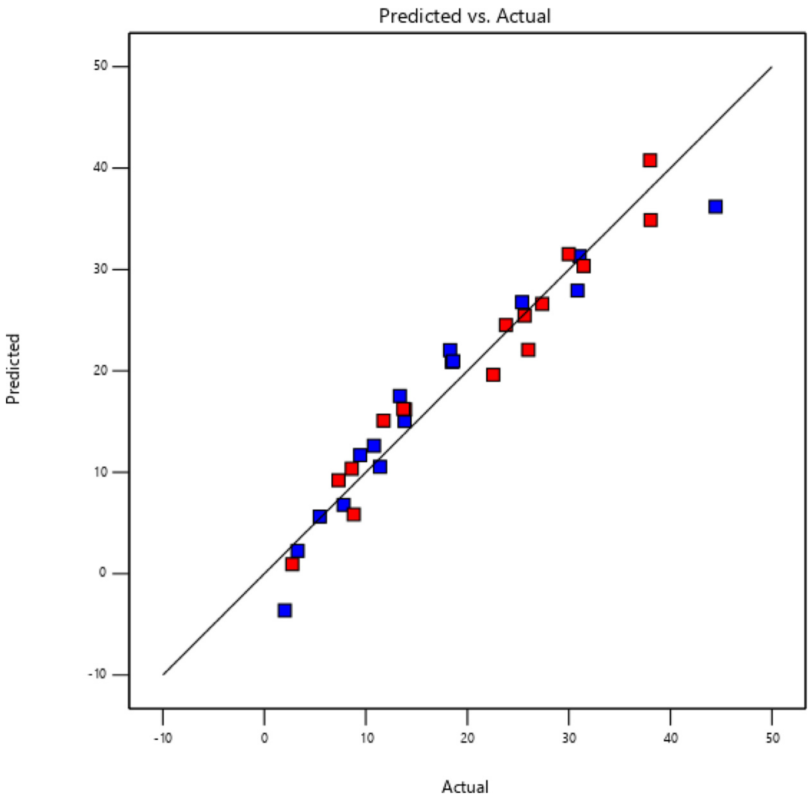

Fig. 2. Predicted versus actual plot of the influential variables over the biochar yield obtained from sugarcane bagasse through microwave pyrolysis.

significantly influencing the product yield with p value < 0.05. The first order equation for predicting the biochar yield as shown in Table 2 by fitting the experimental data is provided in Eq. (3).

$$\text{Biochar yield (\%)} = +18.57 + 7.87A - 4.38B - 0.2456C + 2.03D + 2.70E + 4.96F \tag{3}$$

where, A represents the feedstock amount; B represents the feedstock size; C represents the moisture content; D represents the catalyst dosage; E represents the microwave power and F represents the time. The constant terms for each of the factors represent the specific coefficient in the coded equation. A positive coefficient shows synergistic effects while a negative coefficient shows an antagonistic effect.

The coefficient of regression (R^2) of 0.9365 shows a good correlation between the experimental and predicted values. The predicted R^2 of 0.8960 is in reasonable agreement with the adjusted R^2 of 0.9213; (*i.e.*) the difference is less than 0.2, showing the reliability of the model. Adequate precision measures greater than 4 indicated the model to be adequate with the lack of unwanted errors. Further, the predicted versus actual graph (Fig. 2) showed goodness of fit of the proposed model with adequate correlation between the experimental and predicted results.

Even though the linear regression model considers the errors to be normally distributed and near zero, substantial amount of error might still lie between the experimental data and the predicted estimates (Behera et al., 2020b). The diagnostic plots were utilized to analyse the level of errors in the model. Lack of pure errors/ residuals and model adequacy was also justified by the distribution of experimental values linearly over the normal probability line in Fig. 3a. The residual versus predicted response plot (Fig. 3b) shows a random scatter, supporting the constant variance assumption and lack of heterogeneity. Also, randomized pattern was obtained in the case of residual versus experimental run order plot (Fig. 3c). These plots indicate the lack of substantial errors in the distribution of data and also the absence of outlier, and uncontrolled variable over the response is relatively small (Supraja et al., 2020).

3.3. Effect of individual parameters on response

3.3.1. Effect of individual parameter on temperature and heating rate

The final temperature of pyrolysis in each of the runs during the experiment has been detected using an infrared pyrometer. The least temperature was found to be 62 °C under the pyrolysis condition of 2 g of feedstock amount with 1.5 cm particle size containing 8% moisture content and 30% catalyst addition at 360 W after 5 min, while the highest temperature recorded was 185 °C with a feedstock amount of 10 g, 0.015 cm particle size having a moisture content of

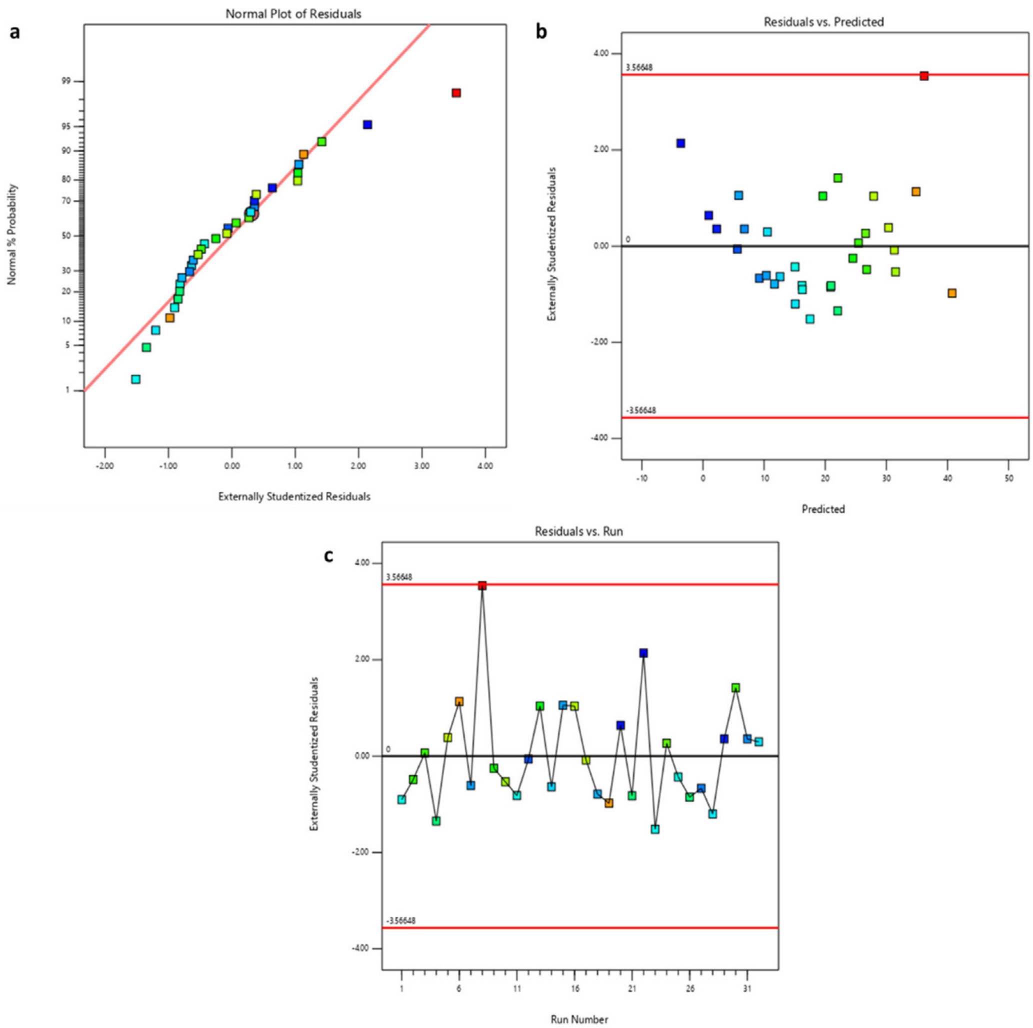

Fig. 3. (a). Normal probability plot (b). Residual versus predicted (c). Residual versus run plot of externally studentized residual.

16% and added with 10% catalyst dosage at 720 W and time of 20 min. Similar to the present study, Masek et al. (2013) showed that microwave pyrolysis could also occur nearly at a temperature of 200 °C even with a lower residence time, resulting in a char yield of 27.3% obtained from willow chips using biomass load of 130 g with constant microwave power of 1.2 kW. At higher microwave power, the surface temperature is maximum and since the biomass is of smaller particle size, the heating rate is faster which facilitate the pyrolysis reaction. As stated by Li et al. (2018), temperature of 180 °C is sufficient enough to initiate pyrolysis reaction under the influence of microwave. For run 20, even after the addition of 30% carbon, no pyrolysis occurred at 360 W for 5 min. This is owing to the reason of insufficient temperature which means that electric field is not intensive that could agitate the molecules to reach the desired temperature under low power and time and also due to less efficient synergistic effect of carbon catalyst and biomass. Similar findings was also reported by Salema and Ani (2012) stating that no pyrolysis happened at 300 W even after the addition of microwave absorber of up to 50% and less moisture content which is not also able to build the pressure restricting the temperature to lower value that could not initiate the pyrolysis reactions. In a nutshell, it could be concluded that at higher microwave power of 720 W and time of 20 min, the biomass bed surface temperature reached the maximum temperature required for biochar product formation that results in increased yield whereas at lower power and time, due to insufficient temperature, pyrolysis reactions like secondary cracking, volatilization could not happen that results in insignificant product yield.

The heating rate of the sample is influenced by particle size and microwave power. In case of particle size, the heating rate was 33.6 °C min^{-1} for initial 5 min, however, when time proceeds, the heating rate drops to 8.9 °C min^{-1} for 0.015 cm sample at 20^{th} min whereas the heating rate ranges from 29.8 °C min^{-1} to 8.75 °C min^{-1} for 1.5 cm sample at 720 W respectively. This is owing to the fact that powdered biomass sample could able to mix with catalyst which promotes the higher heating rate. At 360 W power, heating rate ranges from 16.6 °C min^{-1} to 6.1 °C min^{-1} for 1.5 cm sample under

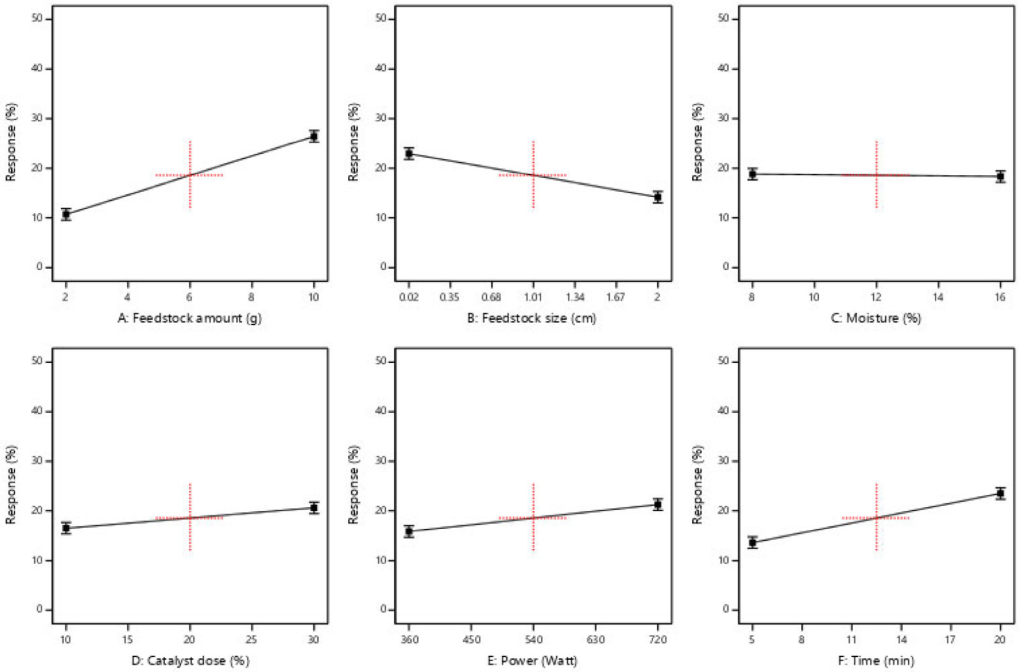

Fig. 4. Influence of individual factor ranges over the biochar yield obtained from sugarcane bagasse through microwave pyrolysis.

the same conditions whereas it ranged from 21.2 °C min^{-1} to 6.16 °C min^{-1} for 0.015 cm respectively. The heating rate obtained at 360 W is lower than that obtained at 720 W owing to the fact that at higher microwave power, the microwave absorption will be higher which leads to higher heating rate.

3.3.2. Effect of individual parameter on biochar yield

The runs carried out for detecting the influential parameters has been given in Table 2. The influence of individual factors over the biochar yield can also be inferred from the interaction plots shown in Fig. 4. Feedstock amount was found to have the greatest positive impact over the biochar yield. As shown in table, with the increase in feedstock amount, more biomass will be available to absorb the available microwave irradiation, thus resulting in increased conversion to biochar formation. Microwave time is the next most significant factor influencing the biochar yield. With the increase in time from 5 min to 20 min, the conversion of biomass has been increased since residence time of 5 min is insufficient for complete decomposition of cellulose and hemicellulose. Rex et al. (2020) observed that no product yield was obtained even maintained for 20 min with 20% of catalyst addition. Feedstock size was found to show negative impact over the biochar yield, (*i.e.*) with the increase in size of the particle, a decline in biochar yield was observed. The result obtained in the present study is contradictory with the trend reported by Zhu et al. (2015) and Wu et al. (2019) during microwave assisted pyrolysis without microwave absorber. However, during slow pyrolysis in the presence of a microwave absorber, contact heat transfer based reactions dominate during low temperature thermal cracking process (Mohamed et al., 2016). Thus, in the present study, MAP done with smaller particle size feedstock with external added biochar catalyst was uniformly mixed, thus providing better surface area of contact and uniform distribution of microwave resulting in higher biochar yield, also reported by Mong et al. (2020). But in case of large sized particles, the inappropriate and non-uniform contact between the microwave absorber and the feedstock hindered efficient heat transfer, resulting in incomplete pyrolysis reactions, declining the biochar yield.

Microwave power was found to be the third most essential factor influencing the biochar yield during the pyrolysis. Studies have reported that with the increase in microwave power beyond the threshold limit, often there is a decline in biochar yield as the heating rate becomes very rapid resulting in formation of more bio-oil and gaseous by-products (Salema and Ani, 2012; Rex et al., 2020). In the present study, for the 2-level factors for microwave power considered, it was evident that with an increase in power, the conversion into solid carbonaceous residues were significantly higher. Since at low power, there is no appreciable increase in temperature which could not initiate pyrolysis reaction. Biochar, the carbonaceous material acts as the catalyst/microwave absorber due to efficient dielectric properties. The microwave absorber was found to have a positive influence over the biochar yield, as the increase in its concentration, absorbs more microwave irradiation, thereby facilitating heat transfer and the required temperature for conversion of biomass and results in increased biochar yield. In the present study, keeping the moisture within the range of 8%–16%, does not have

Table 4
Set of solutions obtained via numerical optimization of microwave pyrolysis of sugarcane bagasse with different desirability.

S. No.	A	B	C	D	E	F	Response	Desirability
1	10.00	0.02	8.00	30.00	720.00	20.00	40.76	0.913
2	9.99	0.02	8.33	30.00	719.55	19.75	40.57	0.908
3	9.99	0.04	8.14	29.98	715.13	20.00	40.56	0.908
4	9.99	0.05	8.00	29.91	720.00	19.90	40.53	0.908
5	9.97	0.02	10.83	29.88	719.86	19.96	40.48	0.906
6	9.88	0.02	8.98	30.00	719.67	20.00	40.47	0.906
7	9.99	0.02	10.75	29.12	717.25	20.00	40.35	0.903
8	9.97	0.02	13.43	30.00	719.99	19.89	40.31	0.902
9	9.99	0.06	9.33	28.83	719.99	19.91	40.18	0.899
10	9.93	0.05	13.31	30.00	720.00	19.99	40.16	0.899

A, B, C, D, E and F represents feedstock amount (g), feedstock size (cm), moisture content, microwave power and time; Response corresponds to biochar yield in %.

any significant influence over the biochar yield even though moisture is regarded as an efficient absorber for microwave irradiation. A low moisture content of 8% is expected to absorb the requisite microwave power, resulting in higher biochar yield, which on further increase is expected to decline the biohar yield, due to endothermic reactions, declining the heating rate and formation of more gaseous phase compounds. Similar results were also reported in the study by Beneroso et al. (2014), who suggested that high moisture content often favours syngas generation during microwave assisted pyrolysis of municipal solid sludge.

It is noteworthy to mention that the screening designs or fractional factorial designs are generally used to screen and identify the effect of prominent individual factors over the output/response. Thus, the present study was limited to identify the most significant individual factors affecting the response. However, the combined effect of the identified significant factors will further be evaluated using the central composite rotatable design (CCRD) in future in a large scale microwave pyrolysis reactor.

3.4. Model validation and point prediction

Numerical optimization was carried out with the aim to increase the biochar yield by keeping all the factors at the desired range with the aim to improvise the process feasibility. Similar optimization methodology was also followed by Binnal and Babu (2017). Numerical optimization protocol was also provided by 100 solutions (only the top 10 shown in Table 4) obtained with the desirability value ranging from 0.913 to 0.775. The first solution with the highest desirability having the process parameter combination as 10 g feedstock with 0.015 cm feedstock size, having a moisture content of 8%, exposed to 720 W for 20 min was selected. The experimental conditions were validated again in the laboratory. A biochar yield of 37.70% was obtained having a standard deviation of 2.16, compared to that of 40.76% predicted by the model. The biochar yield obtained was comparable (within a difference of $\pm$ 10%) to that predicted by the model, suggesting the adequacy of the optimization model in predicting the significant parameters. Also it is noteworthy to mention that the yield obtained via numerical optimization was lower than that of the 44.46% at the combination using 10 g biomass, with an average particle size of 0.015 cm, moisture content of 16% and addition of 10% microwave absorber at 720 W for 20 min. The decrease in moisture content is expected to decline the heating rate and thereby the biochar yield, however the addition of higher amount of catalyst could effectively balance the requisite heating and facilitate the biochar production. The cost linked with the catalyst could be brought down by recycling the biochar formed during MAP as the microwave absorber for subsequent pyrolysis.

3.5. Characteristic features of biochar produced under optimal conditions

The powdered biomass samples with an average particle size of 0.015 cm had 77.98 $\pm$ 2.36% volatile matter, ash content of 10.47 $\pm$ 0.12% and fixed carbon of 11.54 $\pm$ 2.48%. The biomass sample with the particle size of 1.5 cm had 72.6 $\pm$ 4.40% volatile matter, ash content of 9.75 $\pm$ 1.14% and fixed carbon of 17.6 $\pm$ 3.25%. The calorific value of the biomass was found to be 12.44 MJ kg^{-1}. The pH of the sugarcane bagasse is 4.4 whereas it got increased after biochar formation and found to be 4.8 which is acidic in nature owing to formation of carbonates and release of alkali salts of organic matter and decreasing of –COOH groups (Behera et al., 2020a). The electrical conductivity of biochar was found to be 104.1 $\mu S\ cm^{-1}$. The biochar contains volatile matter, ash and fixed carbon content of 27.99%, 12.76% and 59.23% respectively. The H/C and O/C ratio were identified to be 0.43 and 0.12 respectively which is less than values recommended by International Biochar Initiative and European Biochar Foundation (Klasson, 2017). The heating value of the biochar was found to be 19.14 MJ kg^{-1}, similarly reported by Webber III et al. (2018) which was produced at 343 °C. The scanning electron microscopic image of biochar (Fig. 5a) shows that the surface is porous in form of honeycomb and rough structures. The elemental composition of biochar was identified through energy dispersive X-ray analysis. The biochar has carbon and oxygen content of 75.43% and 21.11% respectively, whereas in addition, trace quantities of potassium, calcium, iron content of 1.26%, 0.55%, 0.71% has also been detected (Fig. 5b). From these entries, it could be comprehended that the sugarcane bagasse biochar produced through microwave pyrolysis could be used as soil amendment in alkaline soil, solid fuel and other applications.

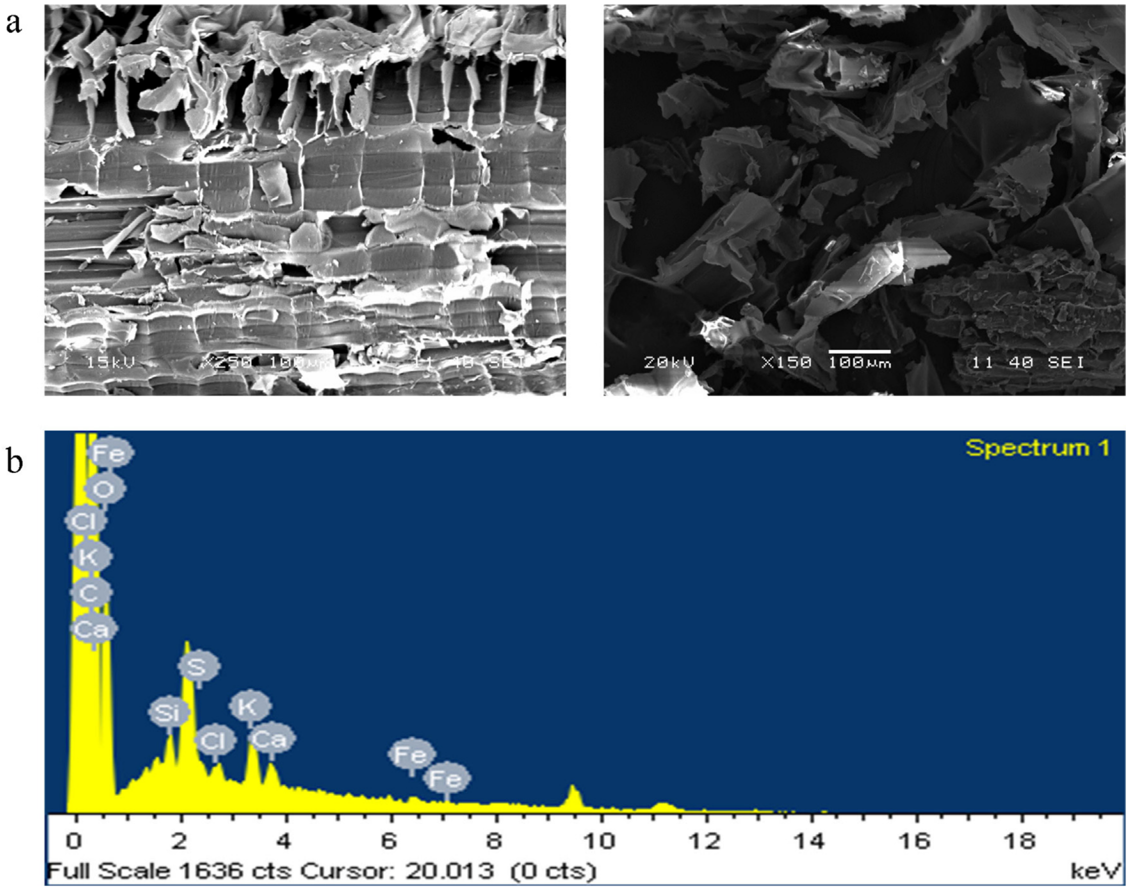

Fig. 5. (a) Scanning electron microscopic image of sugarcane bagasse biochar at different magnifications; (b). Energy dispersive X-ray analysis of sugarcane bagasse biochar.

4. Conclusion

Preliminary screening based optimization model with the analysis of the half normal plot and the Pareto chart showed the MAP to be mostly influenced by feedstock amount, time, feedstock size and microwave power. The half fractional factorial design was found to be significant with a R^2 of 0.9360, and having a relatively lower distribution of experimental errors. The model detected no interaction between the factors selected for the study at their respective range taken under consideration. A comprehensive optimization of the significantly influential variables through central composite rotatable design is further expected to improve the process efficacy and economics.

CRediT authorship contribution statement

Mari Selvam S.: Conceptualization, Experimentation, Investigation, Writing – original draft, Final approval of the article. **Balasubramanian Paramasivan:** Conceptualization, Supervision, Writing – review & editing, Final approval of the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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