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Pyrolysis of Mango (*Mangifera Indica*) Shells for Medium-Grade Fuels and Chemicals Production

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***Abstract*: This study uses a fixed-bed reactor to investigate the influence of temperature and time on bio-fuel yields from the pyrolysis of mango (Mangiferaindica) shells. Proximate and ultimate analyses revealed favorable characteristics for biofuel production, including 47.63% volatile matter, 32.44% fixed carbon, 47.19% carbon, and a higher heating value of 20.74 MJ/kg. To optimize yields, the experiment was designed using Design Expert 12.0.1.0 version software, with varied pyrolysis temperatures (300–500°C) and residence times (10–30 minutes). Analysis of variance (ANOVA) and statistical modeling that determined the significant effects of these parameters was established, achieving a maximum bio-oil yield of 42.56 wt% at 450°C for 30 minutes. Mango shells demonstrated superior performance with cellulose, hemicellulose, and lignin contents of 21.70%, 28.70%, and 25.50% compared to existing studies. The findings highlight mango shells' potential as a sustainable feedstock for medium-grade bio-fuel production, offering an effective solution for waste utilization and advancing clean energy technologies.**

***Keywords*: pyrolytic conversion, mango shells, biofuel, bioenergy, environmental sustainability, waste management.**

1. Introduction

A reliable energy supply is essential for smooth industrial operations, yet the growing fuel consumption has outpaced supply, leading to a global energy crisis. This crisis has renewed interest in developing renewable energy alternatives to address the increasing energy demands of the developing world (Bhan*et al*., 2020). Consequently, there has been a global persuasion to develop technologies that utilize energy-rich and readily available resources such as agricultural and bio-process residues to meet present energy needs while safeguarding the energy needs of future generations. Among these efforts, pyrolysis of organic materials, such as biomass, has emerged as a promising solution for sustainable and environmentally friendly fuel production. This process involves heating biomass at elevated temperatures without oxygen to produce bio-fuels, including bio-oil, bio-char, and bio-gas and has gathered significant attention as a pathway to renewable energy (Soria *et al*., 2019).

Mango shells, a significant crop residue, hold the potential for thermochemical processing to produce grade fuel. Predominantly cultivated in tropical regions, with India leading global production, mangoes are also widely grown in Pakistan, Thailand, China, Mexico, the Philippines, Indonesia, Brazil, and Africa, including Nigeria. Mango processing industries generate solid waste, including mango seeds, which are often discarded, contributing to environmental pollution and health risks. In Nigeria and similar regions, these discarded mango shells represent an underutilized renewable fuel and chemical production resource. Thermal conversion through fast pyrolysis, without oxygen, can transform mango shells into bio-oil, serving as a feedstock for clean-burning fuels (Okekunle*et a*l., 2018).

The mango seed consists of an outer fibrous layer known as the shell, which protects the inner kernel containing the embryo and nutrient reserves (Roy *et al*., 2018). The shell is rich in cellulose, hemicellulose, and lignin, while the kernel primarily contains cellulose and fatty acids (Lazzari*et al*., 2016). Depending on the fruit variety, Mango seeds account for 30-45% of the total fruit weight, making them a substantial component of mango waste. This waste comprises two primary elements: the shell and the kernel. Pyrolysis of the mango shells presents a valuable opportunity to transform this abundant agricultural residue into medium-grade fuels, offering the dual benefits of reducing harmful emissions and minimizing environmental pollution. This process also addresses critical issues such as feedstock wastage and greenhouse gas emissions by converting waste into bio-oil, bio-char, and biogas.

Extensive research has been conducted on the pyrolysis of various feedstocks, focusing on optimizing the yields of biofuels and other value-added products. By investigating the potential of mango shells as a feedstock, this study contributes to sustainable waste management and supports the development of renewable energy technologies. Hence, the study reported in this paper aligns with global efforts to address pressing energy

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needs and environmental concerns, paving the way for innovative solutions to enhance energy security while mitigating ecological impacts. The remaining parts of this manuscript are organized as follows: Section 2 details the materials and methods used in the study; Section 3 presents the results along with an in-depth discussion; and Section 4 provides the study's conclusions.

2. Materials and Method

A. Feedstock Processing and Characterization

Mango shells (Mangiferaindica) were locally sourced from the Ministry of Agricultural and Natural Resources Agric Farm Settlement in Ogbomoso South Local Government, Oyo State, Nigeria. The shells were sun-dried to reduce moisture content, weighed, and sealed in airtight bags to prevent reabsorption of moisture, then stored at room temperature before pyrolysis experiments. Proximate analysis was conducted to determine the shell's moisture content, volatile matter, ash content, and fixed carbon content. Moisture content, volatile matter, and ash content were evaluated following ASTM standards (Method D, 2013, and Practice D 346). Fixed carbon content was calculated using the formula:

$$\%FC = 100 - (MC + AC + VC) \quad (1)$$

The elemental composition of mango shells was analyzed using titration and gravimetric methods. Sulfur content was measured with a spectrometer, while oxygen content was calculated by summing the percentages of total carbon, nitrogen, and sulfur and subtracting the total from 100:

$$\%oxygen = 100 - (\%\, of\ C + N + S) \quad (2)$$

B. Experimental Setup and Procedure

Pyrolysis of mango shells was performed using a fixed-bed pyrolysis system comprising a retort, condensate receiver, and gas collection unit, all fabricated from mild steel, as shown in Figure 1. The mango shells, shown in Figure 2, were pyrolyzed in the oxygen-free fixed-bed reactor. For each run, 100 g of mango shells were loaded into the retort, following parameters set by Design Expert Version 12.0.0. The system was sealed with bolts, nuts, and a gasket to prevent gas leakage. The retort was then placed in a clay-brick-lined electric furnace, and pyrolysis was carried out by varying the temperature from 300 to 500 °C in 50 °C increments, with residence times ranging from 10 to 30 minutes in 5-minute intervals.

The retort was connected to the condensate receiver via an insulated galvanized pipe, and the receiver's valve was initially closed to condense a substantial portion of gas into a liquid. Once condensation was achieved, the valve was opened to release uncondensed gases into the gas collection unit. After the designated holding time, the pyrolysis process was terminated, and the biochar was removed from the retort, allowed to cool, and weighed using an Ohaus top-loading balance. Biochar, bio-oil, and bio-gas yields were calculated as percentages of the initial weight of the mango shells using equations (3), (4), and (5).

$$\%Bio-char\ yield = \frac{Mass\ of\ the\ char\ obtained}{Mass\ of\ the\ raw\ samples} \times 100 \quad (3)$$

$$\%Bio-oil\ yield = \frac{Mass\ of\ the\ liquid\ obtained}{Mass\ of\ the\ raw\ samples} \times 100 \quad (4)$$

$$\%Bio-gas\ yield = 100 - (\%Bio-char\ yield + \%Bio-oil\ yield) \quad (5)$$

As outlined in the experimental design, the procedure was repeated for all samples across varying pyrolysis temperatures and residence times. The temperature and holding time that yielded the highest bio-oil production were identified and recorded for further analysis and evaluation.

Fig. 1. Pyrolysis equipment setup

Fig. 2. Mango shells

C. Bio-oil Characterization and Ultimate Yield Analysis

The elemental composition of the bio-oil was determined using a CHONS Elemental Analyzer, with sulfur content measured via a spectrophotometer. Oxygen content was calculated by summing the percentages of carbon, sulfur, nitrogen, and hydrogen, then subtracting from 100, as described in Equation 2. The study also evaluated the pyrolysis yield performance using the Signal-to-Noise Ratio (SNR), a statistical measure that compares the desired signal level to background noise. A high SNR is desirable for optimal pyrolysis product efficiency, and it was calculated using Equation 6 (Başar*et al*., 2022).

$$SNR = -10 \log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \times 100 \quad (6)$$

The yield percentage (y_i) of each pyrolysis product was calculated using Equations (3), (4), and (5), where *n* represents the total number of experimental runs.

3. Results and Discussion

A. Physicochemical Composition of Raw Mango Shells

The proximate analysis of mango shells is summarized in Table 1. The moisture content was 14.51%, higher than the 9.14% reported for peanut shells (Ibrahim *et al*., 2023). Moisture content in biomass feedstock influences the heat required to raise the material to pyrolysis temperature and affects the overall temperature dynamics due to exothermic evaporation (Adeleke *et al*., 2019). The ash content of mango shells was 5.41%, lower than the 7.10% reported for cashew nutshells (Shrirame*et al*., 2021). Low ash content reduces slagging and fouling effects and is associated with higher heating values. Additionally, biomass with low ash content maximizes bio-oil yield, as certain elements and alkali metals in ash catalyze thermal decomposition (Boateng *et al*., 2006).

The volatile matter content of mango shells was 47.63%, higher than the 41.00% reported for palm kernel shells (Nizamuddin *et al*., 2015). High volatile content enhances ignition properties and facilitates pyrolysis by contributing to higher combustible volatile yields (Shariff *et al*., 2016). The fixed carbon content was 32.44%, slightly exceeding the 31.33% reported for palm kernel shells (Nizamuddin *et al*., 2015). Fixed carbon is an intermediate product between carbon residue and ash, and higher levels indicate a richer carbon source, making mango shells a promising feedstock for pyrolysis (Adeleke *et al*., 2019, Sangotayo *et al.,* 2017).

Table 1
Result of physical and chemical composition of mango shells

Materials	Properties	Unit	This study	Other Author
Mango shells	Moisture content	%	14.51	9.14[1]
	Volatile content	%	47.63	7.10[3]
	Ash content	%	5.41	41.00[4]
	Fixed Carbon content	%	32.44	31.33[4]

B. Results of the Ultimate Composition of Mango Shells

The ultimate analysis of mango shells, presented in Table 2, revealed elemental compositions of 47.19% carbon, 19.23% hydrogen, 10.54% nitrogen, 0.14% sulfur, and 22.90% oxygen. The high carbon content indicates good potential for fuel gas production, as it enhances the formation of combustible constituents during combustion. The carbon content was higher than previously reported for mango stone shells by Ola *et al*. (2014), while the oxygen content was comparatively lower, suggesting moderate combustibility. Hydrogen content, critical for generating water gas as a fuel, was significantly higher than that of cashew nutshells by Shrirame *et al*. (2021), indicating enhanced fuel efficiency. The nitrogen content was also higher than other mango-derived biomass, contributing to more significant producer gas potential. The sulfur content was minimal, reducing the risk of harmful sulfur dioxide emissions and promoting environmental sustainability.

The cellulose content of mango shells was 21.70%, with hemicellulose of 28.70%, comparable to other agricultural residues like mango seed shells and corn cobs. The relatively high concentration of cellulose and hemicellulose suggests the potential for high pyrolytic oil yields during pyrolysis. Lignin content was 25.50%, slightly lower than mango seed shells but higher than corn cobs. Lignin primarily contributes to char formation and is a source of phenolic compounds that degrade into tar. These properties enhance the feedstock's value for biochar production. The higher heating value (HHV) of mango shells was determined to be 20.74 MJ/kg, surpassing the HHV of corn cobs (16.46 MJ/kg) and palm kernel shells (18.10 MJ/kg). This indicates a high energy potential for mango shells as a biomass feedstock. The results highlight mango shells as a promising resource for pyrolysis, with significant potential for bio-fuel and bio-char production.

Table 2
Ultimate composition and characteristics of mango shells

Material	Properties	Unit	This study	Other Authors
Mango shell	Carbon content	%	47.19	44.6[1]
	Oxygen content	%	22.90	41.77[3], 52.75[4]
	Hydrogen content	%	19.23	5.96[5]
	Nitrogen content	%	10.54	0.53[1]
	Sulfur content	%	0.14	0.54[3], 0.41[1]
Lignocellulose	Cellulose	%	21.70	39.56[9]
	Hemicellulose	%	28.70	39.4[8]
	Lignin	%	25.50	26.94[9]
Higher Heating Value	Higher Heating Value	MJ/kG	20.74	16.46[8]

C. Statistical Analysis Models

1) Mango Shells

The biochar yield from mango shells was analyzed and predicted using Design Expert (12.0.1.0) software, which developed statistical models to evaluate pyrolysis outcomes. The significance and reliability of these models were validated through the F-test analysis of variance (ANOVA), as detailed in Equations (7), (8), and (9).

$$B_C = 31.19 + 15.85A(1) + 5.31A(2) - 0.9476A(3) - 7.56A(4) - 0.0236B(1) + 0.4044B(2) - 0.2216B(3) - 0.1256B \quad (7)$$

$$B_O = 33.23 - 9.56A(1) - 2.76A(2) + 01.18A(3) + 7.00A(4) - 0.6428B(1) + 0.1412B(2) + 0.5792B(3) + 0.2932B(4) \quad (8)$$

Table 3
Analysis of variance (ANOVA) for the product yield (bio-char, bio-oil, and bio-gas) from mango shells

Response	Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value
Bio-char (%)	Model	2489.70	8	311.21	121.57	<0.0001
	A	2488.55	4	622.14	243.02	<0.0001
	B	1.15	4	0.2876	0.1124	0.1124
	Residual	40.96	16	2.56		
	Cor Total	2530.66	24			
Bio-oil (%)	Model	837.12	8	104.64	90.10	<0.0001
	A	832.16	4	208.04	179.13	<0.0001
	B	4.96	4	1.24	1.07	0.4046
	Residual	18.58	16	1.16		
	Cor Total	855.70	24			
Bio-gas (%)	Model	600.45	8	75.06	17.41	<0.0001
	A	594.51	4	148.63	34.47	<0.0001
	B	5.94	4	1.48	0.3444	0.8440
	Residual	69.00	16	4.31		
	Cor Total	669.45	24			

Table 4
Model comparison statistics of product yield (bio-char, bio-oil, and bio-gas) from mango shells

Bio-Char Yield			
Standard Deviation	1.60	R^2	0.9838
Mean	31.19	Adjusted R^2	0.9757
C.V. %	5.13	Predicted R^2	0.9605
		Adeq Precision	30.3459
Bio-Oil Yield			
Standard Deviation	1.08	R^2	0.9783
Mean	33.23	Adjusted R^2	0.9674
C.V. %	3.24	Predicted R^2	0.9470
		Adeq Precision	27.4909
Bio-Gas Yield			
Standard Deviation	2.08	R^2	0.8969
Mean	35.61	Adjusted R^2	0.8454
C.V. %	5.83	Predicted R^2	0.7484
		Adeq Precision	12.8528

$$B_G = 35.61 - 6.33A(1) - 2.53A(2) - 0.2716A(3) + 0.6384A(4) + 0.6284B(1) - 0.5736B(2) - 0.3856B(3) - 0.1956B(4) \quad (9)$$

Where,
B_c = Bio-char yield from mango shells (wt%),
B_O= Bio-oil yield from mango shells (wt%),
B_G= Bio-gas yield from pyrolysis of mango shells (wt%),
A = Temperature (degree), B = Time (min).

The quadratic models for biochar, bio-oil, and bio-gas yields, as indicated by probability values (prob > F) less than 0.05 in Table 3, were statistically significant at a 95% confidence level. The F-statistic values further validated the significance of these models. Key model terms, including A, B, A2, B2, and AB, significantly influenced the yields of biochar, bio-oil, and biogas. These findings demonstrate the strong predictive capability of the models.

Statistical parameters from the ANOVA, shown in Table 4, confirmed the accuracy of the developed models. The biochar yields model exhibited a high determination coefficient (R^2 = 0.9838) and a low coefficient of variation (C.V. = 5.31), indicating close alignment with the experimental data. Similarly, the bio-oil yields model had an R^2 of 0.9783 and a C.V. of 3.24, while the bio-gas yields model showed an R^2 of 0.8969 and a C.V. of 5.83. Model adequacy was further supported by adjusted R^2, predicted R^2, and adequate precision values, with Signal-to-Noise Ratios (SNR) of 30.3459, 27.4909, and 12.8528 for biochar, bio-oil, and bio-gas yields, respectively. These SNR values, exceeding the desirable threshold of 4, confirm the models' suitability for navigating the design space. Table 5 presents the design matrix for mango shells pyrolysis, using temperature and time as factors, with product yields (bio-char, bio-oil, and bio-gas) as the responses.

Table 5
Design matrix of mango shells using temperature and time as factors and the product yield (bio-char, bio-oil, bio-gas) as response

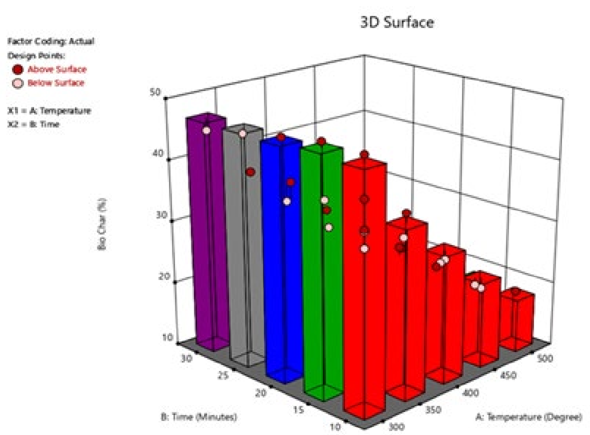
Run	A	B	B_c	B_o	B_g
1	450	15	23.75	38.63	37.62
2	400	25	30.41	34.78	34.81
3	500	10	19.04	36.94	44.02
4	500	25	19.86	37.27	42.87
5	500	30	17.45	36.47	46.08
6	400	15	30.02	35.53	34.45
7	300	30	45.03	22.04	32.93
8	350	25	33.84	30.28	35.88
9	300	20	47.35	23.76	28.89
10	350	15	38.07	30.95	30.98
11	400	10	28.72	33.89	37.34
12	300	10	48.24	23.67	28.09
13	450	20	24.05	40.41	35.54
14	500	15	17.74	37.17	45.09
15	350	20	35.97	31.48	32.55
16	450	10	21.91	38.57	39.52
17	400	30	33.21	33.44	33.36
18	350	10	37.94	29.85	32.21
19	300	25	46.21	24.32	29.47
20	500	20	18.62	38.97	42.41
21	450	25	25.02	40.95	34.03
22	300	15	48.41	24.56	27.03
23	450	30	23.42	42.56	34.52
24	400	20	28.87	34.41	36.72
25	350	30	36.69	29.77	33.78

D. *Effect of Pyrolysis Parameters on the Product Yields*

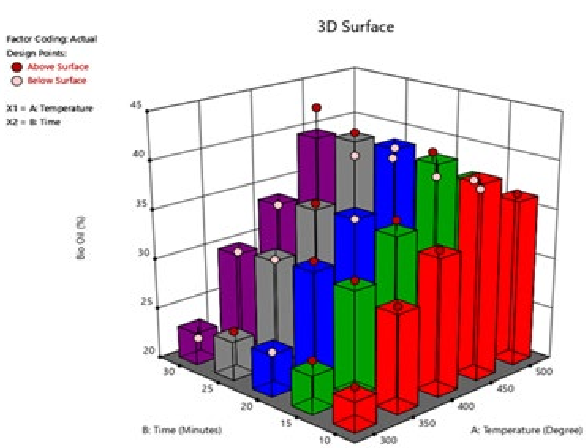
1) *Mango Shells*

Figure 3 illustrates the three-dimensional response surfaces and contour plots of mango shells pyrolysis product yields, showing the combined effects of temperature and residence time on biochar, bio-oil, and bio-gas production. The data reveals that biochar yield decreases with increasing Pyrolysis temperature; this observation is consistent with pyrolysis conventions. The maximum biochar yield of 48.24% was obtained at 300 °C with a residence time of 10 minutes, as shown in Figure 3(a). This aligns with the findings by Ola et al. (2014), which demonstrated that higher temperatures result in lower biochar yields due to more significant thermal decomposition.

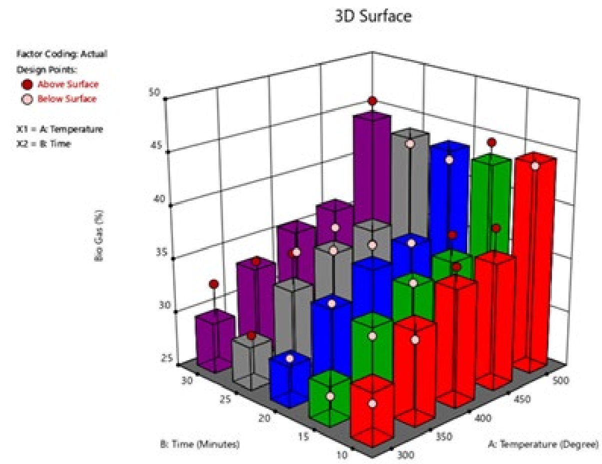
Bio-oil yield, as shown in Figure 3(b), increased with temperature up to 450 °C and then declined at 500 °C. The maximum bio-oil yield of 42.56% was achieved at 450 °C with a residence time of 30 minutes, as presented in Table 5. Meanwhile, bio-gas yield steadily increased with both temperature and residence time, reaching a peak of 46.08% at 500 °C and 30 minutes, as depicted in Figure 3(c). These trends confirm findings from Lazzari et al. (2016) and Rivas et al. (2020), which noted that higher temperatures favor bio-oil and bio-gas production while reducing bio-char yield.



(a)



(b)



(c)

Fig. 3. Response surface 3D plot showing the interaction and effects of temperature and time on yields from pyrolysis of mango shells; (a) bio-char, (b) bio-oil, (c) bio-gas

4. Conclusion

This study demonstrated the potential of mango shells as a sustainable feedstock for bio-fuel production through pyrolysis, with the effects of temperature and time on bio-fuel yield being thoroughly analyzed. The feedstock analysis revealed a high carbon and hydrogen content alongside low sulfur levels, essential attributes for efficient biofuel generation. Proximate analysis of mango shells indicated favorable values for moisture content (14.51%), volatile matter (47.63%), ash content (5.41%), and fixed carbon (32.44%), while ultimate analysis further supported their suitability with high carbon (47.19%) and hydrogen (19.23%) content and a substantial higher heating value of 20.74 MJ/kg. These characteristics position mango shells as a valuable resource for bio-fuel production, leveraging their inherent properties to minimize reliance on fossil fuels.

The optimum bio-oil yield of 42.57% was achieved at 450 °C and a pyrolysis time of 30 minutes, underscoring the potential of mango shells for efficient thermal conversion. These findings highlight the viability of employing mango shells, often treated as agricultural waste, in addressing energy and environmental challenges. By integrating appropriate conversion technologies. Mango shells can be transformed into medium-grade bio-fuel products suitable for domestic and industrial use. This approach mitigates waste and environmental concerns and supports the transition toward cleaner and more sustainable energy alternatives.

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