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Yield and Energy Modeling for Biochar and Bio-Oil Using Pyrolysis Temperature and Biomass Constituents

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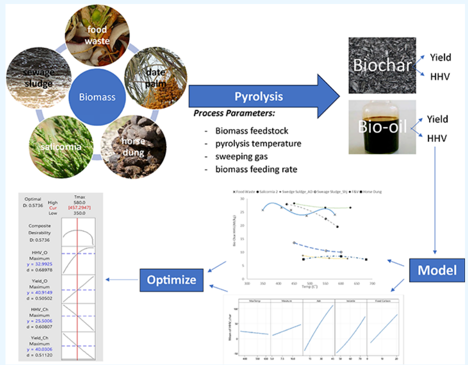
ABSTRACT: Pyrolysis offers a sustainable and efficient approach to resource utilization and waste management, transforming organic materials into valuable products. The quality and distribution of the pyrolysis products highly depend on the constituents' properties and set process parameters. This research aims to investigate and model this dependency, offering decision-makers a tool to guide them when designing the process for a particular application. Experimental data on the pyrolysis of various types of feedstocks processed at a wide range of pyrolysis temperatures (350−650 °C) are utilized to develop the prediction models. Four variables are modeled: the yield and energy content for both the biochar and bio-oil as a function of the pyrolysis temperature and feedstock characteristics. The models developed had very good prediction power with the coefficient of determination above 90%. The results highlight the advantages of food waste (leftover) as a suitable feedstock to produce biochar at the pyrolysis temperature within the range of 450−550 °C. Furthermore, the biofuels produced from food waste are found to be of good quality, with the bio-oil exceptionally high in energy content (HHV = 34.6 MJ/kg), which is almost 80% of that of diesel. The developed models provide a tool for predicting the biofuel yield and quality based on the feedstock selection and process temperature.



1. INTRODUCTION

According to the International Energy Agency (IEA), total energy consumption will rise at an annual rate of 1.5%, while fossil fuels are still the main energy source.[1] The development of green fuel as a viable source of energy has been at the forefront of research. Due to its environmental advantages, biochar and bio-oil generated from biomass have gained much attention in the last few decades. Pyrolysis is a thermochemical process used to convert biomass into biofuel, biochar, and gas by heating dried biomass at elevated temperatures (300−650 °C) in the absence of oxygen. The conversion process results in biochar, a volatile matter that can be partially condensed to the liquid phase (bio-oil), and noncondensable gases such as carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4).[2] Mahari et al.[3] provided an extensive review of various pyrolysis techniques for valorizing municipal wastes. One of the main limitations of pyrolysis is the release of harmful gases like CO and CH_4 that should be properly managed.[4] This is in addition to batch-to-batch biochar content variability.[5]

The final chemical and physical characteristics of biochar significantly influence its optimal application. Thus, characterizing the end product of pyrolysis becomes essential. For instance, the suitability of biochar for energy applications depends on its carbon and ash content, while its effectiveness in agricultural and wastewater uses requires possessing a high surface area and a large adsorption capacity,[6−9] as well as an appropriate alkali and alkaline earth metallic content.[10] Domene et al.[11] demonstrated the significant impact of temperature and biomass feedstock on soil respiration and collembolan reproduction properties. Controlling the pyrolysis operating conditions such as the residence time, temperature, pressure, catalyst, and heating rate allows for the production of a preferred phase of product (solid, liquid, or gas) and influences both the biochar yield and quality.[12] Increasing the residence time at low temperatures results in a higher yield of solids, while increasing the temperature negatively affects the biochar yield. Low heating rate ensures that thermal cracking of biomass would not occur.

Pyrolysis can be performed in various ways including slow, fast, flash, vacuum, intermediate, and hydro pyrolysis. Among these, slow and fast pyrolysis are the most common forms of biomass conversion.[13] Slow pyrolysis generates the largest quantity of high-quality biochar from biomass compared with other processes. Onay and Kockar[14] recommended employing slow pyrolysis with low heating rates (10−30 °C/min) to maximize the biosolid or char yield. In slow pyrolysis, vapors

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Table 1. Summary of Surveyed Biomass Pyrolysis Optimization Research

		variables and (optimal settings)							response		
ref.	biomass	temp (°C)	heating rate (C/min)	N flow rate (L/min)	holding time (min)	particle size (μm)	feeding rate (g/h)	process	bio-oil yield (%)	char yield	HHV (MJ/kg)
19	acid-treated rice husk	300−600 (427)	10	0.87−15 (0.8)	20−60 (45)	<300		slow	35.5	49.2	14.6
37	corn, eggshell, and HDPE	50−900 (700)	0.2−3.35 (3.35)		20	710		Co			
38	spent coffee waste	400−800 (500)	3−15 (10)	0.1−0.3 (0.15)	10−90 (30)			slow		30.0	22.6
21	banana pseudostem	470−540 (500)			0.9−1.2 (1.02)	400−600	300	fast	39.4		5.35
36	eucalyptus and LDEP	300−600 (524)			90−150 (118)				17.3		
39		300−600 (507)	15−40 (38)	0.04−0.08 (0.045)	30−90 (60)				34		
40	tomato peel waste	450- 650 (600)	5−25					slow	40		22.5
41	palm shell	400 −600 (500)				300−600 (600	100	fast	60		
42	Acacia nilotica	220−280 (252)	5−15 (5)	0.045	20−60 (60)	7000−1250					
18	Sal wood sawdust	500	80						46		36.1
5	date palm	400	5		60			slow			
43	Salicornia	600−800 (700)	15	0.1	20				18.1−22.7	36.7−45.7	10.2−17.6
44	sewage sludge	300−700 (300)							72−52		

are confined and extensively react with the solid phase, resulting in a high char yield in the end.[15] While fast pyrolysis can also be used in biochar production, it is mainly employed for bio-oil production, yielding a higher quantity of bio-oil and biochar as coproducts.[13] In a study by Kambo and Dutta,[6] a comparison was drawn between slow pyrolysis and the hydrothermal carbonization (HTC) of biomass, i.e., the biomass is treated with hot water instead of drying. The authors suggested that HTC char exhibits reduced alkali and alkaline earth content, heavy metal content, and a high heating value (HHV) compared to biochar.

Numerous researchers have conducted studies to optimize the pyrolysis process. Morales et al.[16] utilized published data from various samples to explore the correlation between properties and develop predictive models for biochar properties. The authors concluded that an arbitrary selection of biomass or pyrolysis temperature is unlikely to yield the desired biochar properties. Similarly, Luo et al.[17] investigated the combined effects of heating temperature, time, rate, and atmosphere (airflow, air-limited, and N_2) on the physicochemical properties of biochar, utilizing pine sawdust, maize straw, and sugarcane bagasse as feedstock. Their findings suggested that production temperature and atmosphere are the predominant factors influencing biochar properties, while heating time and rate had minimal effects on the functional group compositions of biochar under N_2 atmosphere. Additionally, Mishra and Mohanty[18] explored the impact of catalytic pyrolysis enhancements, such as calcium oxide (CaO), copper oxide (CuO), and aluminum oxide (Al_2O_3), on boosting the yield and improving the characteristics of both biochar and bio-oil.

Various materials used as feedstock worldwide to produce biochar include food waste (FW),[19−23] sewage sludge (SS),[24−28] algae,[29,30] and animal waste.[31] However, depending on the application, the yield and quality of the pyrolysis products should be tailored through the manipulation of process setting and selection of the biomass material.[32,33,19,11] The efficiency of biochar production from biomass significantly relies on factors such as pyrolysis temperature, heating rate, feedstock type and composition, particle size, and reactor conditions.[34,35] Table 1 provides a summary of recent work related to the optimization of the pyrolysis process. Most of the research focused on optimizing temperature and heating rate. Das and Goud[19] employed the response surface method (RSM) to maximize bio-oil yield by investigating the impact of pyrolysis temperature, nitrogen flow rate, and holding time on the yield. Results suggested that the optimum conditions for yield maximization are 427 °C, 800 mL/min, and 45 min, respectively. These settings resulted in a maximum bio-oil yield of 35.5 wt % with a biomass conversion of 50.8 wt %. To ensure a sufficient supply of feedstock, some researchers mix biomass with other recyclable materials.[36,37] Liew et al.[37] evaluated the synergistic effects and kinetic parameters for binary mixtures of corn cob and high-density polyethylene (HDPE) in copyrolysis in the presence of renewable chicken and duck eggshell catalyst using a thermogravimetric analysis (TGA) approach at various heating rates and a temperature range of 323−1173 K. Vanapalli et al.[36] employed a sustainable waste management approach by combining single-use low-density polyethylene (LDPE) with eucalyptus biomass (EuBm) to generate viable byproducts. The resulting chars exhibited a high volatile matter content (68%), and their pores were filled with partially pyrolyzed products.

The summarized literature in Table 1 indicates that modifying feedstocks and adjusting the pyrolysis temperature significantly influence biochar yield and its chemical properties. However, there is a notable gap in research focusing on investigating how the biomass constituents specifically impact the yield and energy value of char and bio-oil. In the aforementioned studies, a limited number of feedstock

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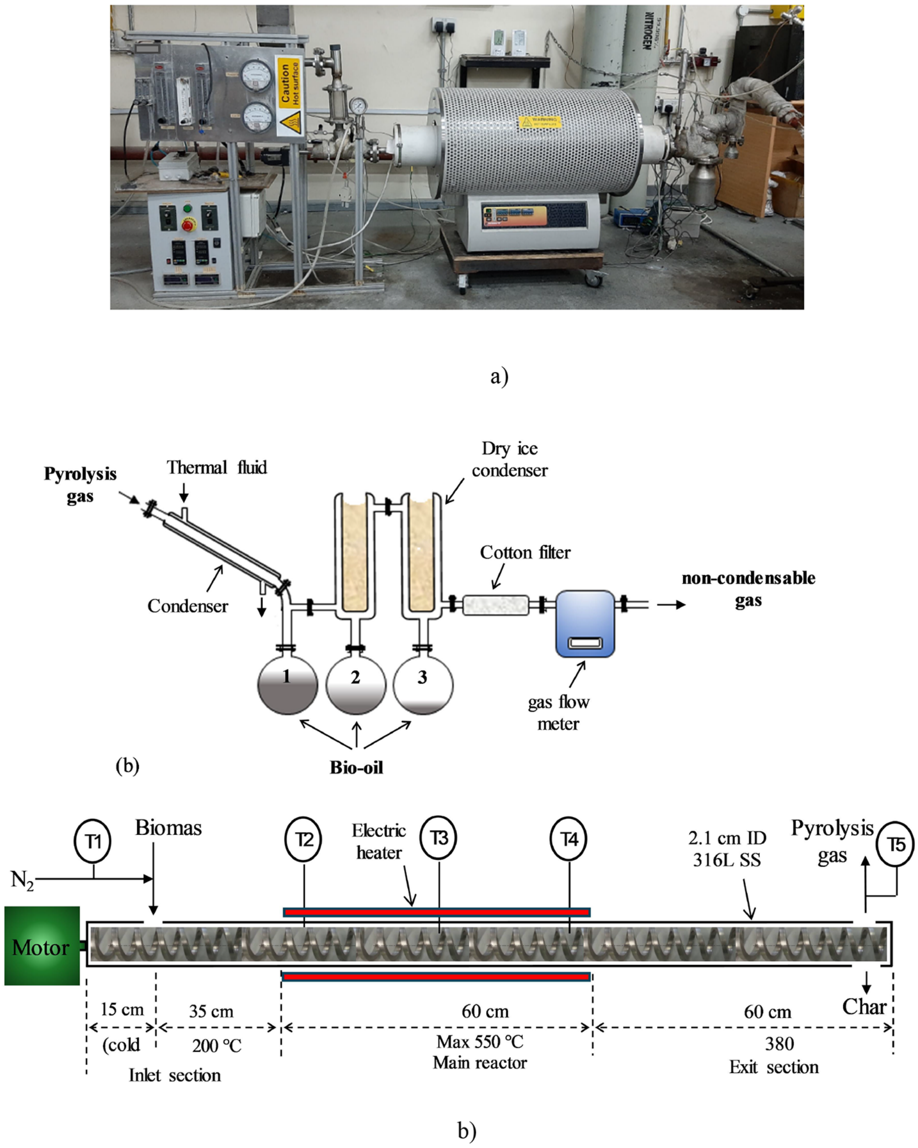

Figure 1. (a) Photo of the complete setup [Author]. (b) Schematic of the reactor and compensation setup.[47]

materials were examined, with the primary focus on process parameters rather than establishing a correlation between the individual constituents of the biomass and their respective effects on the biochar and bio-oil produced. This research aims to address this gap by utilizing experimental data from various feedstocks to construct models predicting the energy content of biochar and bio-oil, as influenced by feedstock constituents and pyrolysis temperature. The development of such models will not only reduce the necessity for conducting physical pyrolysis experiments with new feedstocks but also enable the anticipation of the effects of mixing the existing ones. This will provide valuable insights into optimizing biochar and bio-oil production processes.

The objective of this research is to investigate and model the influence of biomass constituents and process parameters, specifically the pyrolysis temperature, on biochar and oil production quantity and heating content. To incorporate a wider range of properties in the analysis, five different organic waste feedstocks are investigated. Additionally, this study proposes an optimization method that determines the optimal temperature settings to achieve specific desired biochar or bio-oil properties. This research will assist decision-makers in providing the details of biochar production, including critical assessment and selection of a suitable biomass source from the available organic waste. The research makes a threefold contribution. First, it presents a comparison of various feedstocks under similar conditions; very few researchers conducted such an analysis based on the surveyed literature. Second, some nonconventional feedstocks that have not been thoroughly examined before such as Salicornia and date palm[45,45] are investigated. Lastly, very few studies attempted modeling the final product properties resulting from different feedstocks based on their constituents and pyrolysis temperature.

2. MATERIALS AND METHODS

In this research, five different organic waste feedstocks are analyzed and investigated to build the energy content prediction models. The feedstocks are food waste (FW), Salicornia, sewage sludge (SS), fruits and vegetables (F&V), and horse dung (HD). Details on the methodology followed to

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prepare and characterize the samples are provided in the following subsections.

2.1. Sample Collection. Food waste samples were collected from four different restaurants and a hospital. Two of these restaurants are part of hotels, one is in a university, while the last one is a factory restaurant. The samples were dried using a dehydrated machine at 75 °C for 8 h. Similarly, the F&V were collected from a local fruit and vegetable market in Sharjah, United Arab Emirates (UAE) and dried outside, with the average external temperature of 30 °C. The date palm and Salicornia were collected from trees located in Sharjah and Dubai, respectively, and dried outside in air and at an average external temperature of 30 °C. The sewage sludge samples were collected from two different treatment plants: one is in Sharjah and the other one in Abu Dhabi. Finally, the horse dung was collected from a local farm in Sharjah, UAE.

2.2. Biomass Preparation. Prior to pyrolysis, the biomass moisture content and particle size are analyzed to ensure a safe and efficient operation of the reactor. Wet biomass of moisture content >10% mass was subjected to drying using open air. Moreover, biomasses of particle size >3 mm were subjected to size reduction using a shredding and grinding machine. Following drying and grounding, all biomasses were sieved to achieve a particle size distribution within the range of 0.3−3 mm.

2.3. Pyrolysis Process. The biochar production was carried out in an auger reactor; see Figure 1. The reactor was designed for a maximum processing capacity of 500 g/h and a maximum operating temperature of 750 °C, while the processing occurred at 500 °C. The experimental unit consisted of two main sections: (i) a tubular reactor with a screw (auger reactor) heated by an electric furnace and connected to a continuous biomass feeder and a biochar collection pot and (ii) a pyrolysis gas condensation system for collection of the bio-oil and fuel gas. The experimental setup comprised a hopper, biomass feeding system, reactor screw, heating furnace, cyclones, biochar collection pot, gas discharge, cooling system, and a control panel. The gas discharge pipe was equipped with a sampling point to allow the collection of gas samples at fixed intervals for composition analysis. This biomass pyrolysis system is fully automated and equipped with computer data logging. The complete system is automated and connected to a computer for data logging and to a gas chromatograph (Mico-GC) for online gas analysis. For more details on the pyrolysis system please refer to.[46] Nitrogen was used as the main sweeping gas.

The reactor was operated with five different feedstocks. The processing parameters are summarized in Table 2. Nitrogen is used as the main sweeping gas. Three thermocouples upstream, middle, and downstream of the reactor were used to measure the pyrolysis temperature. Both the average and maximum temperatures were recorded.[1]

Table 2. Pyrolysis Experimentation Operating Parameters

variables	range of operating conditions
biomass feedstock	FWSSSWP, SSF&V, HD
biomass particle size	0.5−3 mm max
reactor temperature	350−650 °C
operation mode	fast−intermediate
sweeping gas	nitrogen
sweeping gas flow rate	0.5−0.7 L/min
biomass feeding rate	200−500 g/h
average gas residence time (s)	2.0
average solid residence time (s)	50.0

2.4. Yield Characterization. The pyrolysis percentage yield of the liquid and biochar was calculated using eq 1:

$$\%\text{Yield} = \frac{\text{Mass of product collected}}{\text{Total mass of biomass reacted}} \tag{1}$$

The percentage yield of noncondensable gas was calculated by the difference from 100%. The proximate analysis of the feedstock was determined by using a muffle furnace. The volatile content was determined following the standard method CEN/TS 15148:2005, with the furnace operated with nitrogen to allow for the inert degradation of the samples at up to 900 °C. The fixed carbon content was determined by the difference from 100%. The ultimate analysis was carried out using an elemental analyzer (EuroVector Euro EA 3000 EA) to determine the carbon, hydrogen, nitrogen, sulfur, and oxygen contents in the sample. The oxygen content was not measured but determined by the difference ($O_2\% = 100\% - \text{ash}\% - C\% - H_2\% - N_2\%$). The high heating value (HHV) was determined by using an automated oxygen bomb calorimeter. The proximity analysis was performed by using a tubular reactor heated in an inert environment to determine the volatile content. The ash and moisture contents were obtained in a furnace, while the fixed carbon was obtained by the difference (FC% = 100% − volatile% − moisture% − ash%).

2.5. Modeling and Optimization. Each feedstock was tested at different temperature settings, and the properties of biochar and bio-oil are modeled using polynomial regression to describe the output property as a function of maximum pyrolysis temperature and biomass significant constituents. Since there are several properties that need to be optimized simultaneously, a multiresponse optimization is conducted using the desirability technique.[48−50] The desirability function approach is one of the most frequently used multiresponse optimization techniques in practice. The method makes use of an objective function D called the composite desirability function and transforms each individual response into a scale-free value (d_i) called individual desirability. Both the composite and individual desirability range from zero (least desirable) to one (most desirable), indicating the achievement of the desired objective. Mathematically, composite desirability D can be defined as shown in eq 2:

$$D = (d_1 \times d_2 \times d_3 \times \cdots \times d_n)^{1/n} = \left(\prod_{i=1}^{n} d_i\right)^{1/n} \tag{2}$$

In our case, the goal is to maximize individual desirability d_i since they represent yield and HHV. As a result, d_i is modeled as

$$d_i = \begin{cases} 0 & f(1) \le L_i \\ \left(\dfrac{f(1) - L_i}{H_i - i}\right)^{wt1} & L_i \le f(1) \le H_i \\ 1 & f(1) \ge H_i \end{cases} \tag{3}$$

where L_i and H_i are the lower- and upper-bound response, $f(1)$ is the mathematical model, and w_{ti} is a weight factor range from 0.1 to 10 and controls the shape of the desirability function. In this study, $w_{ti} = 1$, so individual desirability d_i will

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Table 3. Feedstock CHNOS and Proximity Analysis

	CHNOS							proximate analysis %			
feedstock	N	C	H	S	O2 ash free	O/C ash free	H/C	moisture	ash	volatile	fixed carbon
FW	3.73	48.02	7.06	0.89	33.14	0.52	1.76	6.20	7.92	74.11	11.76
DP	0.88	42.5	5.78	0.19	38.98	0.69	1.63	12.30	10.06	57.22	18.38
SS	4.88	49.23	7.60	0.00	23.34	0.36	1.85	6.95	14.95	70.00	8.10
SWP	0.86	33.36	5.41	0.00	40.13	0.90	1.95	9.78	20.24	64.69	5.30
AD-SEW	5.89	29.14	5.79	0.00	19.79	0.52	2.35	5.15	39.67	52.73	2.46
SHJ-SEW	7.13	29.72	5.92	0.00	26.28	0.62	2.31	6.41	31.38	58.70	3.51
F&V	1.10	52.10	8.43	0.00				7.65	9.35	62.50	20.50
HD	3.39	69.35	7.66	0.00				6.13	45.70	46.11	2.06

Table 4. Pyrolysis Temperature and Biochar and Bio-Oil Yield and HHV for Different Feedstocks

feedstock	average temp. (°C)	maximum temp. (°C)	char yield (%)	char HHV (MJ/kg)	bio-oil (%)	oil HHV (MJ/kg)	C&O−HV (MJ/kg)
FW	300	350	48.1	25.8	36.1	29.3	23.0
	350	410	44.2	26.7	44.7	31.7	26.0
	400	440	42.4	25.8	37.1	34.5	23.7
	450	490	36.1	23.6	40.1	31.5	21.2
	500	550	33.4	26.5	45.6	34.7	24.7
	500	580	31.6	24.0	44.4	34.0	22.7
DP	450	525	31.0	21.3	46.0	25.5	18.3
SS	350	431	39.8	26.7	26.1	24.1	10.6
	350	427	43.2	27.9	26.0	24.7	12.1
	400	468	33.2	16.2	31.0		
	450	521	36.7	22.6	29.1	26.1	8.31
	450	550	29.2	22.5	35.3	25.9	6.57
	500	588	25.4	19.5	33.0	24.8	4.95
SWP	500	550	32.9	16.6	4.23	29.3	6.70
AD-SEW	450	478	59.6	8.75	30.7	32.7	15.2
	550	563	51.3	7.77	35.5	32.8	15.6
	600	6203	50.2	7.67	34.3	33.0	15.2
SHJ-SEW	550	5623	47.1	10.6	43.6	27.7	16.9
F&V	450	4603	39.8	28.3	6.40	27.4	13.0
	550	5653	39.6	26.7	8.41	29.4	13.0
	600	6303	33.5	26.7	7.95	28.8	11.2
HD	450	4803	58.4	7.39	5.46	28.3	5.86
	550	6003	57.2	8.50	8.26	28.0	7.17
	650	6803	56.1	7.31	5.43	28.6	5.66

vary from 0 to 1 in a linear fashion for all responses. Considering all n responses, clearly one wishes to choose the settings for process parameters to maximize D. A value of D close to 1.0 implies that all responses are simultaneously in a desirable range simultaneously. The objective is to maximize char and oil yield and HHV.

3. RESULTS AND DISCUSSION

Various biomasses abundant in reasonable quantities in the United Arab Emirates (UAE) were tested, namely food waste (FW), mixture of date palm (DP), Salicornia seeds (SS), Salicornia plant (SWP), sewage sludge from two different cities (Abu Dhabi (AD-SS) and Sharjah (SHJ SEW)), fruits and vegetables (F&V), and horse dung (HD). All biomass samples were collected from various local sources within the UAE. Table 3 provides a summary of the biomass characterization using both CHNOS and proximate analysis:

The characteristics of the samples tested are summarized in Table 4. The biochar and bio-oil energy output heating value (C&O−HV) is estimated using eq 4:

$$\mathrm{C\,\&\,O - HV}_i = \mathrm{CharYield}_i.\ \mathrm{CharHHV}_i + \mathrm{OilYield}_i.\ \mathrm{OilHHV}_i \tag{4}$$

It is assumed that the energy output from biogas is utilized as the input energy for the pyrolysis process. As a result, biogas energy was not included in eq 4. Some of the experiments have been repeated for FW, SS, and SHJ-SEW three times and resulted in a reproducibility of 8, 5, 6, and 8% for char yield, char HHV, bio-oil yield, and bio-oil HHV, respectively. The results are deemed acceptable, given the nature of pyrolysis and variability of feedstocks.

Based on the proximate analysis, the ash content is low in FW, Salicornia seeds, and F&V, while food waste and Salicornia seed are significantly higher in volatiles. In pyrolysis, a feedstock of a high volatile content is highly desirable to increase the bio-oil yield through pyrolysis. The more volatiles, the more condensable are the components in the pyrolysis vapor into oil. This is evidenced when the bio-oil yield of FW and SS is compared with HD. The volatiles in the FW and SS are higher than in HD, which resulted in a higher bio-oil yield.

On the other hand, ash, which ends up in the biochar, contributes to cracking the pyrolysis gas and hence lowers the

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bio-oil yield. The ash has a catalytic effect on pyrolysis in terms of breaking the heavy bio-oil compounds into gases.[51] The more ash in the feedstock, the more gas at the expense of the oil. This is evidenced by comparing the bio-oil yield of F&V and SWP. Both feedstocks have similar volatiles, but F&V has almost half of the ash content of SWP and double the bio-oil yield.

Based on the surveyed literature and initial experimentation, a wide range of temperature is investigated for FW, SS, AD-SEW, F&V, and HD to capture the wider performance of outcome. In the case of SHJ-SEW, one temperature was investigated which is the one that resulted in the highest C&O HV for the AD-SEW case. Moreover, the repeatability of the tests is investigated once in the case of FW at 500 °C and twice in the case of SS at 350 and 450 °C and deemed acceptable.

The thermal profiles of the feedstocks investigated in this study are listed in Figure 2. The results suggest a significant variation in the thermal behavior of various biomasses. The date palm waste clearly shows a distinguishable and gradual mass loss during the drying stage due to its relatively high moisture content. This feedstock also has a volatile content within the intermediate range, as indicated by the limited mass loss. The horse dung has a very limited mass loss (∼30%), and this is consistent with the proximate analysis which shows this biomass to have the least volatile and highest ash. The biomasses with the highest mass loss are the Salicornia seed and food waste. The TGA profiles indicate that the food waste devolatilization ceases at around the temperature of 400−500 °C, while for Salicornia this occurs at a much higher temperature around 600 °C and a wider temperature range.

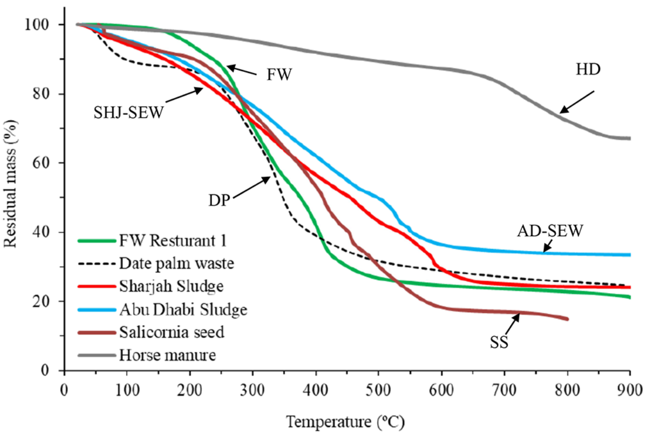

Figure 2. Residual mass profiles of biomasses investigated using TGA [Author].

Based on the results, sewage sludge pyrolysis resulted in the highest char yield, while FW provided the highest oil yield. In terms of HHV, F&V resulted in highest char HHV while FW provided highest oil HHV. As a result, the maximum total C&O energy output is gained from FW biomass.

To better quantify the relationship between constituents and the final product properties, correlation coefficients are estimated. Pearson coefficients are used to investigate the hypothesis that a linear relationship between the biomass constituent and yield or HHV exists within the limits of the experiment (sample size) and the desired confidence (p-value). $r = 1$ or -1 indicates a perfect positive and negative correlation, respectively, while r close to zero indicates no correlation. A p-value below the significance level ($\alpha = 0.1$) provides evidence for the correlation. Alternately, the Spearman correlation evaluates the monotonic including nonlinear relationship between two continuous or ordinal variables. In a monotonic relationship, the variables tend to change together but not necessarily at a linear rate. Table 5 provides a summary of correlation and p-values. Based on the results, there is strong evidence of positive linear correlation between biomass ash and char yield. Similarly, there is stronger evidence of negative nonlinear correlation between volatiles and yield. In terms of char HHV, there is strong evidence of linear correlation between both volatiles and fixed carbon and char HHV. There is also stronger evidence of negative nonlinear correlation between the ash content and char HHV.

Next, regression models were developed to predict the yield and HHV for both char and oil using temperature and biomass constituents as predictors. Eqs 5-8 present the prediction model along with the coefficient of determination R^2 which is an indicative of how good the model is in terms of explaining the variability of data.[52]

$$\begin{aligned}\text{CharYield} = {} & 184.2 - 0.0547\ \text{Temp} - 33.02\ \text{Moisture} \\ & - 1.927\ \text{Ash} + 2.07\ \text{Volatile} + 0.759 \\ & \text{Moisture}^2 - 0.01536\ \text{Vol}^2 + 0.0234\ \text{T.} \\ & \text{Moisture} - 0.002304\ \text{Temp. Volatile} \\ & + 0.294\ \text{Moisture. Ash}\ (R^2 \\ & = 93.8\%)\end{aligned} \tag{5}$$

$$\begin{aligned}\text{CharHHV} = {} & -882 + 0.813\ \text{Temp} + 30.3\ \text{Moisture} \\ & + 7.44\ \text{Ash} + 7.28\ \text{Volatile} + 5.34 \\ & \text{FixedCarbon} + 0.01146\ \text{Volatile}^2 - 0.045 \\ & \text{Temp. Moisture} - 0.00519\ \text{Temp. Ash} \\ & - 0.00679\ \text{Temp. Volatile}\ (R^2 \\ & = 97.6\%)\end{aligned} \tag{6}$$

Table 5. Biomass Constituents' and Biochar Properties' Correlation Summary

property	H/C	ash	volatiles	moisture	fixed carbon
char yield	0.1 (0.80)	**0.89 (0.003)**	−0.87 (0.005)	−0.55 (0.16)	−0.77 (0.026)
char HHV	−0.17 (0.54)	−0.93 (0.003)	**0.765 (0.045)**	0.23 (0.60)	**0.89 (0.007)**
oil yield	−0.12 (0.70)	−0.48 (0.022)	0.30 (0.82)	0.06 (0.35)	0.37 (0.45)
oil HHV	0.38 (0.40)	0.21 (0.60)	0.05 (0.60)	−0.544 (0.007)	−0.27 (0.35)

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Table 6. Comparison of Results with the Surveyed Literature

this study						surveyed literature						
feedstock	avg. temp (°C)	char yield (%)	char HHV (MJ/kg)	bio-oil (%)	oil HHV (MJ/kg)	ref	feedstock	temp (°C)	char yield (%)	char HHV (MJ/kg)	bio-oil (%)	oil HHV (MJ/kg)
FW	400	42.4	25.8	37.1	34.5	19	rice husk	427	35.5	14.56	49.2	
FW	500	31.6	24.0	44.4	34.0	38	coffee	500	30.0	22.6		
FW	500	31.6	24.0	44.4	34.0	21	banana	500	39.4	5.35		
FW	500	31.6	24.0	44.4	34.0	40	tomato peel	507	40	22.5		
SWP	500	32.9	16.6	4.23	29.3	43	Salicornia	600	41.2	13.5	20.1	
AD-SEW	550	51.3	7.77	35.5	32.8	44	SEW	500	57.9		45.3	
AD-SEW	600	50.2	7.67	34.3	33.0	44	SEW	700	52.4			
SHJ-SEW	550	47.1	10.6	43.6	27.7	44	SEW	500	57.9			
HD	450	58.4	7.39	5.46	28.3	31	HD	450	33.0			24
HD	550	57.2	8.50	8.26	28.0	31	HD	550	32.0	27		27
HD	650	56.1	7.31	5.43	28.6	31	HD	650	29.0			25

Table 7. Char Yield Analysis of Variance

source	DF	SS	contribution	Adj MS	*F*-value	*P*-value
regression	9	2487	93.8%	276	35.3	0.000
MaxTemp	1	1.12	0.04%	3.38	0.43	0.519
moisture	1	503	19.0%	95.4	12.2	0.002
ash	1	1615	60.9%	35.6	4.54	0.045
volatile	1	174	6.56%	22.2	2.84	0.107
Moisture*Moisture	1	5.11	0.19%	32.8	4.19	0.053
Volatile*Volatile	1	0.01	0.00%	25.0	3.20	0.088
MaxTemp*Moisture	1	42.6	1.61%	29.4	3.75	0.067
MaxTemp*Volatile	1	102	3.85%	71.6	9.13	0.006
Moisture*Ash	1	43.9	1.65%	43.9	5.60	0.028
error	21	165	6.21%	7.84		
lack-of-fit	19	93.8	3.54%	4.94	0.14	0.995
pure error	2	70.8	2.67%	35.4		
total	30	2651	100%			

Table 8. Char HHV Analysis of Variance

source	DF	SS	contribution	Adj MS	*F*-value	*P*-value
regression	9	1528	97.6%	1528	71.9	0.000
MaxTemp	1	402	25.7%	55.5	23.5	0.000
moisture	1	144	9.19%	54.6	23.1	0.000
ash	1	873	55.8%	56.4	23.9	0.000
volatile	1	19.6	1.25%	50.0	21.2	0.000
fixed carbon	1	13.4	0.86%	43.5	18.4	0.001
Volatile*Volatile	1	15.6	1.00%	14.1	5.97	0.027
MaxTemp*Moisture	1	8.67	0.55%	46.0	19.5	0.000
MaxTemp*Ash	1	0.00	0.00%	47.3	20.1	0.000
MaxTemp*Volatile	1	51.7	3.30%	51.7	21.9	0.000
error	16	37.8	2.41%	37.8		
lack-of-fit	14	30.8	1.97%	30.8	0.63	0.761
pure error	2	6.98	0.45%	6.98		
total	25	1566	100%			

$$\mathrm{OilYield} = 5368 - 20.52\ \mathrm{Moisture} - 86.35\ \mathrm{Ash} - 12.73\ \mathrm{Volatile} - 78.58\ \mathrm{FixedCarbon} - 3.914\ \mathrm{Moisture}^2 + 0.2751\ \mathrm{Ash}^2 - 0.4602\ \mathrm{Volatile}^2 + 0.000395\ \mathrm{Temp.\ Volatile}\ (R^2 = 97.6\%) \quad (7)$$

$$\mathrm{OilHHV} = -359 + 0.0937\ \mathrm{Temp} + 7.85\ \mathrm{Moisture} - 19.01\ \mathrm{Ash} + 30.66\ \mathrm{Volatile} - 11.15\ \mathrm{FixedCarbon} - 0.000081\ \mathrm{Temp}^2 - 0.918\ \mathrm{Moisture}^2 + 0.2223\ \mathrm{Ash}^2 - 0.3008\ \mathrm{Volatile}^2\ (R^2 = 91.0\%) \quad (8)$$

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Table 9. Oil Yield Analysis of Variance

source	DF	SS	contribution	Adj MS	F-value	P-value
regression	8	5630	98.0%	704	95.4	0.000
moisture	1	309	5.37%	142	19.2	0.000
ash	1	832	14.5%	1335	181	0.000
volatile	1	292	5.08%	82.0	11.1	0.004
fixed carbon	1	2647	46.0%	1379	187	0.000
Moisture*Moisture	1	53.7	0.93%	332	45.1	0.000
Ash*Ash	1	544.4	9.47%	643	87.2	0.000
Volatile*Volatile	1	884.3	15.4%	933	126	0.000
MaxTemp*Volatile	1	67.9	1.18%	67.9	9.20	0.008
error	16	118	2.05%	7.38		
lack-of-fit	14	99.3	1.73%	7.09	0.75	0.703
pure error	2	18.8	0.33%	9.39		
total	24	5748	100%			

Table 10. Oil HHV Analysis of Variance

source	DF	SS	contribution	Adj MS	F-value	P-value
regression	9	194	91.0%	21.6	14.6	0.000
MaxTemp	1	0.066	0.03%	8.42	5.71	0.033
moisture	1	47.4	22.2%	2.93	1.98	0.182
ash	1	18.3	8.55%	7.03	4.76	0.048
volatile	1	0.402	0.19%	35.4	24.0	0.000
fixed carbon	1	8.20	3.84%	4.15	2.81	0.118
MaxTemp*MaxTemp	1	3.03	1.42%	6.71	4.55	0.053
Moisture*Moisture	1	81.9	38.3%	2.71	1.83	0.199
Ash*Ash	1	18.4	8.60%	18.4	12.5	0.004
Volatile*Volatile	1	16.8	7.88%	16.8	11.4	0.005
error	13	19.2	8.98%	1.48		
lack-of-fit	11	9.99	4.68%	0.908	0.20	0.972
pure error	2	9.20	4.31%	4.60		
total	22	214	100%			

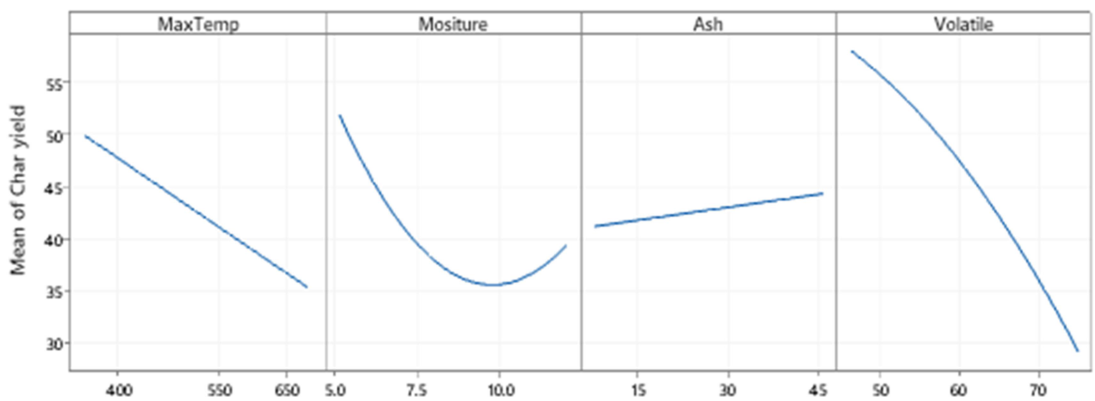

Figure 3. Main effect plots of pyrolysis temperature and biomass properties on char yield [Author].

Tables 7, 8, 9, and 10 summarize the analysis of variance (ANOVA) which indicates the significance level of each term in prediction models along with the contribution percentage. For example, ash can explain 60% of variability of char yield, as indicated by the contribution in Table 6. Figures 3–6 depict the main effect plots of temperature and biomass constituents on the four responses measured. To maximize biochar yield, low moisture, temperature, and volatile are needed, as seen in Figure 3, while maximizing char HHV requires low temperature and high ash and moisture, as shown in Figure 4. In terms of oil yield, low temperature and constituents provide the maximum yield revealed in Figure 5. Finally, Figure 6 shows that low moisture, ash, fixed carbon, and intermediate volatile provide the maximum oil HHV.

Since the biochar yield is inversely proportional to temperature, a linear model is used to predict yield as a function of temperature. For example, the coefficient of determination R^2 of food waste is 98.2%, indicating that 98% of biochar yield variability can be explained by this simple model. It is worth noting here that some of the models are based on three temperatures only, which is deemed to be of low sample size. However, the general monotonic linear trend is maintained. The models for the two Salicornia samples are intersecting, indicating no statistical difference between the

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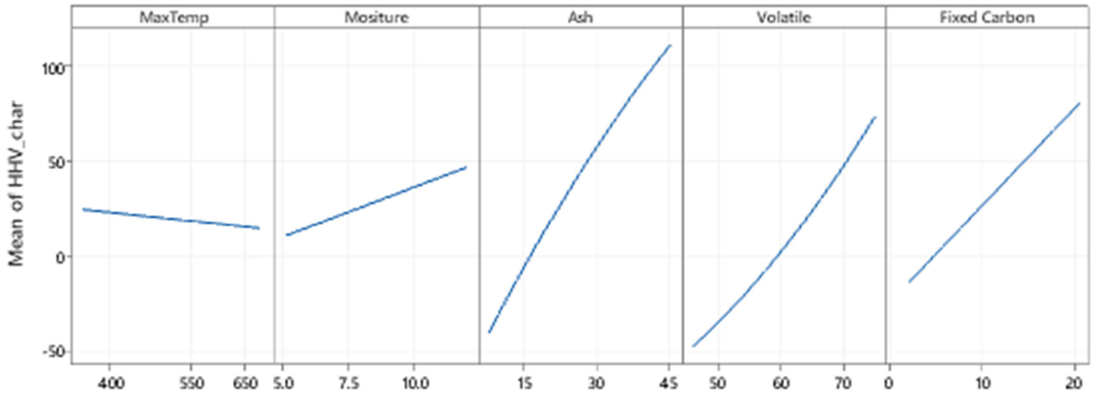

Figure 4. Main effect plots of pyrolysis temperature and biomass properties on char HHV [Author].

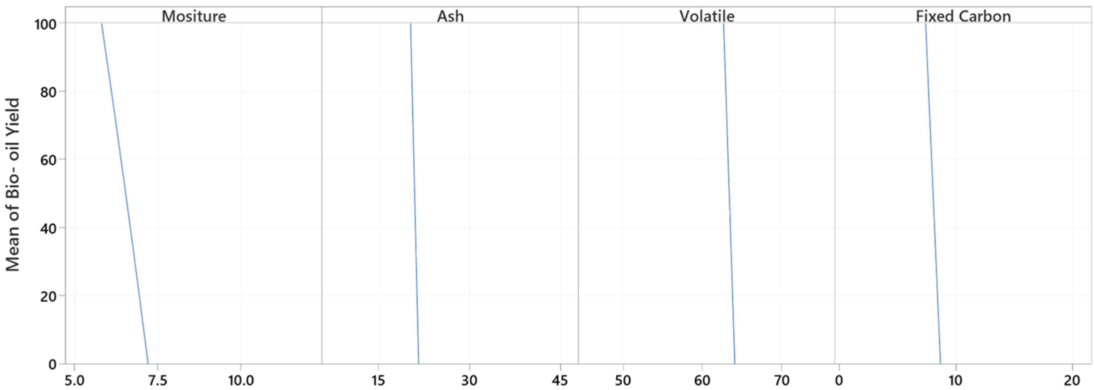

Figure 5. Main effect plots of pyrolysis temperature and biomass properties on bio-oil yield [Author].

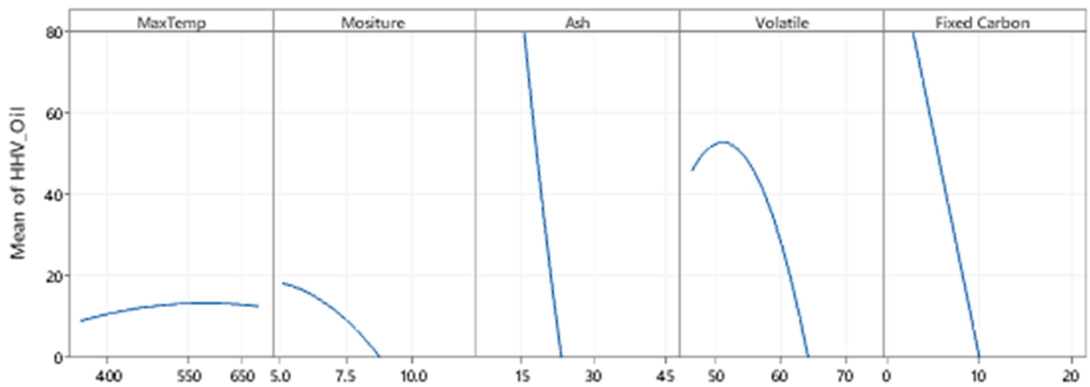

Figure 6. Main effect plots of pyrolysis temperature and biomass properties on bio-oil HHV [Author].

two samples at low temperatures. Alternately, the sewage sludge from Abu Dhabi shows a higher biochar yield than that from Sharjah. Results are in line with the study of Singh et al.[42] who investigated the impact of temperature, residence time, and heating rate on Acacia nilotica base biochar in a fixed-bed reactor. They found that yield and heating energy were highly influenced by temperature, whereas residence time and heating rate had minimal impact.

To explain the yield performance of different biomass feedstocks, thermal profile analysis is conducted to some of the feedstocks. This analysis is important as it gives an indication of the biomass degradation stages and the mass loss at a range of pyrolysis temperatures. It is noticed that the biomasses with the most mass loss are the Salicornia seed and food waste. The mass loss in the case of Abu Dhabi sewage sludge is the least. Concerning the Salicornia seed, which has the highest volatile content, the optimum pyrolysis temperature for the maximum bio-oil yield is around 600 °C, and the major devolatilization stage appears to take place at a wide range. Figure 7 depicts the linear regression charts of biochar in terms of temperature. The chart suggests lower yields at higher temperatures, especially for FW and SS, regardless of the source. The negative trend of yield with temperature is in line with the results obtained by Hossain et al.[44] who reported the biochar yield decrease of 72.3, 63.7, 57.9, and 52.4% at 300, 400, 500, and 700 °C, respectively. Similarly, Tsai et al.[31] examined the yield of biochar produced from dried horse manure and reported a similar negative trend. Such a decrease is attributed to the loss of chemically bound H_2O content and destruction of organic

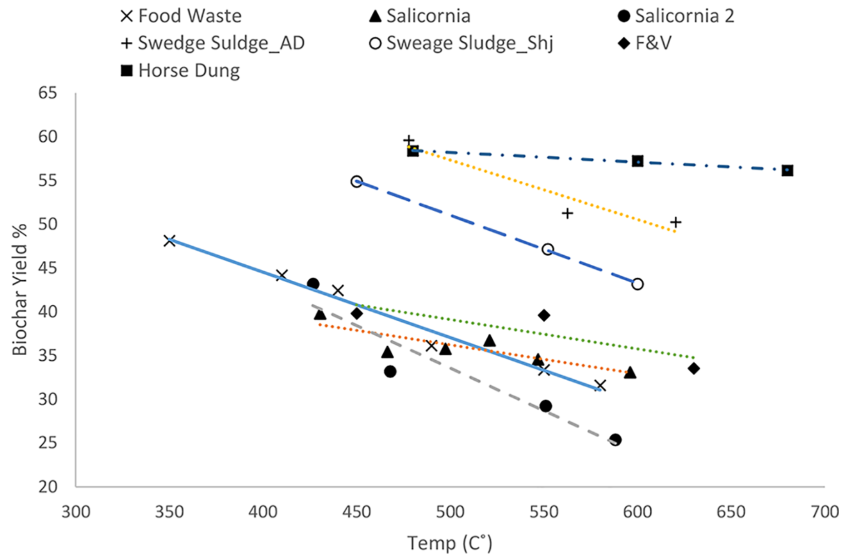

Figure 7. Regression plot of biochar yield vs temperature [Author].

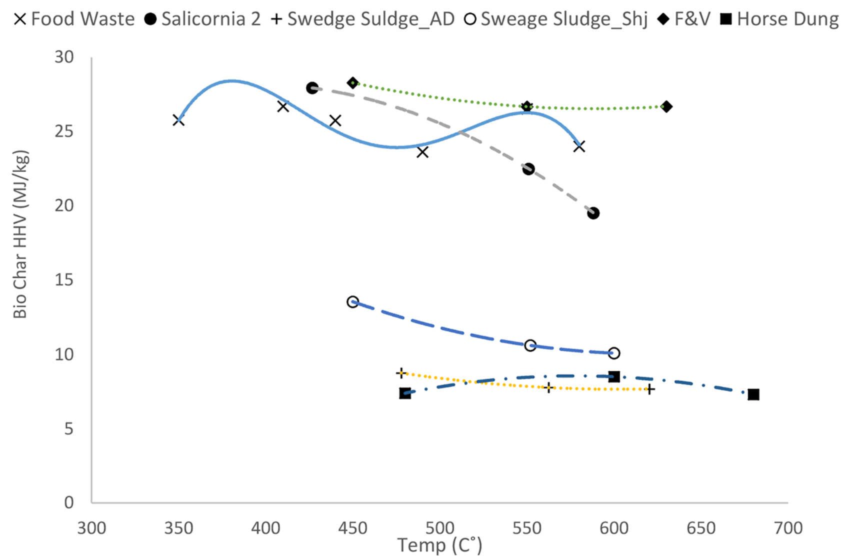

Figure 8. Biochar HHV produced at various pyrolysis temperatures [Author].

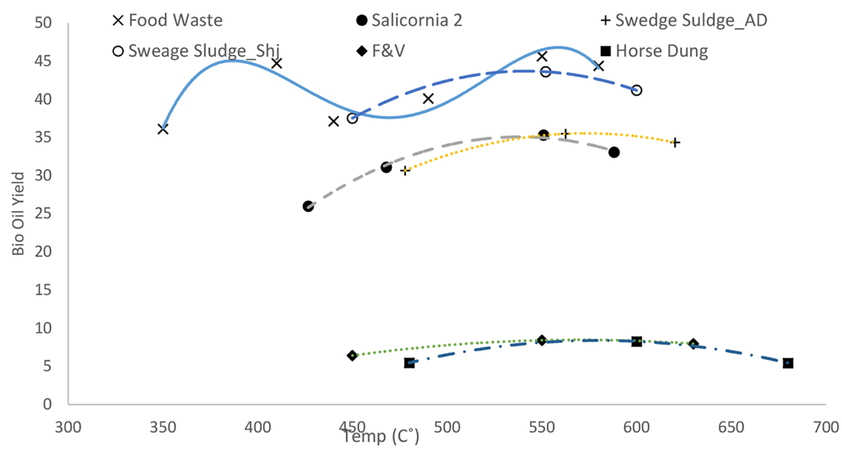

Figure 9. Regression plot of food waste bio-oil vs temperature [Author].

matter accompanied by the development of the aromatic structure.[53]

Figure 8 shows the measured heating values of all of the biochar samples produced in this study. Food waste has more

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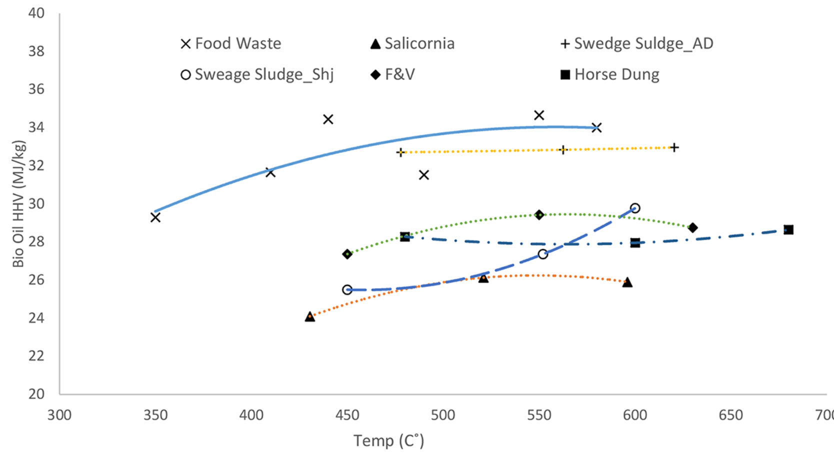

Figure 10. Bio-oil HHV produced from different feedstocks [Author].

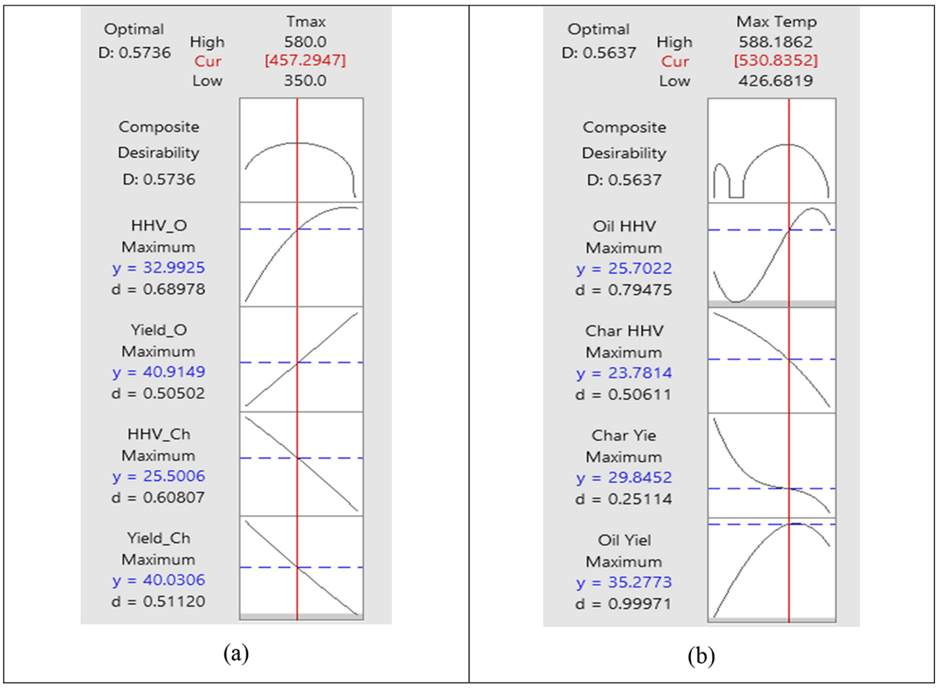

Figure 11. Desirability Optimization for (a) FW and (b) Salicornia [Author].

testing samples compared to other feedstocks which enable us to investigate higher order regression models. As a result, different polynomial regression models were investigated for food waste, and the third order polynomial with two deflection points provided the best results in terms of error minimization. It is clear that SS, Salicornia, and HD biochar are all of low energy content (<15 MJ/kg). Noticeably, these are the biochar produced from the biomasses of the highest ash content, which makes it less desirable as fuel. It is also noticeable that the impact of temperature on the HHV of these chars is limited. Unlike the heating values of the chars from the FW, Salicornia, F&V, and SS showed a drop in HHV as the temperature increases. The HHV of these chars fall within a reasonable range of 19.5−27.0 MJ/kg, which is comparable to the HHV of biochar produced from most woody materials.

Similarly, the bio-oil is modeled using a second order since yield increases with temperature increase until a certain point and then starts decreasing with temperature except for food waste which shows two deflection points (Figure 9). The highest bio-oil yield was obtained using the food waste and sewage sludge of Sharjah, while the lowest is obtained from horse manure and F&V. There is a difference between SS of Sharjah and Abu Dhabi by an average of 10%. Results are in line with the study of Ghorbannezhad et al.[41] who developed bio-oil from palm shell and suggested that higher temperatures improved the bio-oil yield. They also suggested that the higher the temperature, the higher the carboxylic acids (acetic acid and propionic acid) and furans and the lower the aromatics. Similarly, Gautam and co-workers[43] examined the impact of temperature on the bio-oil yield and noted an increase in yield from 600 to 700 °C and then a decrease beyond that. They attributed the increase to reactions such as thermal cracking and dehydration which result in volatile formation which will, in return, crack at a higher temperature into noncondensable gases such as CO_2, CO, and CH_4.

One should note that the trends are only valid within the temperature range tested and may change at higher temperatures.[54] Shahbeik et al.[55] modeled the big data of sludge and

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reported an optimum bio-oil yield between 500 and 600 °C. At higher temperatures (700−800 °C), a transition was observed in the product distribution toward more syngas.

Like biochar, the HHV for bio-oil produced at different temperatures was measured and modeled. Figure 10 shows the measured heating values of all of the bio-oil samples produced in this study along with their prediction models. FW bio-oil provided the maximum HHV along with SS from Abu Dhabi, while Salicornia, horse manure, and FV provided a lower energy content (<30 MJ/kg). The HHV value increases with temperature in the case of FW and SS of Sharjah, while temperature did not show a significant impact on other feedstocks.

Table 6 provides a comparison between the results of our experiments and the ones found in the literature. The results were comparable in the cases of FW and sewage to some extent. However, there is a noticeable difference in the HD. This difference can be attributed to many reasons such as the difference in feedstock characteristics, type of reactor, and pyrolysis parameters, such as residence time.

Next, two scenarios are explored: optimizing a single feedstock and using a mixture of stocks. In the first scenario, the temperature is optimized in a way that the total heat value is maximized. The latter scenario focuses on the prediction of yield and HHV for different mixtures. Several researchers advocated the use of a mixture of feedstocks to achieve favored results. For example, Taherymoosavi et al.[27] pointed out that biochar produced from a single feedstock at the highest heating temperature might not produce the optimum yield. Similarly, Suliman et al.[56] suggested that a mixture of selected biomass feedstocks with appropriate pyrolysis conditions may optimize biochar properties. Moreover, Narzari et al.[57] investigated the yields and properties of biochar from three different feedstocks: bioenergy byproducts, lignocellulose biomass, and a noxious weed, using a fixed-bed slow pyrolysis tubular reactor. They observed that high water-holding capacity and pH biochar are obtained at higher temperatures. The optimization method used here is the desirability method due to its simplicity and efficiency. Figure 11 summarizes the desirability optimization and indicates that the optimal setting for FW is 457 °C. Based on this temperature, 40% of FW biomass will convert into biochar with 25.5 MJ/kg, while another 40.9% will convert into bio-oil with HHV of 33 MJ/kg. In the case of Salicornia, around 29.9% will convert into biochar with HHV of 23.8 MJ/kg, while another 35% will convert into bio-oil with HHV of 25.7 MJ/kg. Although the optimization objective used here is based on maximizing all four outcomes (char yield, char HHV, oil yield, and oil HHV), it is industry-specific. Each industry such as automotive or chemicals or oil have a different objective. In some industries, the focus might be on maximizing the oil production with the highest HHV or quality only. In this case, the bio-oil production comes at the expense of biochar production. Regardless of the scenario, it can be achieved by changing the feedstock and pyrolysis temperature.

4. CONCLUSIONS AND PROSPECTS

In this work, experimental data for five different pyrolysis feedstocks were investigated. Prediction models of biochar and bio-oil yield and HHV as a function of biomass constituents and temperature were developed. These regression models serve as a valuable tool to identify which biomass constituents are capable of achieving the desired yield or HHV value. Different feedstocks could be mixed together to alter the biomass properties, as needed. The developed models were then used to optimize single feedstocks and predict the properties of feedstocks based on their constituents. Among the feedstocks, food waste emerges as the highest total energy value feedstock (33.3 MJ/kg), while a combination of sewage sludge and food waste provides a more economical and sustainable means of bioenergy production. These prediction models assist decision-makers in selecting the appropriate biomass considering their characteristics along with the pyrolysis temperature to predict the final product yield and energy content. Utilizing these models promises to save both time and resources.

For future research, investigating the variability in the total heat values of other feedstocks and their mixtures warrants further investigation. Additionally there is a need for further investigation into the integration of advanced modeling techniques like machine learning to optimize the pyrolysis processes. Few recent studies such as those by Shahbeik et al.,[55] Shafizadeh et al.,[58] Xia et al.[59] and refs 60−63 have focused on the deployment of these advanced techniques in bioenergy. However, it is imperative to further explore this research frontier, drawing on these examples or additional relevant works, to underscore the significance of such supplementary assessments in guiding the forthcoming studies. Lastly, the results are focused on correlating the feedstock constituents and temperature with yield and HHV. However, there are other factors that may affect the product characteristics such as the residence time in the reactor, particle size, and pyrolysis condition (fast, slow, etc.). Therefore, further research is recommended to investigate the impact of these factors on the final product characteristics.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

GHG Greenhouse gas
HD horse dung
HHV higher heating value
HTC hydrothermal carbonization
FW food waste
SS sewage sludge
F&V fruits and vegetables
HDPE high-density polyethylene
SWP Salicornia whole plant
LDEP low-density polyethylene
RSM response surface methodology
TGA thermogravimetric analysis
EuBm eucalyptus biomass
EC electric conductivity
CEC citation-exchange capacity
AD Abu Dhabi
SHJ Sharjah
ANOVA analysis of variance

ADDITIONAL NOTE

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