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Element Characteristic Tolerance for Semi-batch Fixed Bed Biomass Pyrolysis

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Biomass pyrolysis to bio-oil is one of the promising sustainable fuels. In this work, relation between biomass feedstock element characteristic and crude bio-oil production yield and lower heating value was explored. The element characteristics considered in this study include moisture, ash, fix carbon, volatile matter, C, H, N, O, S, cellulose, hemicellulose, and lignin content. A semi-batch fixed bed reactor was used for biomass pyrolysis with heating rate of 30 °C/min from room temperature to 600 °C and the reactor was held at 600 °C for 1 h before cooling down. Constant nitrogen flow (1bar) was provided for anaerobic condition. Sago and Napier glass were used in the study to create different element characteristic of feedstock by altering mixing ratio. Comparison between each element characteristic to crude bio-oil yield and low heating value was conducted. The result suggested potential key element characteristic for pyrolysis and provide a platform to access the feedstock element acceptance range.

1. Introduction

Over dependent of fossil fuel for energy and downstream product demand has led to environmental pollution and global warming. Search for alternative resources is one of the main focuses in current stage of research and development to promote environmental friendly approaches such as achieving sustainability. Biomass is one of the promising alternative renewable resources. However, implementation of biomass in industry scale is yet to be feasible due to high transportation cost and unique property of each biomass species. Several researches have been conducted to relate performance of biomass processes with respect to biomass element characteristics. For example, minimum of 50 wt% of moisture content required for combustion to be feasible (Mohammed et al., 2011). Lower moisture content resulting higher energy output due to less energy used in vaporising water from the feedstock. He et al. (2014) concluded that higher hydrolysis yield of corn stover and higher ethanol yield was due to lower ash content of biomass feedstock. Based on the pretreatment proposed by Li et al. (2009) research in simultaneous saccharification and fermentation on lignocellulosic biomass, Goh et al., (2010) proposed that bio-ethanol yield can be estimated based on cellulose and hemicellulose content of the biomass feedstock. Kotarska et al. (2015) suggested that decomposition of lignocellulosic raw material in biomass which consists of cellulose, hemicellulose and lignin increase production yield of ethanol from corn straw in Simultaneous Saccharification and Fermentation (SSF) process.

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Similarly, impact of biomass element characteristic to process yield and operation in biomass pyrolysis were conducted. Rabacai et al. (2014) reported that production of light gas in pyrolysis is governed by cellulose content. In addition, char and tar are governed by hemicellulose and lignin content. Azargohar et al. (2014) studied the chemical and structural properties of biomass to the effect of fast pyrolysis to produce bio-char. The study proposed that biomass with lower H/C and O/C ratio, and ash content is appropriate as feedstock for activated carbon production. Giudicianni et al. (2014) conducted research on the relation of cellulose, hemicellulose and lignin to Arundo donax steam assisted pyrolysis. The result shows that more lignin content increases yield of bio-oil and reduce yield of char. Presence of steam promotes char gasification thus reducing char yield. Phan et al. (2014) evaluated bio-oil production from Vietnamese biomasses via fast pyrolysis. The study shows that bigger biomass feedstock size decreases bio-oil yield. Bagasse yielded highest bio-oil production of 67.22 % with lowest water content of 17 % in bio-oil. From element characteristic, bagasse has highest combustible, cellulose, and lignin content, and lowest ash content. With a systematic knowledge of relation between feedstock element characteristic and production yield and quality, data can be used as a platform to select optimum biomass for the system. For example, element targeting is used by Lim and Lam (2014a) to integrate biomass supply chain via element characteristic; the approach is further improved in Lim and Lam (2014b) to consider underutilised biomass including process waste.

In this work, relation of biomass feedstock element characteristic to crude bio-oil production yield and low heating value (LHV) in semi-batch fixed bed pyrolysis is studied. The objective of the work is to identify key element characteristic of the feedstock and propose an element acceptance range (EAR) for the pyrolysis process. EAR act as a platform to determine the amount of biomass feedstock and the mixtures based on element characteristic to ensure consistency in the production. The element characteristic considered include moisture content (MC), volatile matter (VM), ash (AC), fixed carbon (FC), carbon (C), hydrogen (H), nitrogen (N), oxygen (O), sulphur (S), cellulose (Cell), hemicellulose (Hcel) and lignin (Lig). Two biomasses with different mixing ratio were used as the feedstocks, creating unique element characteristic for the feedstock. Both bio-oil yield and LHV of crude bio-oil was compared and key element characteristic for the process was identified.

2. Materials and procedures

Two species of biomasses are used in this work, Napier grass stem (NGS) obtained from Crop For the Future field research centre in Semenyih, Malaysia and Sago biomass (Sago) consists of fibre and starch collected from waste water in sago flour process plant in Pusa, Sarawak, Malaysia. Both materials were oven dried upon received according to BS EN 14774-1 standard and element characteristic is conducted and shown in Table 1. A fixed bed tubular reactor was used for the pyrolysis process under inert atmosphere. Biomass was heated up at 30 °C/min to 600 °C and the temperature was held for 1 h. Volatiles generated were cooled rapidly in ice bath and oil was collected in a container. Bio-oil yield was calculated based on Eq(1). LHV of bio-oil was determined via bomb calorimeter - series 6100 by Parr Instrument Company. In determination of the LHV of bio-oil, commercial grade diesel was mixed with the bio-oil to ensure complete combustion of bio-oil and the actual LHV of bio-oil was calculated using Eq(2).

Table 1: Element characteristic of Napier Grass Stem and Sago Biomass

Biomass	MC	AC	VM	FC	HHV	C	H	N	S	O	Cell	Hcel	Lig
Sago	9.19	11.63	73.97	5.21	19.07	39.66	6.61	0.19	0.00	53.54	23.03	73.06	6.75
NGS	9.26	1.75	81.51	16.75	18.05	51.61	6.01	0.99	0.32	41.07	38.75	19.76	26.99

$$bio\_oil\ yield(wt\%) = \frac{bio\_oil\ collected(g)}{total\ biomass\ feedstock(g)} \times 100\% \quad (1)$$

$$LHV\ of\ bio\_oil = \frac{\left[total\ sample(g) \times sample\ heat\ value\ \left({}^{MJ}/_{kg}\right)\right] - \left[mass\ of\ diesel(g) \times heat\ value\ of\ diesel\ \left({}^{MJ}/_{kg}\right)\right]}{mass\ of\ bio\_oil(g)} \quad (2)$$

Several mixtures of sago and NGS are produced to create unique element characteristic of feedstock in each cases. Table 2 summaries the composition of biomass in each case of study and Table 3 presents the element characteristic for each case. The oil-bio yield and LHV from each case are compared to determine the relationship to biomass feedstock element characteristic of this pyrolysis process.

Table 2: Biomass composition in each case study

Case	1	2	3	4	5	6	7	8
Sago (wt%)	100.0	30.5	30.3	20.3	19.9	10.1	9.7	0.0
NGS (wt%)	0.0	69.5	69.7	79.7	80.1	89.9	90.3	100.0

Table 3: Element characteristic of biomass feedstock in each case study

Case	MC	AC	VM	FC	HHV	C	H	N	S	O	Cell	Hcel	Lig
1	9.19	11.63	73.97	5.21	19.07	39.66	6.61	0.19	0.00	53.54	23.03	73.06	6.75
2	9.24	4.76	79.21	13.23	18.36	47.97	6.19	0.75	0.22	44.87	33.96	36.01	20.82
3	9.24	4.74	79.23	13.25	18.36	47.99	6.19	0.75	0.22	44.84	33.99	35.89	20.87
4	9.25	3.75	79.98	14.40	18.26	49.18	6.13	0.83	0.26	43.60	35.56	30.58	22.88
5	9.25	3.71	80.01	14.45	18.25	49.23	6.13	0.83	0.26	43.55	35.62	30.36	22.96
6	9.25	2.74	80.75	15.58	18.15	50.40	6.07	0.91	0.29	42.33	37.16	25.14	24.95
7	9.25	2.71	80.78	15.62	18.15	50.45	6.07	0.91	0.29	42.28	37.22	24.94	25.02
8	9.26	1.75	81.51	16.75	18.05	51.61	6.01	0.99	0.32	41.07	38.75	19.76	26.99
Standard deviation	0.02	3.07	2.34	3.58	0.32	3.71	0.19	0.25	0.10	3.87	4.88	16.56	6.29

3. Results and discussions

Table 4 tabulated crude bio-oil production yield and its respective LHV for each case. The relation between each element to crude bio-oil yield and LHV are presented in Figure 1 and Figure 2. In general, a linear relation is observed in the relation between feedstock element characteristic with crude bio-oil yield and LHV. From the analysis, it is shown that case 1 are inconsistence with the general trend of the graph. This could be due to human error or faulty equipment during the experiment. Thus case 1 is to be excluded in the graph and discussion.

Table 4: Crude bio-oil production yield and LHV

Case	1	2	3	4	5	6	7	8	Standard deviation
Crude bio-oil yield (wt%)	43.66	32.13	36.21	33.62	24.93	50.63	34.61	57.21	10.62
LHV of crude bio-oil (MJ/kg)	12.41	9.53	7.03	11.74	8.53	15.29	16.90	12.03	3.32

More MC, VM, FC, C, N, S, Cell and Lig, and less AC, VM, HHV, H, O, and Hcel in biomass feedstock resulting in higher yield of crude bio-oil production and higher LVH of bio-oil in the pyrolysis process. Similar result in terms of relation between lignin content in biomass feedstock to bio-oil yield is reported by Giudicianne et al. (2014). It is reported that more lignin content favours higher bio-oil yield and lower char yield. From the trend of the crude bio-oil yield with respect to the ash content in biomass feedstock, more ash content resulting in less bio-oil. More ash content in biomass increases char production, thus less bio-oil production is expected which is also reported by Choi et al. (2014) in pyrolysis of seaweed. As for the comparison of feedstock element characteristic in terms of LHV of crude bio-oil, fixed carbon and carbon content is in parallel with LHV of bio-oil such that more FC and C content increases LHV of bio-oil. There is an interesting finding of an inverse relationship between biomass feedstock HHV and crude bio-oil LVH. No pretreatment conducted on crude bio-oil generated, thus it contains moisture that affects the bio-oil heating value analysis. Part of the energy is used to evaporate moisture content within crude bio-oil. Thus, depending on the amount of moisture content within the crude bio-oil, the LHV from the analysis will be affected. Thus, comparison of HHV of biomass feedstock with HHV of bio-oil will be more constructive and accurate. HHV of bio-oil can be estimated provided that the moisture content in the crude bio-oil is determined. This will be verified in future work.

Another comparison of the biomass feedstock element characteristic with crude bio-oil yield and LHV are conducted based on standard deviation presented in Table 3 and Table 4. The data shows that Hcel has the highest standard deviation of 16.56 as compared to other element characteristic. The value is relatively low as compared to the standard deviation for crude bio-oil yield and LHV which is at 10.62 and 3.32. This suggests that Hcel is potentially has less impact to the bio-oil yield and LHV. Besides, it

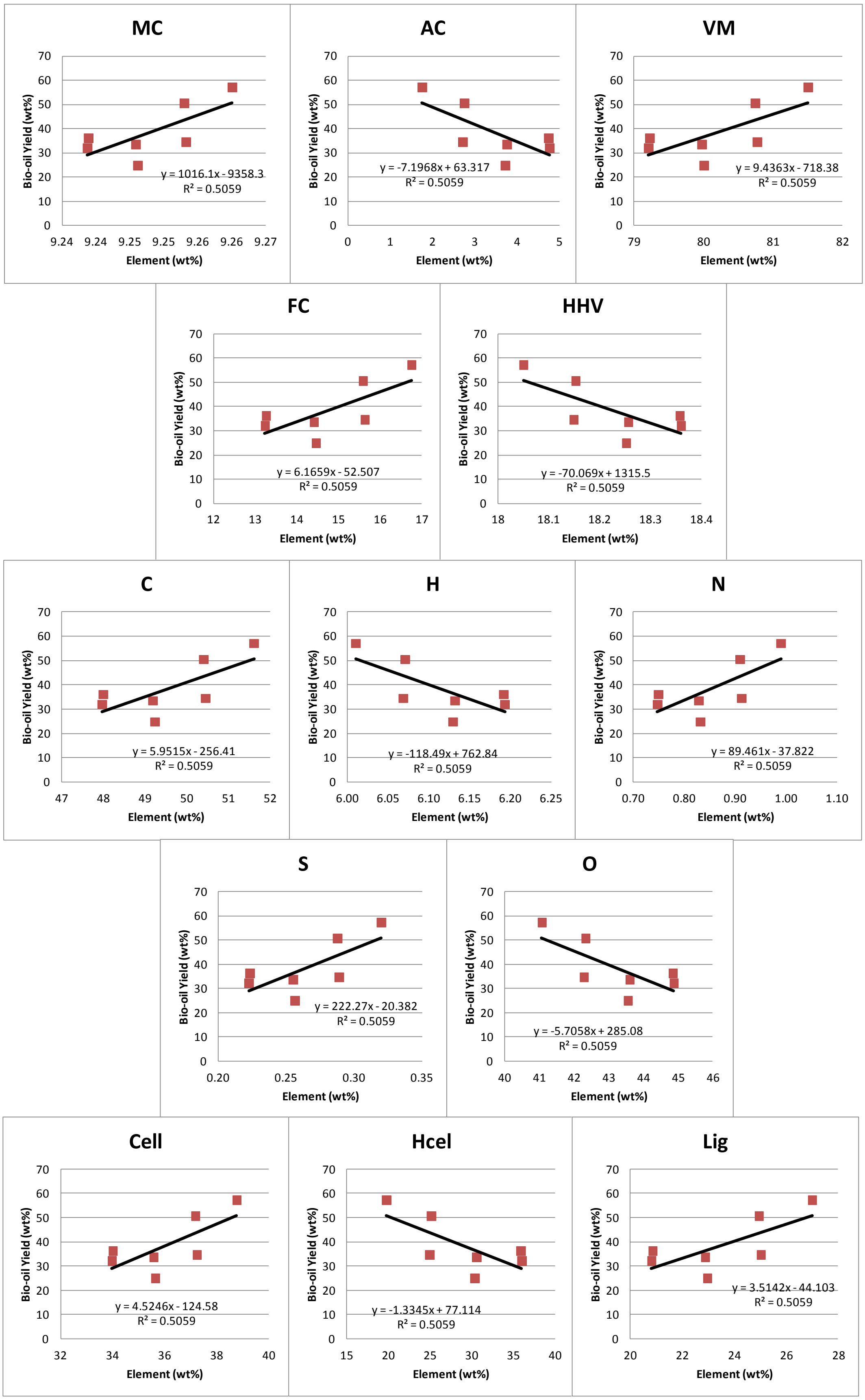

Figure 1: Relation of feedstock element characteristic to crude bio-oil yield

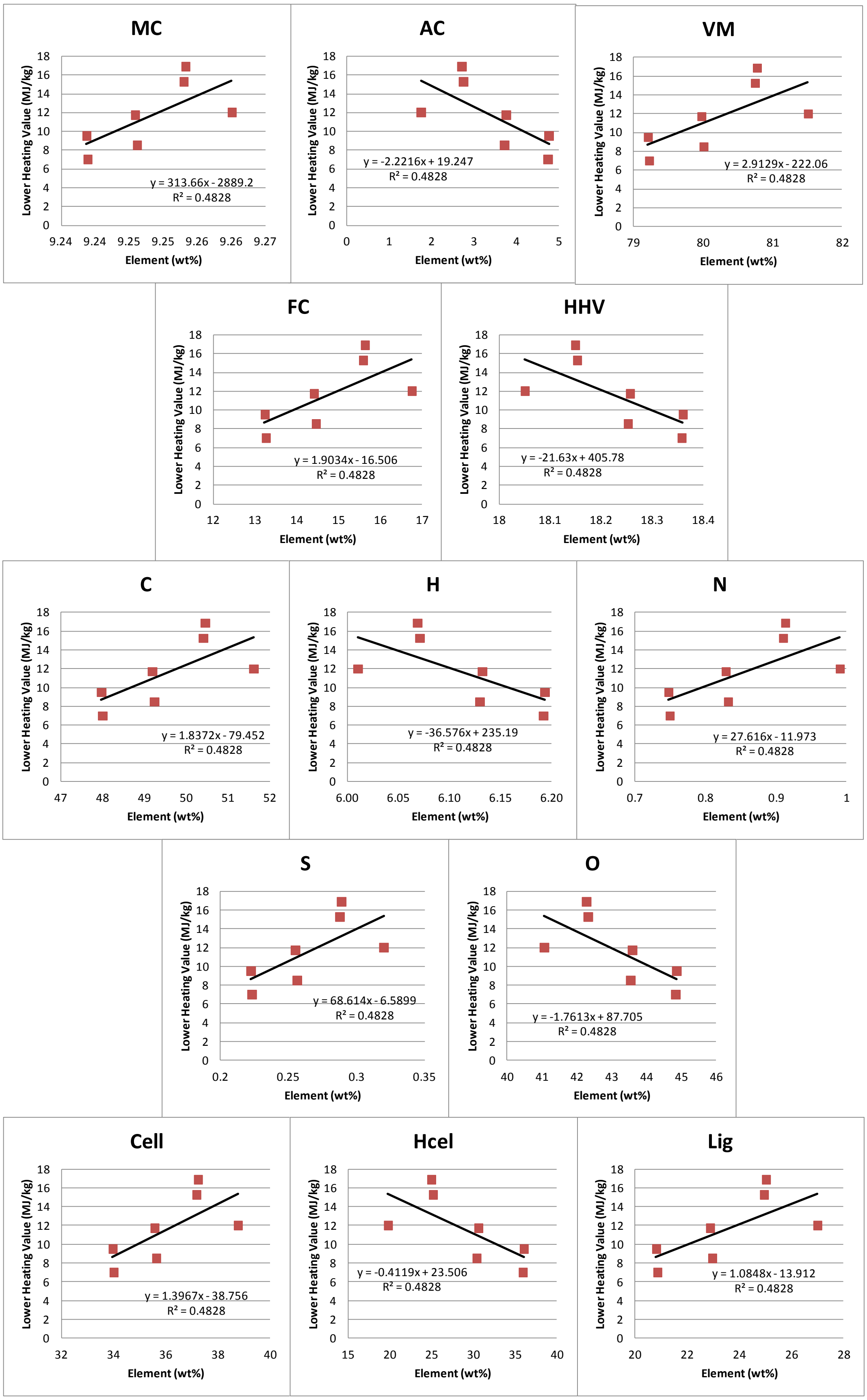

Figure 2: Relation of feedstock element characteristic to crude bio-oil LHV

is shown that standard deviation of AC, FC, C, and O (3.07, 3.58, 3.71, and 3.87) are similar to standard deviation of crude bio-oil LHV of 3.32. This suggests that these element characteristic of biomass are potentially the key element characteristic in this pyrolysis process and have direct impact to the LHV of biomass. Any significant fluctuation in these element characteristic will resulting fluctuation in bio-oil quality. This reflects the tolerance of feedstock selection for the pyrolysis such that smaller element acceptance range should be implied on AC, FC, C, and O to ensure consistency in LHV of bio-oil. Wider element acceptance range of Hcel is unlikely to give major impact to the crude bio-oil production yield. However, more experiment should be conducted to further verify the impact of remaining biomass feedstock element characteristic to crude bio-oil production yield and LHV in pyrolysis. Experiment will be improved in future such as better control for consistency in reaction and in procedure to minimise human errors. These are believed to be the cause of outlier such Case 1 as discussed above and the high R^2 value in each graphs presented in Figure 1 and 2. More biomass species will be considered in future work to create more dimensions in the mixing to create more variation in feedstock element characteristic.

4. Conclusions

Two biomass species of NGS and Sago are used as biomass feedstock for pyrolysis to produce bio-oil. Mixing ratio of the biomasses is altered to create unique element characteristic of biomass feedstock. The relation between feedstock element characteristic and crude bio-oil production yield and LHV is studied. The result shows that in general, increases of MC, VM, FC, C, N, S, Cell, and Lig increases the crude bio-oil yield and LHV. While fluctuation of Hcel content in feedstock has less impact to crude bio-oil yield, fluctuation of AC, FC, C, and O in feedstock is relatively close to the fluctuation of LHV based on standard deviation. Thus, these suggest that SC, FC, C, and O are potentially be the key element characteristic of the pyrolysis process. This proposed that the element acceptance range of pyrolysis of AC, FC, C, and O should be controlled for consistency in bio-oil LHV. More biomass species will be used in future work to create more dimensions in biomass mixing and feedstock element characteristic.

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