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Novel Input-Output Prediction Approach for Biomass **Pyrolysis**

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1. Abstract

- 17 Biomass pyrolysis to bio-oil is one of the promising sustainable fuels. In this work, relation between
- 18 biomass feedstock element characteristic and pyrolysis process outputs was explored. The element
- characteristics considered in this study include moisture, ash, fix carbon, volatile matter, carbon, hydrogen, 19
- 20 nitrogen, oxygen, and sulphur. A semi-batch fixed bed reactor was used for biomass pyrolysis with heating
- 21 rate of 30 ℃/min from room temperature to 600 ℃ a nd the reactor was held at 600 ℃ for 1 hour before
- 22 cooling down. Constant nitrogen flow rate of 5 L/min was provided for anaerobic condition. Rice husk,
- 23 Sago biomass and Napier grass were used in the study to form different element characteristic of
- 24 feedstock by altering mixing ratio. Comparison between each element characteristic to total produced bio-
- 25 oil yield, aqueous phase bio-oil yield, organic phase bio-oil yield, higher heating value of organic phase
- 26 bio-oil, and organic bio-oil compounds was conducted. The results demonstrate that process performance
- 27 is associated with feedstock properties, which can be used as a platform to access the process feedstock
- 28 element acceptance range to estimate the process outputs. Ultimately, this work evaluated the element
- 29 acceptance range for proposed biomass pyrolysis technology to integrate alternative biomass species 30 feedstock based on element characteristic to enhance the flexibility of feedstock selection.

2. Keywords

32 Biomass element characteristic; element targeting; element acceptance range; fixed-bed pyrolysis

3. Introduction

- 34 Global warming and environmental issues are becoming the main concern of the world. Search for cleaner
- 35 processes and sustainable resources are very critical in current stage of research and development to
- 36 tackle the issue. Many leading researchers is targeting at the improvement of sustainable process
- 37 integration (Klemeš et al., 2011). Among the renewable resources, biomass is one of the promising
- 38 alternative sustainable resources. For example, palm biomass is one of the main-stream biomass
- 39 developed to aim at the concept of Waste-to-Wealth (Ng et al., 2012). Conversion of biological waste into
- 40 useful downstream product or energy further improves the quality of waste management (Klemeš and
- 41 Varbanov, 2013). However, implementation of biomass in industry scale is yet to be feasible in many
- 42 regions, especially on non-mainstream biomasses due to high transportation cost and unique properties of
- 43 each biomass species. Distinctive properties of each biomass species further constraints biomass
- 44 applicability, especially integration of underutilised biomass or non-mainstream biomass species into
- 45 existing process technologies. The potential value of these underutilised biomasses is not being optimised
- 46 and leading to potential environmental issue such as accumulative process waste. This is a very critical
- 47 gap to achieve overall optimisation of system and at the same time increases waste management cost. On
- 48 the other hand, supply chain management and logistic issue also contribute to the delay of biomass

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implementation, such as in bio-energy production (Gold and Seuring, 2011). Lim and Lam (2016) proposed element targeting approach to integrate alternative biomass into existing process technology to enhance the flexibility of feedstock. Several researches have been conducted to relate performance of biomass processes with respect to biomass element characteristics. For example, biomass combustion is only feasible if the moisture content of biomass is less than 50 wt% (Mohammed et al., 2011). Lower moisture content results higher energy output due to less energy used in vaporising water within 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. Utilising the pretreatment study 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.

Several studies on the impact of biomass feedstock element characteristic to pyrolysis process outcomes were also conducted by researchers. For example, 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 activated carbon production favours biomass feedstock with lower H/C and O/C ratio, and ash content. 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. Giudicianni et al. (2014) conducted research on the relation of cellulose, hemicellulose and lignin to Arundo donax steam assisted pyrolysis. The study concluded that higher content of lignin in the feedstock 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. From the analysis above, it is clear that biomass process technology outcomes are closely related to the feedstock element characteristic. However, less effort has been focused on analysing the boundary of the element acceptance range of pyrolysis. With a systematic knowledge of relation between feedstock element characteristic and process outcomes, this information can be used as a platform to select optimum biomass for the system. Further application into biomass supply chain management is possible as per the study by Lim and Lam (2014) to consider underutilised biomass into the existing system.

The insight of this paper is an extension work to evaluate element targeting proposed by Lim and Lam (2014) and Lim and Lam (2016) in laboratory scale. This work extends on analysis of the concept of element targeting and feasibility of implementation in real life case scenario. In this work, impact of biomass feedstock element characteristics to semi-batch fixed bed pyrolysis outputs is studied. The process outputs to be considered in this paper includes total produced bio-oil yield, aqueous phase bio-oil yield, organic phase bio-oil yield, higher heating value of organic phase bio-oil and several functional groups of organic phase bio-oil compound. The objectives of this work is to analysis and constructs relation between biomass feedstock element characteristics and pyrolysis output, and propose an approach to estimate pyrolysis output based on feedstock element characteristic properties. This allows integration of underutilised biomass into the existing biomass process technology, in this case, biomass pyrolysis. The element characteristics to be considered include moisture content (MC), volatile matter (VM), ash (AC), fixed carbon (FC), high heating value (HHV), carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulphur (S). Three biomass species are used in this study including rice husk, Napier grass and sago biomass. Many developments have been conducted on rice husk process technologies, however mass implementation is yet to be feasible due to general supply chain issues. Both Napier grass and sago biomass are considered to be underutilised biomasses. Napier grass are generally available in many regional area, but with limited availability and de-centralised accessibility. Nevertheless, Napier grass has potential as raw material for downstream product, such as bio-fuel (Isah et al., 2015). On the other hand, sago biomasses collected from process effluent from sago flour production consists of sago fibre and starch normally treated as process waste. However, less research and development is conducted in both biomass species thus resulting less implementation on biomass. In this paper, rice husk, Napier grass and sago biomass are used as the feedstock for biomass pyrolysis. This provides opportunity to evaluate application of underutilised biomasses into exiting process technology as alternative resources. Mixing ratio of the biomasses is altered to create unique element characteristic of feedstock. The relations is analysed to construct element acceptance range (EAR) of the process. EAR act as an estimation

106 platform, such that as long as the biomass feedstock is within the proposed range, no significant fluctuation in process outputs are expected.

4. Materials and procedures

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Three species of biomasses are used in this work, Napier grass stem (NGS) and Rice Husk (RH) obtained from Crop for the Future field research centre in Semenyih, Malaysia, and Sago biomass (Sago) consists of fibre and starch collected from sago flour process plant effluent in Pusa, Sarawak, Malaysia. Due to high moisture content of the as-received-biomass (range from 50 wt% to 80 wt% depending on the weather and condition and collection period), all materials were oven dried upon received according to BS EN 14774-1 standard and element characteristic is conducted to preserve the biomass sample and shown in Table 1. Noted that after exposed to atmosphere, air humidity in tropical country revert moisture content of predried biomasses back to approximately 10 wt%. A stainless steel fixed bed tubular reactor (115 cm length and 5 cm inner diameter) was used for the pyrolysis process under inert atmosphere. Constant nitrogen flow at 5L/min was provided to create inert environment. Approximate 100 g of biomass sample was placed at center of the reactor and heated up at 30 °C/min to 600 °C and the temperature was held for 1 hour. Volatiles generated were cooled rapidly in a coil condenser connected to cooling water system at 3 °C and oil was collected in a container. Total produced bio-oil yield is calculated based on Eq(1). The produced bio-oil is separated into aqueous phase and organic phase. The bio-oil is carefully decanted to remove majority of the aqueous phase bio-oil from organic phase bio-oil. The remaining aqueous phase bio-oil is then slowly removed using syringe to extract as much aqueous phase bio-oil from organic phase bio-oil. Production yield of each phases are calculated based on the same formulation in Eq(1). HHV of organic phase of produced bio-oil was determined via bomb calorimeter - series 6100 by Parr Instrument Company. The compound of organic phase bio-oil is further analysed using a gas chromatograph-mass spectrometer (GC-MS) system (PerkinElmer ClarusR SQ 8, USA) with a quadruple detector and PerkinElmer-EliteTM-5ms column (30 m x 0.25 mm x 0.25 µm). The oven is programmed at an initial temperature of 40 °C, ramp at 5 °C /min to 280 °C a nd held there for 20 min. The injection temperature, volume, and split ratio were 250 °C, 1 μ L, and 50:1 respectively. Helium was used as carrier gas at a flow rate of 1 mL/min. The bio-oil samples in chloroform (10%, w/v) were prepared and used for the analysis. MS ion source at 250 °C with 70 eV ionization energy was used. Peaks of the chromatogram were identified by comparing with standard spectra of compounds in the National Institute of Standards and Technology (NIST) library.

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

Biomass	MC	AC	VM	FC	HHV	С	Н	N	S	0
	(wt%)	(wt%)	(wt%)	(wt%)	(MJ/kg)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
NGS	9.26	1.75	81.51	16.75	18.05	51.61	6.01	0.99	0.32	41.07
RH	11.71	13.16	72.27	14.57	16.56	40.67	6.79	0.44	0.87	51.23
Sago	9.19	11.63	73.97	5.21	19.07	39.66	6.61	0.19	0.00	53.54

$$bio_oil\ yield(wt\%) = \frac{bio_oil\ collsctsd(g)}{total\ biomass\ feedstock(g)} \times 100\% \tag{1}$$

Several cases of NGS, RH and sago mixtures are created to replicate unique element characteristic properties of feedstock. Table 2 summaries the composition of biomass in each case of study and Table 3 presents the element characteristic for each case. The total produced bio-oil yield, aqueous bio-oil yield, organic bio-oil yield, HHV of organic bio-oil, and bio-oil compound from each case are compared to determine the relationship to biomass feedstock element characteristic to the pyrolysis process outputs.

Table 2: Biomass composition in each case study

Case	1	2	3	4	5	6	7
NGS (wt%)	100	0	0	50	0	50	30
RH (wt%)	0	100	0	50	50	0	40
Sago (wt%)	0	0	100	0	50	50	30

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

Case	MC (wt%)	AC (wt%)	VM (wt%)	FC (wt%)	HHV (MJ/kg)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)
1	9.26	1.75	81.51	16.75	18.05	51.61	6.01	0.99	0.32	41.07

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2	11.71	13.16	72.27	14.57	16.56	40.67	6.79	0.44	0.87	51.23
3	9.19	11.63	73.97	5.21	19.07	39.66	6.61	0.19	0.00	53.54
4	10.48	7.45	76.89	15.66	17.30	46.14	6.40	0.71	0.60	46.15
5	10.45	12.39	73.12	9.89	17.81	40.16	6.70	0.32	0.43	52.38
6	9.22	6.69	77.74	10.97	18.56	45.63	6.31	0.59	0.16	47.31
7	10.22	9.27	75.55	12.42	17.76	43.65	6.50	0.53	0.44	48.87

5. Results and discussions

Table 4 tabulated bio-oil production yield, aqueous phase bio-oil yield, organic phase bio-oil yield and HHV of organic phase bio-oil for each case. The relation between each feedstock element characteristic to produced bio-oil yields are presented in Figure 1. Similarly, the relations of feedstock elements with respect to HHV are presented in Figure 2. In general, a linear relation is observed in the relation between feedstock element characteristic with respect to the pyrolysis outputs. Besides, compound of organic phase bio-oil is analysed and the chromatogram is presented in Figure 3. More than 20 compounds are identified in each case. Table 5 presented the composition of the major functional groups identified within the organic phase bio-oil in each case.

Table 4: Bio-oil production yield and HHV

Case	1	2	3	4	5	6	7
Total produced bio-oil yield (wt%)	41.91	31.51	37.98	35.86	45.55	39.54	34.13
Aqueous phase bio-oil yield (wt%)	29.56	30.70	36.87	32.66	36.60	35.51	31.98
Organic phase bio-oil yield (wt%)	12.34	0.82	1.11	3.20	8.95	4.03	2.14
HHV of organic phase bio-oil (MJ/kg)	26.23	19.73	17.95	20.11	23.35	19.45	17.87

155 Table 5: Main functional groups of organic phase bio-oil

Case	1	2	3	4	5	6	7
Phenols (wt%)	51.60	58.20	64.26	72.38	70.88	71.43	67.89
Aldehydes (wt%)	16.14	2.64	13.11	16.81	9.13	3.20	3.20
Acids (wt%)	13.07	4.29	5.47	0.00	3.41	13.50	13.50
Ketones (wt%)	9.57	10.52	2.29	4.54	2.14	0.00	0.00
Hydrocarbon (wt%)	0.00	8.50	3.19	0.00	2.01	6.35	6.35
Alcohols (wt%)	2.52	8.99	2.06	0.00	9.02	0.00	0.00
Benzene derivatives (wt%)	2.17	2.60	2.26	2.08	1.47	0.00	0.00
Others (wt%)	4.66	4.26	7.36	4.19	1.95	0.00	9.06

5.1 Feedstock impacts to produced bio-oil yield

From the results, it is observed that more VM, HHV, C, and N, and; less MC, Ash, FC, H, S, and O in biomass feedstock resulting in higher yield of produced bio-oil production. However, noted that these relations are not all similar in the comparison cases of aqueous and organic phase bio-oil. The general linear relation of aqueous phase and organic phase is not parallel in comparisons of Ash, VM, FC, C, H, N, and O. Based on the trend of produced bio-oil yield with respect to the ash content in biomass feedstock, more ash content resulting in less bio-oil. This finding is comparable to the work by Choi et al., (2014) in pyrolysis of seaweed. Similar trend is found in VM analysis, where higher VM content resulting high yield in bio-oil. In pyrolysis, VM within biomass evaporated upon heating, heavier components at the produced gas condensed into bio-oil within the cooling system and remaining lighter gas is produced as syngas and light hydrocarbon gas. However, depending on the operating condition and thermal cracking of the biomass, possible lower bio-oil yield in high VM biomass feedstock due to more light gas is produced as syngas. Nevertheless, this is more likely to happen in the present of oxidation agent, such as in gasification process.

5.2 Feedstock impacts to produced organic phase bio-oil HHV

As the aqueous phase of bio-oil is generally consist of more acids and moisture, heating value is expected to be lower compared to organic phase of bio-oil. Thus, in this study, only the HHV of organic phase bio-oil is analysed for potential use as fuel. Based on the comparison, lower MC, Ash, HHV, H, and O, and; higher VM, FC, C, N, and S favours higher HHV value in the organic phase bio-oil. This analysis also highlights the key elements of the process. Key elements are the main element constraints that govern the

176 process output. Similarly, non-key elements are the feedstock elements characteristic that has less effect 177 to process output. For example, noted that MC, HHV and S content of the biomass feedstock has little 178 impact to the HHV of organic phase bio-oil, which a closed to horizontal line in this element analysis is 179 observed in Figure 2. Most of the moisture content within the produced bio-oil is presented in the aqueous 180 phase of bio-oil. This explains the minimum impact of biomass feedstock MC with respect to HHV of 181 organic phase bio-oil. The impact should be more significant if compared to HHV of aqueous phase bio-oil. 182 However, determination of HHV of aqueous phase bio-oil is very difficult due to the relatively high 183 concentration of moisture content which weakens its combustion property. On the other hand, as no 184 pretreatment conducted on the bio-oil, the moisture content may affect the bio-oil heating value analysis. 185 Part of the energy is used to evaporate moisture content within bio-oil. Thus, depending on the amount of 186 moisture content within the bio-oil, the HHV from the analysis will be affected. Therefore, comparison 187 between LHV of biomass feedstock and LHV of bio-oil will be more constructive and accurate. LHV of bio-188 oil can be estimated provided that the moisture content in the bio-oil is determined. This will be verified in 189

5.3 Feedstock impact to organic phase bio-oil compound

From the analysis of organic phase bio-oil compounds, more than 20 compounds are identified including different isomers. In order to simplify the comparisons, all identified compounds are classified into 8 functional groups as per Table 5. Similar to the study on bio-oil yield and HHV, the relation of biomass feedstock element characteristics and organic phase bio-oil functional group compound is constructed as shown in Figure 4(a) and 4(b). However from the analysis, no significant trend or relation is observed. Quality of bio-oil in terms of chemical functional groups seems to be scatter around in the comparison to element characteristics of the feedstock. One of the suggestions to this phenomenon is due to the present of minerals within the ash content of biomass. Researches show that different mineral interacts differently during thermochemical conversion (Ellis et al., 2015). Mineral within different biomass has the potential to react with each other and interferes the overall process reaction. Specific mineral also can be used as catalyst for pyrolysis to control and achieve particular bio-oil quality. However in this research, mineral content is not considered as part of the feedstock properties. Thus, analysis and comparison to the potential key element are unable to be conducted. This suggested that further improvement of current element targeting approach is required, especially to integrate feedstock mineral content to process output such as bio-oil compounds. Catalytic reaction might able to minimise the fluctuation in the relations, which enable proximate estimation of bio-oil compound in the process output.

5.4 Estimation of pyrolysis output

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Upon the discussion on the analysis of relation between biomass feedstock element characteristic with respect to pyrolysis outputs, this section discusses one of the potential application. Based on the constructed relations, pyrolysis outputs can be estimated based on the feedstock element characteristic. In cases of feedstock properties fluctuation or exploration of alternative feedstock, an early stage of process outputs estimation is essential as decision making tool. Upon expansion of same approach in other biomass technologies, it also can be used as a screening platform for research and development to determine potential application of respective biomass species in each technology. However, as the influence of each element characteristic to process outputs are varied, forward estimation might resulting in multiple process outputs or a wide range of estimated which might not be feasible. For instance, a biomass with 10 wt% MC and 72 wt% VM is estimated to generate produced bio-oil yield at 38.27 and 36.37 kg per kg feedstock respectively, which are not identical to each other. Thus, this approach is highly dependence on the key element that governs the process conversion. In this example of bio-oil production via pyrolysis, estimation based on VM is considered to be more accurate as VM are directly proportional to the gaseous product generated in pyrolysis to produce bio-oil in the cooling system. Nevertheless, more experiment and research need to be conducted to identify the impact factor of each element characteristics and generalised a co-relation for process estimation.

5.5 Construction and application of Element Acceptance Range (EAR)

Another application of relation between biomass feedstock element characteristics and process outputs is in the construction of EAR. EAR is the feedstock elemental boundary or limitation of respective process technology in order to maintain operational and process consistency. In other words, as long as the feedstock is within the proposed EAR, no significant process fluctuation is expected. EAR can be constructed by backward estimation from targeted process output. For example in this case, assuming the total produced bio-oil yield is targeted to be in the range of 35 wt% to 40 wt%. Based on the constructed relations as shown in Figure 1 (between feedstock element characteristics and total produced bio-oil yield),

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the element acceptance ranges of this pyrolysis technology are estimated as shown in Figure 5. Noted that EAR of Figure 5 is only applicable to the proposed pyrolysis set up and operating conditions as per described in Section 4. From the proposed element acceptance range, depending on the key elements of the other process outputs, aqueous phase bio-oil yield, organic phase bio-oil yield, HHV of organic phase bio-oil yield can be estimated. For instance, assuming VM to be the main key element in this process, aqueous phase bio-oil yield, organic phase bio-oil yield, and HHV of organic phase bio-oil yield are estimated to be in the range of 31.69 wt% to 36.15 wt%, 0 wt% to 8.31 wt%, and 17.14 MJ/kg to 22.89 MJ/kg. Thus, depending on the process output requirement, element targeting approach enables the identification of element acceptance range of respective technology. The main advantage of the backward estimation is to determine the feasibility of alternative biomass species as potential feedstock via the constructed element acceptance range. The proposed range is also applicable to determine the optimum composition of biomass mixture as feedstock to ensure consistency in process outputs as suggested by Lim & Lam (2016).

Analysis on the relation between feedstock element characteristic and process outputs enables a systematic platform to determine main process constraints. This breakthrough the limitation in conventional technologies, where developed technology only applicable to the respective biomass feedstock or selected few biomass species. Integration and estimation of process outputs based on element characteristic instead of biomass species offer higher flexibility in feedstock selection without compromise the process and operation. With the proposed EAR approach, all biomass technology has the potential to be implemented in any region with diverse biomass resources. Non-main stream biomass species or underutilised biomasses are able to be considered into the system as potential resources as long as the overall element characteristic of biomass feedstock mixture is within EAR of the technology. Another advantage of element targeting is to tackle uncertainties in biomass resources. Uncertainty of biomass availability and quality due to seasonal fluctuation and weather condition can be minimized based on EAR, such that alternative biomass species or mixtures are exploited as temporary solution. No doubt that more research and experimental works are required to construct a systematic co-relation between feedstock element characteristic and process outputs, however, the advantages of element targeting are able to tackle the limitation in biomass technology and supply chain management.

5.6 Limitation of the proposed element targeting approach

Previous discussion has shown promising advantages and application of element targeting approach in biomass processes, especially focused in pyrolysis. However, due to limited biomass feedstock variety in the experiment, the similar boundaries are also reflected in the construction of element acceptance range. Based on the feedstock element characteristics reported in Table 3, overall biomass feedstock properties are limited in this experimental work. Thus, the proposed relations between biomass feedstock element characteristics and process outputs proposed are only applicable to biomass feedstock within the range of element characteristics as presented in Figure 6. Alternative biomass feedstock with element characteristics out of the boundary might result error in the outputs estimation. This study also unable to clearly point out the key elements of the process, but a general acceptance range is proposed instead. Nevertheless, these issue can be easily rectified by including more biomass species into the experimental study. Diversify biomass species as feedstock for the experiment enables the analysis to cover wider feedstock element acceptance range. Study wider range of feedstock element characteristic further enhance the analysis of the impact of each biomass properties to the process output which are essential to determine the key element and construction of general co-relation of pyrolysis process. These extension works could potentially identify and prioritise the impact of each element characteristics to the process performance,

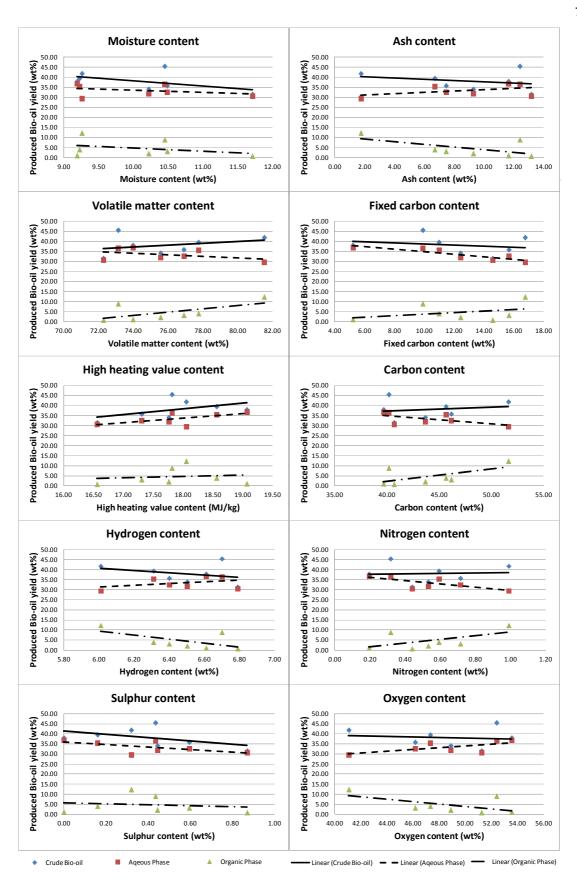


Figure 1: Relation of feedstock element characteristic to bio-oil yields

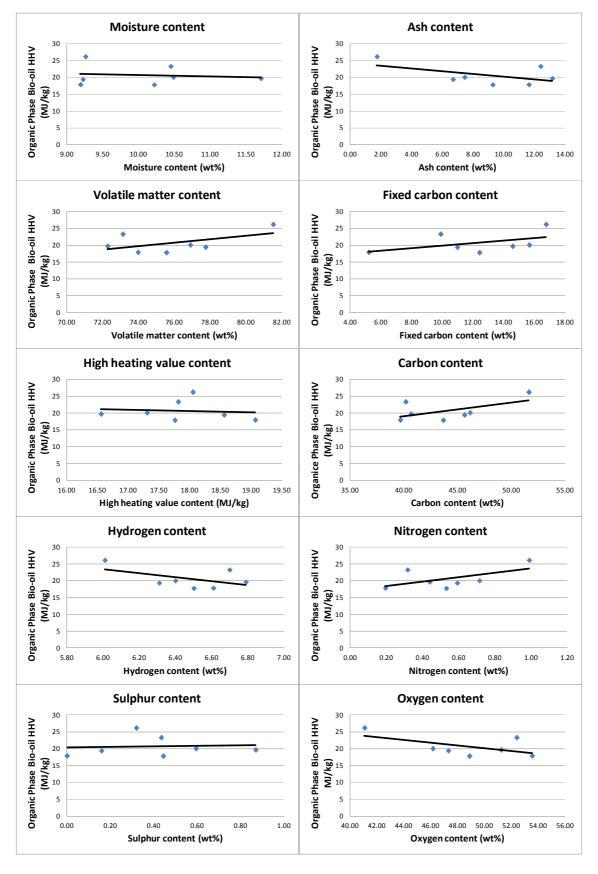


Figure 2: Relation of feedstock element characteristic to organic phase bio-oil HHV

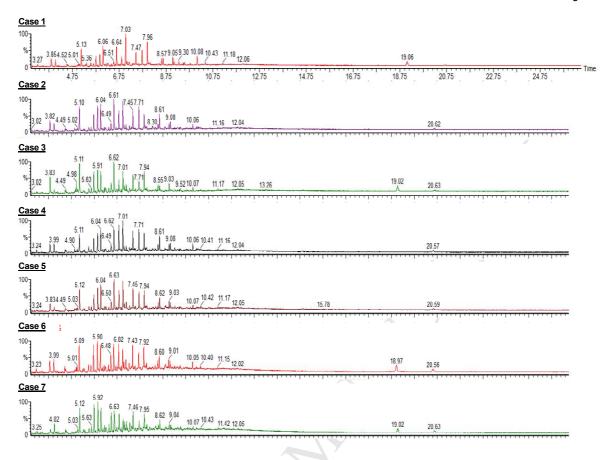
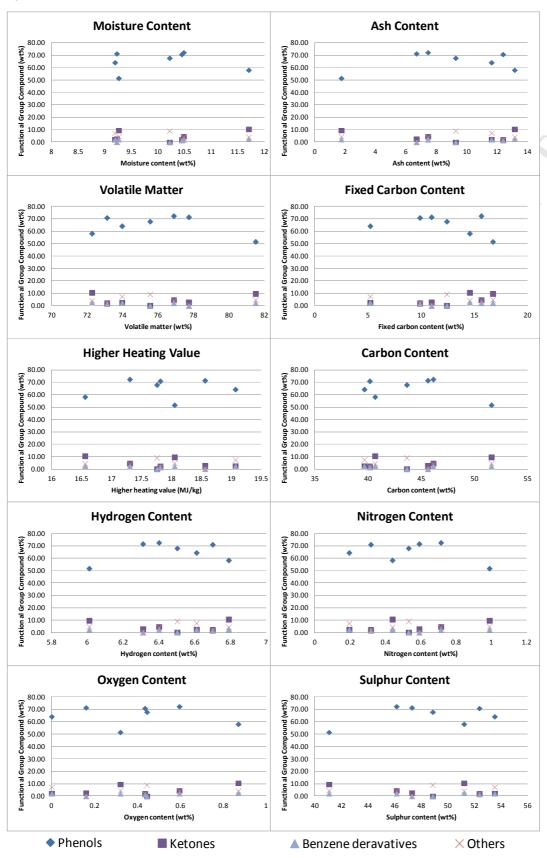


Figure 3: Chromatogram for bio-oil compound analysis



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Figure 4(a): Relation of feedstock element characteristic to organic phase bio-oil functional compounds

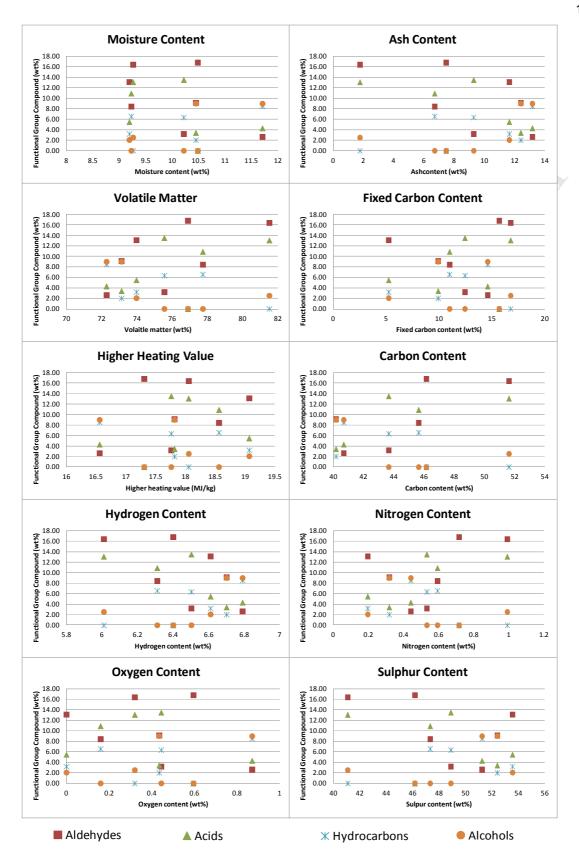
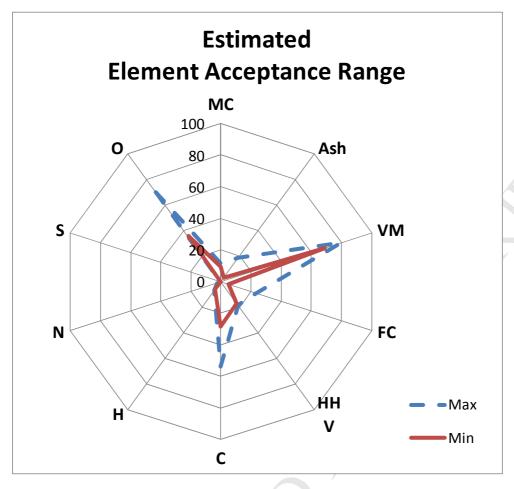
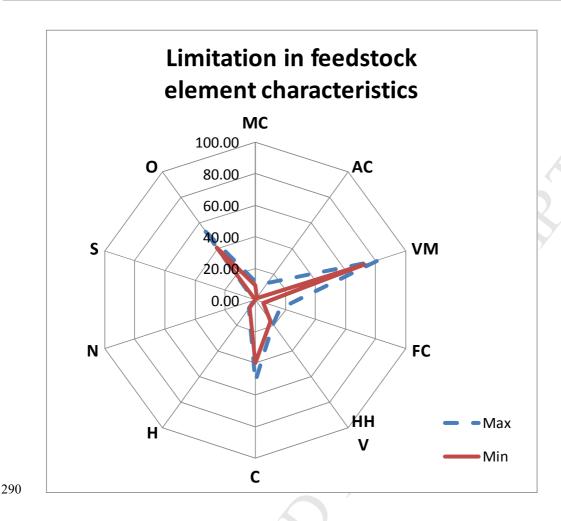


Figure 4(b): Relation of feedstock element characteristic to organic phase bio-oil functional compounds



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Figure 5: Estimated element acceptance range to generate 35wt% to 40wt% of produced bio-oil



291 Figure 6: Research limitation for biomass feedstock element characteristic

6. Conclusions

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Three biomass species are used as biomass feedstock for pyrolysis for bio-oil production including Napier grass stem, rice husk and sago biomass. Mixing ratio of the biomasses is altered to create unique element characteristic of biomass feedstock. The impact of varies biomass feedstock element characteristics to process outputs, including overall produced bio-oil yield, aqueous phase bio-oil yield, organic phase bio-oil yield, and HHV of organic phase bio-oil are analysed. Based on the relations, systematic process output estimation is proposed using element targeting approach. This approach enables construction of element acceptance range for respective technology, in this case fixed bed pyrolysis, to integrate alternative biomass into existing process without major modification. The analysis shows that total produced bio-oil yield, aqueous phase bio-oil yield, organic phase bio-oil yield and organic phase bio-oil higher heating value generally has linear relations with feedstock element characteristics. Nevertheless, no significant relation is observed in the comparison of organic phase bio-oil compounds with respect to feedstock properties. Several advantages of element targeting approach are discussed such as integration of underutilised biomass into existing process. This enhances feedstock flexibility of process technology and at the same time reduces waste management for cleaner production. However, the proposed results are limited to the biomass element characteristics range based on the three biomass species. More experimental work on various biomass species are required to widen the range of element characteristic study in biomass pyrolysis.

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References

- BS EN 14774-1., 2009. Solid biofuels. Determination of moisture content. Oven dry method. Total moisture. British Standards Institution, London, UK.
- Choi, J.H., Woo, H.C., Suh, D.J., 2014. Pyrolysis of seaweeds for bio-oil and bio-char production. Chemical Engineering Transactions, 37,121-126.
- Ellis, N., Masnadi, M.S., Roberts, D.G., Kochanek, M.A., Ilyushechkin, A.Y., 2015. Mineral matter interactions during co-pyrolysis of coal and biomass and their impact on intrinsic char co-gasification reactivity. Chemical Engineering Journal, 279, 402-408.
- Giudicianni, P., Cardone, G., Sprrentino, G., Ragucci, R., 2014. Hemicellulose, cellulose and lignin interactions on Arundo donaz steam assisted pyrolysis. Journal of Analytical and Applied Pyrolysis, 110, 138-146.
- Goh, C. S., Tan, K. T., Lee, K. T., Bhatia, S., 2010. Bio-ethanol from lignocellulose: Status, perspectives and challenges in Malaysia. Bioresource Technology, 101, 4834-4841.
- Gold, S., Seuring, S., 2011. Supply chain and logistics issues of bio-energy production. Journal of Cleaner Production, 19(1), 32-42.
- He, Y., Fang, Z., Zhang, J., Li, X., Bao, J., 2014. De-ashing treatment of corn stover improves the efficiencies of enzymatic hydrolysis and consequent ethanol fermentation. Bioresource Technology, 169, 552-558.
- Klemeš, J.J., Friedler, F., Bulatov, I., Varbanov, P.S., 2011. Sustainability in the Process Industry: Integration and Optimization. The McGraw-Hill Companies, Inc., U.S.
- Klemeš, J.J., Varbanov, P.S., 2013. New developments in Heat Integration and intensification, including Total Site, waste-to-energy, supply chains and fundamental concepts. Applied Thermal Engineering, 61, 1-6.
- Kotarska, K., Świercyńska, A., Dziemianowicz, W., 2015. Study on the decomposition of lignocellulosic biomass and subjecting it to alcoholic fermentation: Study on the decomposition of lignocellulosic biomass. Renewable Energy, 75, 389-394.
- Li, H., Kim, N., Jiang, M., Kang, J.W., Chang, H.N., 2009. Simultaneous saccharification and fermentation of lignocellulosic residues pretreated with phosphoric acid–acetone for bioethanol production. Bioresource Technology, 100, 3245–3251.
- Lim, C.H., Lam, H.L., 2014. Biomass Demand-Resources Value Targeting. Energy Conversion and Management, 87, 1202-1209.
- Lim, C.H., Lam, H.L., 2016. Biomass supply chain optimisation via novel Biomass Element Life Cycle Analysis (BELCA). Applied Energy, 161, 733-745.
 - Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusuf, S., Alshareef, I., Chin, S.A., 2015. Pyrolysis of Napier Grass in aFied Bed Reactor: Effect of Operating Conditions on Product Yiealds and Characteristics, BioResources, 10(4), 6457-6478.
- Mohammed M.A.A., Salmiaton A, Azlina W.A.K.G.W., Amran M.S.M., Razi A.F., Yap Y.H.T., 2011.
 Hydrogen rich gas from oil palm biomass as a potential source of renewable energy in Malaysia.
 Renewable and Sustainable Energy Reviews, 15, 1258-1270.
- Ng, W.P.Q., Lam, H.L., Ng, F.Y., Kamal, M., Lim, J.H.E., 2012. Waste-to-wealth: green potential from palm biomass in Malaysia. Journal of Cleaner Production, 34, 57-65.
- Rabacai, M., Costa, M., Vascellari, M., Hasse, C., 2014. Kinetic modelling of sawdust and beech wood pyrolysis in drop tube reactors using advance predictive models. Chemical Engineering Transactions, 37, 79-84.

ACCEPTED MANUSCRIPT

1. Highlights

- To study impact of feedstock element characteristics to pyrolysis process outputs
- Construction of element acceptance range for fixed bed pyrolysis
- Integrate alternative biomass as feedstock without major process modification
- Estimation of process outputs in the event of feedstock properties uncertainty

