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Organic Waste Valorisation via Graphical Pinch Analysis of Carbon-to-Nitrogen Ratio Number

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Organic waste valorisation processes becoming popular organic waste management strategies in recent years, as resolving the environmental issues caused by organic waste disposal and making it into useful resources. Organic wastes can be valorised by mixing with other organic wastes to fulfil the requirement of designated bioprocesses such as the production of H₂, CH₄ and C₂H₅OH. The amount of carbon and nitrogen was the main factor to be considered in this study, expressed in terms of carbon-to-nitrogen ratio number, Nc:N. The locally available organic wastes were used as the main supply of carbon and nitrogen. As the organic waste produced in different cities varies every day, the local organic wastes might not be able to provide sufficient carbon and nitrogen demanded by the designated bioprocesses. This research will reveal the amount of carbon and nitrogen required from external supplies to mix with the carbon and nitrogen found in local organic wastes. The reversed supply composite curve (SCC) shifting was performed when the total cumulative loading rate of SCC lesser than the demand composite curve (DCC). The reversed SCC shifting revealed the details of external supplies in terms of mass flowrates and the carbon-to-nitrogen ratio numbers. The steps of performing reversed SCC shifting were developed from this research. The reversed SCC shifting began from the ending point of SCC and DCC avoided the outsourcing of pure nitrogen as an external supply. Before performing reversed SCC shifting, linear interpolation calculation was applied to identify the horizontal and vertical distances of SCC from demand vertices. In Case Study 1, 10 kg/d of local resources wasted as the total cumulative loading rate of SCC greater than DCC. Case Study 2 required to outsource 8.33 kg/d pure nitrogen and 11.67 kg/d external supply with 42 N_{C:N} to fulfil the carbon-to-nitrogen ratio number demanded by the designated bioprocesses. To avoid outsourcing pure nitrogen as an external supply, different SCC shifting approaches were developed in Case Study 3. The reversed SCC shifting revealed Case Study 3 required 17.785 kg/d external supply with 12.75 N_{C:N} and 2.215 kg/d external supply with 118.82 N_{C:N}. The carbon-tonitrogen ratio numbers of external supplies required by Case Study 3 able to obtain from typical organic wastes and brown wastes such as woodchips and sawdust. This research developed an Organic Waste Valorisation Pinch Analysis (OWVPA) in terms of carbon-to-nitrogen ratio numbers combined with reversed SCC shifting approaches. This Pinch Analysis is a robust and effective tool to estimate the mass flowrate and carbon-to-nitrogen ratio numbers of external supplies required by the designated demand sides.

1. Introduction

Currently, more than 7 B populations are existing on the earth. With the rapid growth rate, it is expected the population will reach 10 B by the year 2055. The growth of the human population accelerates the food consumption to satisfy the increasing demands. As reported by the Food and Agricultural Organization (FAO), more than one-third of the food including edible and non-edible parts are wasted along the supply chains such as agricultural production, post-harvest handling and storage, processing and packaging, distribution and consumption. Nearly 1,300 Mt of food wasted around the world annually able to feed up to 2 B people. In Malaysia, the most widely used method for food waste disposal is landfill as it is cost-effective and easy to

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execute. Food wastes mainly made up of organic matters that will undergo anaerobic decomposition process and emits greenhouse gases (GHG) such as CH₄ (Lim et al., 2016). CH₄ is known as one of the potent GHG that causing global warming, with the ability to trap heat roughly 30 times more than the CO2 do (Yvon-Durocher et al., 2014). The emergence of organic waste valorisation processes to produce C₂H₅OH, H₂ and CH4 (Uçkun Kiran et al., 2014) becoming a trending solution to mitigate the issue of global warming caused by food waste disposal. The carbon-to-nitrogen ratio (N_{C:N}) plays an important role for the production of these products. Excess N can inhibit cell growth due to NH3 toxicity and shifting of metabolic pathway, whereas low N concentration can compromise cell growth (Anzola-Rojas et al., 2015). The optimal range varies as they are governed by different microorganisms and are dependent on the strains used and the operating conditions. The tolerable N_{C:N} reported in literature for H₂ production goes from 26.2 using microalgae (Xia et al., 2016) and up to 40-190 using mixed consortium (Anzola-Rojas et al., 2015). A Nc:N of 100-250 was reported for the co-production of H₂ and C₂H₅OH with Ethanoligenens and Clostridium sp. as the dominant fermenters (Carosia et al., 2017). The CH₄ production was reported to have an optimal N_{C:N} of 25 for the codigestion of food waste with paper waste (Shahbaz et al., 2020) and a tolerable range of 9-50 for the monodigestion of water buffalo manure (Guarino et al., 2016). Each bioprocess has unique N_{C:N} requirement, codigestion able to adjust the N_{CN} of the feedstock using multiple sources of organic wastes. For biogas generation, co-digestion has higher biogas productivity than mono-digestion (Wiwatwongwana et al., 2020). The daily organic wastes produced varies across different cities and the availability of the organic wastes fluctuated every day. Before valorise the organic wastes into the feed-in materials of bioprocesses, the scale of the project needs to be fixed. With the fluctuated daily organic wastes locally available, this research aims to reveal the required mass flowrates of external supplies with a specific carbon-to-nitrogen ratio number using Pinch Analysis. The fundamental Pinch methodology was adopted from the Water Pinch Analysis (Alwi and Manan, 2007). Pinch Analysis is a well-established technique applied across multiple fields such as Carbon Emission Pinch Analysis (Andiappan et al., 2019), Water Scarcity Pinch Analysis (Jia et al., 2020), Electric System Cascade Analysis (Ho et al., 2014), Financial Pinch Analysis (Roychaudhuri et al., 2017) and Quantitative Decision Framework Pinch Analysis (Basu et al., 2017). Until now, there is no targeting of carbonto-nitrogen ratio using Pinch Analysis, hence in this work the methodology for Organic Waste Valorisation Pinch Analysis (OWVPA) will be developed.

2. Methodology development

In this paper, the carbon-to-nitrogen ratio number will be denoted as $N_{C:N}$. There were 5 types of organic wastes (represent the $N_{C:N}$ of supply sides) and 3 bioprocesses (represent the $N_{C:N}$ of demand sides) were chosen from online literature. The organic wastes were sewage sludge (9 $N_{C:N}$), empty fruit brunch (15 $N_{C:N}$), food waste (24 $N_{C:N}$), dairy manure (29 $N_{C:N}$) and leaves (40 $N_{C:N}$). The designated bioprocesses were production of hydrogen, H₂ (20 $N_{C:N}$), methane gas, CH₄(27 $N_{C:N}$) and ethanol, C₂H₅OH (35 $N_{C:N}$). To satisfy carbon and nitrogen demanded by the designated bioprocesses, the total loading rate of supply and demand sides must be the same. In this research, it was assumed that the mixing among the organic wastes formed a homogeneous mixture. This study only focus on the adjustment of $N_{C:N}$ in the feedstock of designated bioprocesses, other components such as temperature, humidity, substrate to inoculum ratio were not discuss in this work but can be taken into account for future work.

2.1 Case study and data collection

Sets of carbon-to-nitrogen ratio number data for the demand and supply sides in Case Study 1 were as shown in Table 1 and 2. The carbon-to-nitrogen ratio number for each source and demand sides were collected from online literature. The details of supply and demand sides were arranged according to the ascending order of their carbon-to-nitrogen ratio number. The loading rate (kg/d) for each supply and demand sides was calculated using the Eq(1).

Loading Rate = N_{C:N} × Mass Flowrate

(1)

Demand sides	N _{C:N}	Mass	Cumulative	Loading	Cumulative
		flowrate (kg/d)	mass flowrate (kg/d)	rate (kg/d)	loading rate (kg/d)
H ₂	20	50	50	1,000	1,000
CH ₄	27	30	80	810	1,810
C ₂ H ₅ OH	35	40	120	1,400	3,210

Table 1: The N_{C:N} and illustrative mass flowrate for different demands for Case Study 1, 2 and 3

Supply sides	Nc:N	Mass Flowrate	Cumulative	Loading	Cumulative
		(kg/d)	MF (kg/d)	rate (kg/d)	loading rate (kg/d)
Sewage sludge	9	10	10	90	90
Empty fruit brunch	15	20	30	300	390
Food waste	24	30	60	720	1,110
Dairy manure	29	40	100	1,160	2,270
Leaves	40	30	130	1,200	3,470

Table 2: The NC:N and illustrative mass flowrate for different sources for Case Study 1

2.2 Construct a graph of cumulative loadir	g rate versus cumulative mass flowrate with SCC and DCC
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A graph of cumulative loading rate versus cumulative mass flowrate for supply and demand sides was plotted as supply composite curve (SCC) and demand composite curve (DCC) as in Figure 1. The cumulative loading rate and cumulative mass flowrate of SCC higher than DCC which indicated sufficient resources to fulfill the demand sides. A "Top gap" yielded with SCC located at the right side of DCC showed that there was an excessive 10 kg/d of local supplies will be wasted.



Figure 1: Graph of cumulative loading rate against cumulative mass flowrate for Case Study 1.

2.3 Perform SCC shifting to yield pinch point

For Case Study 2, different organic wastes locally available (Table 3) were used to target the same demand sides as in Case Study 1. A graph of cumulative loading rate against cumulative mass flowrate for Case Study 2 was plotted in Figure 2.

Supply sides	N _{C:N}	Mass	Cumulative	Loading	Cumulative
		flowrate (kg/d)	mass flowrate (kg/d)	rate (kg/d)	loading rate (kg/d)
Food waste	24	80	80	1,920	1,920
Leaves	40	20	100	800	2,720

Table 3: The NC:N and illustrative mass flowrate for different sources for Case Study 2

The total cumulative loading rate and total cumulative mass flowrate of SCC lower than DCC, indicating the insufficient local resources to fulfill the demand sides. To reveal the mass flowrates and carbon-to-nitrogen ratio number of external supplies, the SCC had to shift to the right side of the DCC until a pinch point formed while intercepting both curves. As pinch point only occurs at demand vertices, the horizontal distance between the SCC and DCC needs to be calculated via linear interpolation. The value of the horizontal distance is positive if DCC is to the left of the SCC and vice versa. The smallest negative value of horizontal distance indicates how far the SCC had to shift to the right side from the current position to yield pinch point. In Figure 2, two demand vertices located within the cumulative loading rate of SCC. The demand vertices were Point A (50 kg/d, 1,000 kg/d) and Point B (80 kg/d, 1,810 kg/d). The cumulative mass flowrates of SCC obtained from

linear interpolation were 41.67 kg/d (refer to the y-axis of Point A) and 75.42 kg/d (refer to the y-axis of Point B). The horizontal distance between SCC and demand vertices were -8.33 kg/d (from Point A) and -4.58 kg/d (from Point B). The most negative value obtained from the horizontal distances indicated SCC had to shift horizontally by 8.33 kg/d to the right. The pinch point occurred at Point A after SCC shifted.



Figure 2: Graphical illustration before and after SCC shifting for Case Study 2.

2.4 Identify the external supplies required and excess resources

The "Bottom gap" located at the starting point of the shifted SCC and DCC while the "Top gap" located at the ending points of the shifted SCC and DCC. For Bottom gap, if SCC located on the right side of DCC, external supplies are required to satisfy the demands of designated bioprocesses and vice versa. For Top gap, if SCC located on the right side of SCC, the local organic waste available more than required to fulfill the designated bioprocesses and vice versa. Figure 2 shown the Bottom gap and Top gap required 8.33 kg/d and 11.67 kg/d of external supply. In the graph of cumulative C:N ratio loading rate versus cumulative mass flowrate, the gradient of lines representing the carbon-to-nitrogen ratio number. At the Bottom gap, the horizontal line "Outsource 1" with a gradient of 0 formed by joining the starting point of shifted SCC (8.33 kg/d, 0 kg/d) and DCC (0 kg/d, 0 kg/d). The line "Outsource 1" with a gradient of 0 indicated an external supply with 0 N_{C:N} was required. At Top gap, the line "Outsource 2" with a gradient of 42 formed when the ending point of shifted SCC (108.33kg/d, 2720 kg/d) and DCC (120 kg/d, 3210 kg/d) joined together. The line "Outsource 2" indicated the Top gap required an external supply with 42 N_{C:N}. To fulfill the carbon-to-nitrogen ratio number required by the designated bioprocesses in Case Study 2, two external supplies were required to add with the locally available organic wastes. The two external supplies were 8.33 kg/d of supply with 0 N_{C:N} and 11.67 kg/d of supply with 42 N_{C:N}. The source with 0 N_{C:N} is also known as pure nitrogen. The use of pure nitrogen as an external supply not a realistic solution as no organic wastes comprise of pure nitrogen and the use of pure nitrogen is not economically feasible. To avoid that, Case Study 3 was being studied using the same supply and demand data as in Case Study 2. Novel approaches to perform SCC shifting was conducted in Case Study 3. For Case Study 3, the targeting of demand sides starts from the end of DCC, Point D (120 kg/d, 3,210 kg/d)

For Case Study 3, the targeting of demand sides starts from the end of DCC, Point D (120 kg/d, 3,210 kg/d) as shown in Figure 2. To form a pinch point, the last plotted point of SCC, Point C (100 kg/d, 2,720 kg/d) must be overlapped with the Point D of DCC. As illustrated in Figure 3, the SCC shifted horizontally by 20 kg/d to the right and vertically by 490 kg/d upward to form Pinch 1. Pinch 2 formed at (89.09 kg/d, 2148.18 kg/d) when the line S1' (y=24x+10) intercepted with line D3 (y=35x-990). Part of the line S1' that located above DCC will be shifted downward, named as line S1''. The first point and last point of line S1'' identified as Point E (20 kg/d, 490 kg/d) and Point F (89.09 kg/d, 2,148.18 kg/d). Before line S1'' shifted downward, the vertical distance of line S1'' from demand vertices were calculated via linear interpolation. The demand vertices that located below the line S1'' were Point A (50 kg/d, 1,000 kg/d) and Point B (80 kg/d, 1810 kg/d). By referring to

the x-axes of Point A and Point B, the cumulative loading rates located on line S1' vertically above the Point A and Point B were 1,210 kg/d and 1,930 kg/d. The vertical distance obtained between line S1" and demand vertices (Point A and Point B) were 120 kg/d and 210 kg/d. The line S1" shifted downward according to the greatest vertical distance, that was 210 kg/d. While the line S1" shifting downward, the ending point of S1", Point F must intercept with the locus of S2' (y=40x-1590). This is to prevent the use of external supplies comprises of pure carbon composition, which is not commonly found in organic wastes. The gradient for line S1' same as line S1", that is 24.



– – – – Locus of S2'

Figure 3: Graphical illustration after SCC shifting for Case Study 3.

In Figure 4, the line S1" intercept with the DCC at demand vertex of Point A (50 kg/d, 1000 kg/d) formed line S1" with the equation of y=24x-200. To calculate the coordinate of the ending point of S1", the function of S1" (y=24x-200) equalized with the locus of S2' (y=40x-1590). The shifted Point F, named as Point F' located at the coordinate of (86.875 kg/d, 1885 kg/d).



Figure 4: Graphical illustration after second SCC shifting for Case Study 3.

The cumulative loading rate and cumulative mass flowrate of line S1" were 69.09 kg/d and 1658.18 kg/d. The line S1" started to plot from point E' (17.785 kg/d, 226.82 kg/d), intercepted Point A (50 kg/d, 1000 kg/d) and ended at point F'. The point E' and origin formed a straight line "Outsource 1". The Point F' and Pinch 2

formed line "Outsource 2". The line "Outsource 1" indicated 17.785 kg/d of external supply with 12.75 N_{C:N} was required and the line "Outsource 2" indicating 2.215 kg/d of external supply with 118.82 N_{C:N} was required. Case Study 3 required external supplies with N_{C:N} of 12.75 and 118.82 was practicable as they can found in real life. The example of organic waste with high N_{C:N} is brown wastes such as wood chips and sawdust.

3. Conclusions

In this work, a new Pinch Analysis known as the Organic Waste Valorisation Pinch Analysis (OWVPA) is developed to perform targeting of an organic waste valorisation supply chain in term of $N_{C:N}$. The optimization of external resources were done by plotting cumulative loading rate versus cumulative mass flowrate for supply and demand sides. This research provides a robust and effective tool for the decision makers to valorise organic wastes through bioconversions.

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