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Environmental Sustainability Assessment of Palm Lignocellulosic Biomass Pretreatment Methods

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Malaysia produces great quantities of waste lignocellulosic biomass every year from oil palm cultivation. Palm wastes are not currently utilised in a very productive manner because the relatively low price of petroleum-derived fuel has prevented biomass-derived fuel from gaining market share. It is envisaged that taking into account environmental sustainability in addition to cost in the evaluation of the viability of a fuel will make biomass-derived fuels more feasible for adoption compared to the conventional fossil fuels. The environmental sustainability metric Sustainable Process Index (SPI) is applied to several competing lignocellulosic biomass pretreatment methods, namely ozonolysis, ionic liquid treatment, and ammonia fibre expansion (AFEX). These methods are chosen because of the relatively novel processes, which are not commonly used at industrial scale. Existing studies have shown that these processes present possible improvement over conventional methods. Using the SPI methodology, it is determined that the total specific service area, a_{tot}, for AFEX is the lowest, the most environmentally sustainable process for the pretreatment of palm lignocellulosic biomass, followed by ozonolysis and then ionic liquid treatment.

1. Introduction

The sustainable process index (SPI) is an environmental sustainability metric that combines process inputs, outputs, infrastructure and labour into one measurement that can be used alongside cost in strategic decision-making process. In the SPI model, anthropogenic processes are represented by a process that takes in resources from the ecosphere and puts out products that must be assimilated back into the ecosphere. In tracking the input and output flows of a particular process, the surface area as a unit of accounting is used. Since all material resources and energy consumed are represented by the surface area needed in order to generate them in a sustainable manner, the SPI is said to be a sustainability-oriented measure (Narodoslawsky and Shahzad, 2015). Final products are represented by the surface area needed to incorporate them into the environment, based on known rates of deposition and sedimentation (Krotscheck and Narodoslawsky, 1996). Using the SPI methodology, several bioenergy systems had been assessed (Krotscheck et al., 2000). Results show that this methodology is able to capture the difference in sustainability between renewable resources and non-renewable resources. It has also proven useful for optimising existing processes (Shahzad et al., 2017).

One example of a renewable resource is the abundantly available lignocellulosic biomass - a by-product of the production of major cash crops. While other industrial crops like corn have started utilising their biomass waste, the same cannot be said of the oil palm cultivation in Malaysia and neighbouring countries. The processing of biomass waste into higher-value products is an area of active research, with the goal of competing with conventional petrochemical products. Along the waste biomass processing chain, the pretreatment stage consumes a large amount of energy and resources. Faced with growing criticisms of its environmental impact, the oil palm industry needs a tool to systematically and quantitatively evaluate the environmental sustainability of growing oil palm and synthesising its derivative products. The footprint method is a promising tool for analysing the complex web of downstream processing of oil palm products.

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2. Methodology

In this study, the environmental footprint metric developed by Krotscheck and Narodoslawsky (1996), the Sustainable Process Index, is combined with the Lifecycle Impact Analysis (LCIA) in order to systematically evaluate the environmental sustainability of lignocellulosic biomass pretreatment methods. A lignocellulosic biomass pretreatment method is defined as a process that takes in raw lignocellulosic biomass, and produces treated biomass suitable for hydrolysis and fermentation into bioethanol.

Three lignocellulosic biomass pretreatment methods are chosen, with particular focus on chemical and physico-chemical treatment methods. A model reaction system is developed for each pretreatment method by using a previous optimisation study. A material and energy balance is developed based on the data published by each of the optimisation studies. The model reaction is set to be a continuous reaction at the small plant scale, with the functional unit being 100 g/s of oil palm biomass feed.

The total specific service area or total footprint, a_{tot} (m^2.y/kg biomass), is used as a comparative measure of sustainability (Krotscheck and Narodoslawsky, 1996). The a_{tot} of the various biomass pretreatment methods are calculated and compared. From Eq(1), the a_{tot} of a biomass pretreatment method is the ratio between the total embedded area assigned to the streams of material and energy entering or leaving the process, A_{tot} (m^2), and the mass flow of treated biomass, S_{tot}. A_{tot} is defined by Eq(2).

$$a_{tot} = \frac{A_{tot}}{S_{tot}} \tag{1}$$

$$A_{tot} = A_R + A_E + A_P \tag{2}$$

The values for A_R, A_E, and A_P are calculated according to the Eq(3) - Eq(5) listed in Table 1. In these equations, the specific service area terms have the unit m^2.y/kg for a material stream, m^2.y/MJ for an energy stream, and m^2.y/m^3 for the wastewater stream. The stream flow terms have the unit kg/s for a material stream, MJ/s for an energy stream, and m^3/s for the wastewater stream.

Table 1: Equations and descriptions for A_R, A_E, and A_P

Formula	Description	Equation number
$A_R = \sum_i a_{R,i} S_{R,i}$	Area required to supply the raw materials required for the process. It is the sum of the multiplication of the specific service area of the raw material, $a_{R,i}$, and the flow of each raw material stream, $S_{R,i}$,	Eq(3)
$A_E = \sum_i a_{E,i} S_{E,i}$	Area required to supply the energy input required for the process. It is the sum of the multiplication of the specific service area of the energy source, $a_{E,i}$, and the flow of each energy stream, $S_{E,i}$,	Eq(4)
$A_P = \sum_i a_{P,i} S_{P,i}$	Area required to accommodate the by-product of the process. It is the sum of the multiplication of the specific service area of the by-product stream, $a_{P,i}$ and the flow of each by-product stream, $S_{P,i}$,	Eq(5)

Excluded from the calculation of the total area are the area to provide the installation for the process, A_I, and the area required for the staff, A_S. The areas are assumed to be equal for each alternative method, and therefore not calculated.

3. Results and discussion

3.1 Defining the lignocellulosic biomass pretreatment methods

Three lignocellulosic biomass pretreatment methods are chosen based on their novelty and potential, namely ozonolysis treatment, ionic liquid treatment (IL), and ammonia fiber expansion treatment (AFEX).

The model ozonolysis pretreatment process to be analysed is adapted from Wan Omar and Saidina Amin (2016). Total Reducing Sugar (TRS) recovery and lignin degradation are the optimisation goal in this multi-response analysis. The oil palm frond (OPF) is grinded, then wetted with distilled water up to some moisture level. Ozone is then fed into the reaction chamber for the specified treatment time. After the treatment has run its course, the reaction chamber is purged of ozone. The biomass is washed with 5 % sodium hydroxide solution, filtered, and then dried.

A 99.9 % TRS recovery and 84.7 % lignin degradation is obtained by running the pretreatment with a 0.8 mm particle size, 40 wt% moisture content, 75 min reaction time, and 105 mL/min ozone flow rate with 19.5 % ozone consumption. The material flow in the pretreatment is shown in Table 2.

The model ionic liquid pretreatment process to be analysed is adapted from Tan et al. (2011). This study is an optimisation study using OPF as the lignocellulosic biomass, and glucose recovery as the optimisation goal. The OPF is shredded and sieved to have a maximum particle size of 1 mm. The ionic liquid used is 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). The biomass is mixed with the ionic liquid according to the specified solid loading percentage. It has been determined that the cellulose dissolves into the ionic liquid. At the end of the treatment, the dissolved cellulose is reconstituted by adding deionised water as the anti-solvent. The solution is allowed to cool to room temperature as the cellulose precipitates. The precipitate solid is separated and washed with more anti-solvent, then dried. 100 % glucose recovery from cellulose is obtained by running the pretreatment at the temperature of 80 °C, solid loading 10 %, and retention time 15 min. The material flow in this pretreatment process as described in the paper is summarised in Table 3. Ionic liquid has been demonstrated by Ramli et al. (2014) to be highly reusable, with small degradation in performance after each use. For this analysis, it is assumed that 12 % of the IL is replaced after each cycle in accordance with the rate of decrease in performance demonstrated in the previous study.

No optimisation study has been done on AFEX on oil palm biomass. Instead, the process parameter given by da Costa Sousa et al. (2016) is used, in which AFEX is applied to corn stover. The biomass is grinded to a size of 4 mm and added into a vessel. Water and liquid ammonia are added, and the vessel is sealed for the duration of the treatment as the water and ammonia react to give out heat and increase the pressure. After the duration of the treatment, pressure is released through a valve and the solid biomass is dried. The material flow in the process is shown in Table 4.

Table 2: Material balance of the ozonolysis using experimental data from Wan Omar and Saidina Amin (2016)

Stream	Mass flow (g/s)				
	Biomass	Water	Ozone	Residual	Total
Biomass feed	90	10	0	0	100
Water feed	0	50	0	0	50
Ozone feed	0	0	32.9	0	32.9
Reactor outlet	90	60	32.9	0	182.9
Washing feed	0	950	0	0	950
Filtrate	0	942.4	0	55.3	997.7
Filter cake	67.6	67.6	0	0	135.2
Treated biomass	67.6	7.5	0	0	75.1

Table 3: Material balance of the ionic liquid pretreatment using experimental data from Tan et al. (2011)

Stream	Mass flow (g/s)			
	Biomass	Water	[BMIM]Cl	Total
Biomass feed	90	10	0	100
IL feed	0	0	1,000	1,000
IL solution	90	10	1,000	1,100
Water feed	0	1,500	0	1,500
Decanter out	90	1,510	0	1,600
Filter cake	90	90	0	180
Filtrate	0	1,420	0	1,420
Treated biomass	90	10	0	100

Table 4: Material balance of the AFEX using experimental data from da Costa Sousa et al. (2016)

Stream	Mass flow (g/s)			
	Biomass	Water	Ammonia	Total
Biomass feed	90	10	0	100
Water feed	0	100	0	102
Reactor inlet	90	110	0	200
Ammonia feed	0	0	2	202
Treated biomass	92	10.2	0	102.2

3.2 Calculation of specific service areas of various process items

The specific service area Malaysian grid electricity, $a_{E,electricity}$, is calculated by taking the weighted average of the specific service areas of the sources of electricity, using their generation contribution as the weighting factor, as shown in Eq(6). The Malaysian grid electricity is composed of fossil fuel power plants (89.1 %), hydroelectric dams (10.3 %) and others (0.6 %) (Tenaga Nasional Berhad, 2014). The specific service areas of the energy sources are adopted from the SPIonWeb database as shown in Table 5.

$$a_{E,electricity}\ (m^2.y/MJ) = 0.891\ a_{fossilfuel} + 0.103\ a_{hydroelectricity} = 10.34 \quad (6)$$

Oil palm waste biomass is generated as a result of palm oil production. Multiple LCA studies have been done for oil palm plantations. Inventory data collected by Mohammadi Ashnani et al. (2014) and Choo et al. (2011) are used in this study. The specific service area calculation for the production of oil palm lignocellulosic biomass is summarised in Table 6.

Ozone is not suitable for long distance transportation due to its short half-life as well as decomposition and corrosion hazard. It is customarily generated on-site close to where it is used. Chen et al. (2006) stated that an energy yield of 173 g O_3/kWh is possible. Using the specific service area for grid electricity above, the specific service area of ozone generated on-site can be calculated as 215 m^2.y/kg O_3.

As of the writing of this article, no ionic liquid appears to be in the SPIonWeb database. The closest analog present is the entry named “Benzimidazole compounds” with a footprint of 13,405.348 m^2.y/kg. This entry will be used as a stand-in for the ionic liquid used in the one of the pretreatment process. This compound has a far higher specific service area than any other species encountered in this study, which is consistent with the remarks from previous researchers that the ionic liquid is very costly and any effort to reduce its use will be very beneficial.

Table 5: Specific service area values extracted from the SPIonWeb database (Narodoslawsky, 2013)

Item	Specific service area, a (m^2.y/unit)	Unit
Fossil fuel / Diesel	11.6	MJ
Hydroelectricity	0.0065	MJ
Ammonium Nitrate	698	kg
K_2O	467	kg
H_3PO_4	520	kg
$MgSO_4$	169	kg
Wastewater	1,458	m^3
Ozone	552	kg
Benzylimidazole compounds	13,405	kg
Ammonia	137.5	kg

Table 6: Specific service area calculation for the production of oil palm lignocellulosic biomass in Malaysia

Item	Stream, S (unit/y)	Unit	Service area, A (m^2)
--- INPUT ---			
Plantation	2,724	m^2	2,724
Diesel	645.5	MJ	7,488
Electricity (Malaysia)	2.0	MJ	20.67
Ammonium nitrate	25.5	kg	17,800
K_2O	45.5	kg	21,250
H_3PO_4	7.5	kg	3,900
$MgSO_4$	12.7	kg	2,146
TOTAL			55,330
--- OUTPUT ---			
Lignocellulose Biomass	3,190	kg	
Specific service area, a_R	17.34	m^2.y/kg	

3.3 Calculation of total specific service areas of the lignocellulosic biomass pretreatment methods

Using the specific service area values described in Section 3.2, the footprint of each lignocellulosic biomass pretreatment methods is calculated. An inventory table is constructed using the experimental data reported in the previously cited study and described in Section 3.1, detailing all the major material and energy flows into and out of the reaction system model. Every item in the inventory table is assigned a service area, A, by multiplying the specific service area of that item, a, with the amount of flow of that item, S. The total footprint of a process, A_{tot}, is the sum of the footprint of all inventory items in the process. The inventory calculation is shown in Tables 7 - 9. In this model, the energy input of drying is represented by an air-dryer that burns fossil fuel in order to generate the hot dry air, as is the conventional practice in this industry (Choo et al., 2011). Diesel is used as a stand-in for the fossil fuel. The energy input of comminution is represented by a mill powered by electricity.

Table 7: Total specific surface area calculation for ozonolysis pretreatment

Item	Stream, S (unit/y)	Unit	Service area, A (m^2)
--- INPUT ---			
Oil palm biomass	0.1	kg	1.734
Ozone	0.0329	kg	7.079
Diesel	0.30	MJ	3.485
Electricity (Malaysia)	0.00529	MJ	0.05469
--- OUTPUT ---			
Wastewater	0.000998	m^3	0.551
Treated biomass	0.075	kg	
Total specific surface area, a_{tot}	171.8	m^2.y/kg	

Table 8: Total specific surface area calculation for ionic liquid pretreatment

Item	Stream, S (unit/y)	Unit	Service area, A (m^2)
--- INPUT ---			
Oil palm biomass	0.1	kg	1.734
Ionic liquid	0.12	kg	1608
Diesel	0.4	MJ	4.640
Electricity (Malaysia)	0.0024	MJ	0.02493
--- OUTPUT ---			
Wastewater	0.00142	m^3	0.7848
Treated biomass	0.1	kg	
Total specific surface area, a_{tot}	16,160	m^2.y/kg	

Table 9: Total specific surface area calculation for AFEX pretreatment

Item	Stream, S (unit/y)	Unit	Service area, A (m^2)
--- INPUT ---			
Oil palm biomass	0.1	kg	1.734
Liquid Ammonia	0.002	kg	0.2749
Diesel	0.5398	MJ	6.262
Electricity (Malaysia)	0.0000183	MJ	0.000189
--- OUTPUT ---			
Treated biomass	0.102	kg	
Total specific surface area, a_{tot}	80.91	m^2.y/kg	

From the specific service area calculated for the production of every kilogram of pre-treated biomass, it can be surmised that AFEX is the most sustainable at 80.91 m^2.y/kg, followed by ozonolysis at 171.8 m^2.y/kg and finally ionic liquid at 16,160 m^2.y/kg. Ionic liquid pretreatment is clearly unsustainable as its footprint is two orders of magnitude higher than the other two methods.

By examining the components of the total footprint area, one can determine the biggest contributor to unsustainability, and this information helps in the future development of the process. For the ionic liquid pretreatment, the biggest footprint comes from the ionic liquid itself. The first hurdle is getting accurate data in the first place, as in this study a stand-in chemical benzylimidazolium is used because that is the closest analog available in the database. Past that, the next step is clearly to optimise the use of ionic liquid in the process, for example to find an alternative ionic liquid that is capable of higher solid loading and recycle rate.

For the ozonolysis process, the generation of ozone itself is very energy intensive. In all three processes, the heat duty for drying the biomass at the end of the treatment is also significant. Finding a more environmentally sustainable alternative energy source for ozone generation and drying could greatly improve these processes.

The values of specific service area calculated in this study have a large uncertainty and are not complete. Only three out of five service area terms that make up the total service area are calculated, while the other two are assumed to be constant between the alternative pretreatment methods. The specific service area values taken from the literature is also very generic, for example the wastewater is not differentiated between the three pretreatment processes. The process parameters used in this study are from lab-scale experiments. The process parameters from plant-scale operation is expected to be very different. This study serves as a demonstration of the potential value of the SPI analysis. Future studies using this method could be applied to more realistic chemical processing systems.

4. Conclusions

Using the SPI methodology, it is determined that ammonia fibre expansion is the most environmentally sustainable process for the pretreatment of palm lignocellulosic biomass, followed by ozonolysis and ionic liquid treatment. The most significant contributors to the footprint are the special reagent used in the treatment processes and the energy for drying the biomass at the end of treatment. Optimising for lowering these parameters should be the goal of future optimisation studies.

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