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Pre- and Post-Treatment Assessment for the Anaerobic Digestion of Lignocellulosic Waste: P-graph

Yee Van Fan[a,*], Jiří Jaromír Klemeš[a], Chew Tin Lee[b]

[a]Sustainable Process Integration Laboratory – SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 616 00 Brno, Czech Republic
[b]Department of Bioprocess Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM) 81310 UTM Johor Bahru, Johor, Malaysia
fan@fme.vutbr.cz

Lignocellulosic waste is one of the most abundant and potential feedstocks for anaerobic digestion (AD), but the energy efficiency is limited by the lignocellulosic composition which is recalcitrant to biodegradation. Pre-treatment of feedstock and the post-treatment of biogas and digestate play a significant role in enhancing the AD efficiency as well as the product utilisation. This study aims to determine the cost-optimal pre-and post-treatment pathway for an AD of lignocellulosic waste by applying P-graph. The economic balance between the main operating cost, yield and quality of products were considered. The treatment options were overviewed followed by a case study considered a different combination of physical, chemical and biological pre-treatments, biogas post-treatment (combine heat and power, fuel cell, biomethane, biofuel) and digestate treatments. A total of 9 pre-treatments for lignocellulosic waste, 2 digestate post-treatments and 9 post-treatments for biogas were evaluated in this study. Chemical pre-treatment by CaO, post-treatment by H_2S removal with membrane separation for biomethane production and without the composting of digestate is suggested as the optimal treatment pathway for lignocellulosic waste.

1. Introduction

The sustainability of the waste to energy (WtE) technologies is affected by the characteristics of feedstock and the selection of processing pathway. Anaerobic digestion (AD) is one of the most common WtE technologies, producing energy through the biochemical conversion. Lignocellulosic waste is an abundant bioresource (Jönsson and Martin, 2016) and having a higher biogas potential than cattle slurry (15 - 25 m^3/t) and poultry (30 - 100 m^3/t) (NNFCC, 2017). The performance of lignocellulosic materials in anaerobic digestion (AD) is limited due to the recalcitrant characteristics. The energy output of AD is in the form of biogas and digestate as the by-product. The selection of pre-treatment is one of the key players in determining the biogas yield, especially in the case of lignocellulosic feedstocks. Biogas can be used to produce heat, electricity and biofuel. Digestate can be used as composting nutrient source. Post-treatment is usually needed to increase the quality of the product for utilisation or to facilitate the transportation. There are various of studies on identifying the suitable pre- (Rodriguez et al., 2017) or post-treatment (Wu et al., 2016) techniques for the AD. The focus of studies has been given to limited types of treatments and the P-graph approach has not been commonly used.

P-graph, described in Friedler et al. (1992), has been applied in different field of study for process optimisation and problem-solving. The related application of P-graph has been summarised by Klemeš and Varbanov (2015). The P-graph application for waste minimisation and processing is identified as a relatively new area with four studies recorded. Several developments have been recently presented. Atkins et al. (2016) identified the economic efficiency of different wood processing residues for biorefineries where P-graph was implemented. These studies extended the implication of P-graph to an even wider field and highlighted the problem-solving potential for waste processing management. P-graph provides optimised solutions illustrated in a simple framework. The manual selection and interpretation based on the calculated values as presented by Wu et al. (2016) could be challenging for complex problems. Leitner and Lindorfer (2016) evaluated the

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pre-treatment technology structure for wheat straw (lignocellulosic material) applying process network synthesis (P-graph) for maximised energy yield. The scopes of their study are limited to different process configurations of steam explosion pre-treatment and for the combined bioethanol and biomethane facility.

The aim of this study is to determine the cost-optimal pre-and post-treatment pathway for anaerobic digestion of lignocellulosic waste. This study reviews different types of pre-and post-treatment for the AD of high lignocellulosic materials. The available treatment options have been summarised. A case study considers different pre-treatment, digestate treatments and biogas post-treatments for different final utilisation was presented. The novel contribution has been the application of P-graph to simultaneously identifying the optimised pre- and post-treatment pathway for the AD of lignocellulosic waste.

2. Overview on the pre-and post-treatment of anaerobic digestion

The pre-treatment can be divided into physical, chemical, biological and the combined approaches as summarised in Table 1. This includes the increase of accessible surface area, decrystallisation of cellulose, solubilisation of hemicelluloses, solubilisation of lignin, alteration of lignin structure and/or formation of furfural, to improve biomass amenity to enzymes and microbes for further biogas production (Zheng et al., 2014).

Table 1: Pre-treatment approach for enhanced biogas production. Adapted from Montgomery and Bochmann (2014)^a and Zheng et al. (2014)^b

Approach	Method
Physical	• Mechanical (milling, grinding machines)^a • Thermal (liquid hot water)^b • Irradiation (microwave, ultrasound, gamma-ray, electron beam)^b • Extrusion- Friction heating, mixing and vigorous shearing upon pressure release^b • Steam explosion-heated with high pressure saturated steam and swiftly reduced to terminate the reaction^b
Chemical	• Alkaline (NaOH, Ca (OH)$_2$, KOH, NH$_3$.H$_2$O etc)^a • Acid (H$_2$SO$_4$, HCl, HNO$_3$, H$_3$PO$_4$ CH$_3$COOH etc)^a • Oxidative with peroxides^a • Ozonolysis: use of powerful oxidant (Ozone)^b
Biological	• Microbiological (Fungal, Bacteria, Consortium)^a • Enzymatic^a
Combined	• Thermochemical-Heating and use of chemical particularly acids^b • Steam treatment carried out with the addition of catalysts (H$_2$SO$_4$, SO$_2$, NaOH etc)^a • Acid catalysed steam treatment with enzymatic hydrolysis^b • Alkaline with enzymatic hydrolysis^b • Alkaline with ultrasound^b

The utilisation of biogas can be generally divided into heat and electricity production, injection into the natural gas grid or the production of vehicle fuel. Post-treatment improves the purity of biogas by removing the CO_2, H_2S, water etc to enhance the energy value/efficiency or to meet the standard quality requirement e.g. for gas grid injection. H_2S is toxic and corrosive. The removal approaches can be divided based on the H_2S concentration as described by Leme and Seabra (2017), including absorption, biological system and use of regenerable solid or liquid media. The CO_2 and H_2O removal methods include cooling effect dehydration, temperature swing adsorption, pressure water scrubbing, organic physical scrubbing, amine scrubbing, pressure swing adsorption and membrane separation (Leme and Seabra, 2017).

The common pathway for biogas utilisation is the combined generation of heat and power (CHP). Another promising biogas utilisation technology is biogas solid oxide fuel cells (Wu et al., 2016), which offers a higher electrical efficiency and higher tolerance to contaminant compared to the conventional CHP technology. The best utilisation of purifying biogas (in term of energy value) is for injection into the gas grid and vehicle fuel. The feasibility of this utilisation is highly dependent on the countries policies. The handling options of digestate include separation of solid and liquid, direct disposal (landfill), nutrient recovery-direct application to land or composting and biogas recovery (Pöschl et al., 2010). As pre-and post-treatments have a significant impact on the biogas yield, the end product utilisation, the energy input to output ratio as well as the economic feasibility, it is of great interest to study the suitable processing pathway.

3. Case study

The case study suggests the feasible pathway for the utilisation of lignocellulosic waste (LW) through AD by considering 9 types of pre-treatments, 2 digestate treatments and 9 post-treatments for biogas. P-graph (Friedler et al. 1992) Studio Version: 5.2.1.4 have been used to evaluate the optimised pre-and post-treatment pathways. The philosophy and application of P-graph framework are available at P-graph (2015).

The major operating cost of pre-and post-treatment was included in this study. The comparison is done on the same basis although some of the costings are not taken into consideration. E.g. the operation cost (EUR/t) of the AD was excluded for all the pathways with the assumption that the AD system is the same. The capital and maintenance costs are also excluded in the costing. The reported value in the results and discussion did not reflect the actual profit or break-even point from the respective AD pathways. It serves as an indicator for the optimised pre-and post-treatment pathway, where a higher value reflects a higher feasibility. Table 2 and 3 show the type and the input data of different pre-and post-treatment utilised in this study.

Table 2: The output and main operating cost of different pre-treatment for AD

Pre-treatment	Output[c] (m^3 biogas/t)	Reference	Main Operating Cost[a,d] (EUR/t)
1. No treatment (P0)	200	Azman et al. (2015)	-
2. Grinding (P1)	220	Mönch-Tegeder et al. (2014)	1.498
3. Steam explosion (P2)	232	Bauer et al. (2014)	1
4. Water vapour (P3)	208.6	Li et al. (2012)	0.12
5. CaO (P4)	318	Bruni et al. (2010)	10.56
6. NaOH (P5)	256	Sambusiti et al. (2012)	35.2
7. H_2SO_4 (P6)	231	Taherdanak et al. (2016)	2.64
8. Enzyme (P7)	255.8	Ziemiński and Kowalska-Wentel (2015)	11
9. Microbial consortium (P8)	393.26	Zhang et al. (2011)	840[b]

[a]Only the main operating cost of the process e.g. the electric/heat, the chemical cost for chemical treatment, the cost of the enzyme for biological treatment etc. were included. [b]Small scale experimental study, not necessary reflect the large-scale implementation. [c]Calculated based on the reported enhancement of biogas. [d]Price of consumables. CaO = 176 EUR/t, H_2SO_4 = 264 EUR/t, Enzyme = 1.1 EUR/t, NaOH = 352 EUR/t, Peptone = 0.126 EUR/g.

Table 3: The output and main operating cost of different post-treatment for AD

Post-treatment	Output (kWh/m^3 biogas)[b]	Reference	Main Operating Cost[a,c] (EUR/t)
• Biogas			
1. H_2S + Pressure water scrubbing (OP1)	9.500	Leme and Seabra (2017)	0.252
2. H_2S + Organic physical scrubbing (OP2)	9.409	Leme and Seabra (2017)	0.026
3. H_2S + Amine scrubbing (OP3)	9.895	Leme and Seabra (2017)	0.076
4. H_2S + Pressure swing adsorption (OP4)	8.924	Leme and Seabra (2017)	0.036
5. H_2S + Membrane separation (OP5)	9.752	Leme and Seabra (2017)	0.040
6. Post treatment for biofuel- water scrubber+ liquification (PT Biofuel L)	6.370	Larsson et al. (2015)	0.189
7. Post-treatment for CHP (PTCHP)	2.27 (Heat), 1.81 (Electricity)	Wu et al. (2016)	0.015
8. Post treatment for fuel cell (PTFC)	2.31 (Heat), 1.54 (Electricity)	Wu et al. (2016)	0.021
9. No post-treatment (NA)	0.6 m^3 of CH_4/ m^3	-	-
• Digestate			
1. Sterilisation and composting	0.5 t compost/t digestate	Pöschl et al. (2010)	1.26
2. No-treatment	0.9 t digestate/t feedstock	-	-

[a]Only the main operating cost of the process e.g. the electric/heat, water consumption for water scrubbing, the chemical cost for chemical treatment, the cost of the enzyme for biological treatment etc. were included. [b]Unit of the output, unless stated. [c]Water = 0.54 EUR/m^3.

Table 4 shows the important conversion factors and assumptions made. The input of lignocellulosic waste is assumed to be 100 t/y in this study.

Table 4: The assumptions and conversion factors

Assumptions/conversion factors	Reference
The potential biogas yield of lignocellulosic feedstock = 400 m^3/t	NNFCC (2017)
Electricity = 0.14 EUR/kWh	Wu et al. (2016)
Heat energy = 0.04 EUR/kWh	Wu et al. (2016)
Biofuel = 0.119 EUR/kWh	Larsson et al. (2015)
Compost = 3.81 EUR/t	Meyer-Kohlstock et al. (2015)
Digestate = 1.81 EUR/t	De Clercq et al. (2017)
Thermal and electrical efficiency of gas engine = 48.5 % and 38.7 %	Jenbacher Type 2
1 m^3 CH_4 = 10 kWh	Charles (2009)

Conversion rate: 1 BRL = 0.27 EUR; 1 USD = 0.88 EUR; 1 RMB = 0.13 EUR

3.1 Results and discussion

The possible pre-and post-treatment pathways by P-graph for the AD of LW are summarised in Figure 1. The optimal pathway was indicated with the bold line (black). The presented value in Figure 1 is the performance ratio obtained from the literature as listed in Table 2 and 3. The optimal (Bold line in black) flow value was highlighted by the bold font in green. Table 5 shows the other near optimal pathway identified by P-graph.

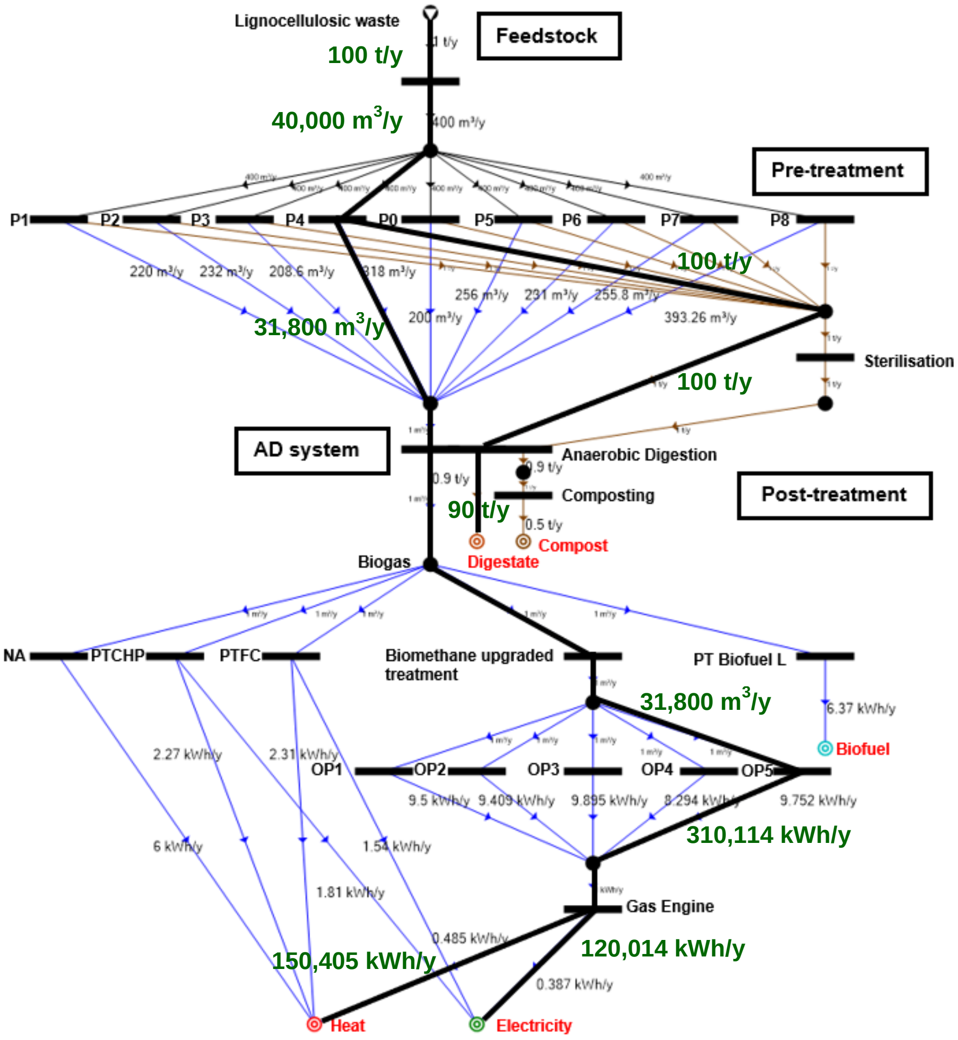

Figure 1: The original and the suggested optimised pathway (bold line in black). The blue line represents the flow of biogas and the brown line is for the flow of digestate. The abbreviation was defined in Table 2 and 3.

Table 5: Top 5 feasible (optimal/near optimal) structures identified by P-graph

Feasible structure	Value (EUR/y) *
P4, OP5 (Biomethane upgraded), without composting (as shown in Figure 1: Black bold line)	20,623.8
P4, OP5 (Biomethane upgraded), with composting	20,505.8
P4, OP2 (Biomethane upgraded), without composting	20,290.4
P4, OP2 (Biomethane upgraded), with composting	20,172.5
P4, OP3 (Biomethane upgraded), without composting	19,840.1

*Indicator for the optimised pathway, where a higher value reflects a higher feasibility. It did not reflect the actual profit. The calculation is based on 100 t/y of lignocellulosic waste.

The alkali pre-treatment by means of CaO (P4) were suggested to be more feasible than grinding (P1), steam explosion (P2), water vapour (P3), NaOH (P5), H_2SO_4 (P6), enzyme (P7), microbial consortium (P8) and no treatment (P0). The CaO treatment (Bruni et al., 2010) offers 59 % enhancement on the yield of biogas (200 m^3/t to 310 m^3/t) although the cost involved is higher than the physical approaches (grinding, steam explosion etc.), see Table 2. It could be a constraint if the investment cost is limited. The investment cost is not considered in this study. The reported retention time for CaO treatment is 10 d. This proposes the need for more holding vessel and higher investment cost for the same capacity to handle the same amount of LW/d. The environment footprints should also be considered in the future study, as that is the major disadvantage of chemical treatments. Based on the analysis, composting of digestate is comparatively less feasible than no treatment. The selling price of compost (3.81 EUR/t) is higher than the digestate (1.81 EUR/t) but the operating cost is significant, yet the product yield is 50 % lesser than the digestate. This could be subjected to the policy and the pricing in different countries. Digestate cannot be applied directly to the soil in some countries. The digestate value could be lower than the value stated in this study or even in negative if ended in the landfill due to tipping fees and transportation cost etc.

Biomethane upgraded (OP) was identified as the most suitable pathway among the no post-treatment (NA), post-treatment for the combined power and heat (PTCHP) and biofuel (PT Biofuel L) utilisation. Specifically, the OP5, H_2S removal with membrane separation as described in Leme and Seabra (2017). The following near optimal options are OP2 (H_2S removal + Organic physical scrubbing) and OP3 (H_2S removal + Amine scrubbing) as shown in Table 5. The upgraded treatment enhanced the quality/purity of methane in the biogas as well as the energy value and selling price. Injection of biomethane into a gas grid has not been considered as there are currently many barriers, both practical and financial (NNFCC, 2017). The distance between the AD plant with the gas distribution network, which is not considered in this study, could significantly affect the outcome. Another feasible post-treatment pathway identified by P-graph after the biomethane upgraded treatment was PT Biofuel L. This is currently not the final predominant use of biogas, except for Sweden and Germany (NNFCC, 2017) and should be promoted. Methane fuelled vehicles have lower emissions including NO_x and particulates (PM2.5 and PM10) compared to petrol and diesel vehicles (NNFCC, 2017).

4. Conclusions

Each treatment has its own advantages and limitations. There can hardly be a universal solution in improving the sustainability of AD. Different scenarios (substrate, scale, demand, policies) have the different constraints and requirement. In this study, P-graph has been used to determine the economical pre-and post-treatment processing balanced with the yield and quality of end-product. Based on the optimisation analysis, alkaline (CaO) pre-treatment, post-treatment for biomethane production (H_2S removal with membrane separation) and without the composting of digestate were identified as the better alternatives for LW. The presented case study subjected to several limitations. The future study should include the environmental footprints analysis, a more detail costing (transportation etc.), sensitivity analysis and expand the study from LW to a wider source of feedstocks. Different WtE technologies including thermochemical (incineration, gasification, pyrolysis), biochemical (sanitary landfill, microbial fuel cell) and chemical (esterification) can also be considered for a more comprehensive identification of optimised pathway.

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