TÉCNICO LISBOA

Biomethane potential laboratory-scale test (BMP) for the determination of biogas production from empty fruit bunches (EFB) derived during palm oil processing via co-digestion with palm oil mill effluent (POME)

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I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the *Universidade de Lisboa*.

To God.

To my parents, Edgar and Elsy, who never stop giving of themselves in countless ways.

To my grandmother and sister, Ana and Maryori, for their moral support during all these years.

To my wife, Diana, the symbol of love, courage, and sacrifice. This is because of you.

This work was accomplished by their hands.

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Abstract

The current thesis investigated biogas production from empty fruit bunches (EFB) as waste-to-energy valorization route using laboratory scale biomethane potential test (BMP), considering EFB pre-treatment and co-digestion with palm oil mill effluent (POME) as main strategies for enhancing methane yield. EFB pre-treatment using NaOH 0.1M at 80°C for 2 h with a recovery of 66.6% was carried out. $Ca(OH)_2$/Ash 60:40 (% wt.) was proposed for pH adjustment, leading to 4.82 ± 0.15 g used per litre of POME to reach a pH of 6.6 and 16.7% reduction on $Ca(OH)_2$ employed. Seven experiments were carried out during 22 days at mesophilic conditions and ambient temperature using the liquid displacement method to quantify CH_4 production. Lowest cumulative methane yield was 7.3 ± 0.3 mL CH_4/g VS for POME under facultative conditions while highest cumulative methane yield was 415 ± 34 mL CH_4/g VS for POME under anaerobic conditions. Alkaline pre-treatment showed no positive effect on biogas production from EFB and pre-treatment conditions should be reconsidered. Cumulative methane yield for co-digestion for POME and unpretreated EFB with a POME:EFB ratio of 6:2 in volatile solid (VS) basis was 369 ± 31 mL CH_4/g VS, equivalent to 46.5 m^3 CH_4 /ton of mixed EFB and POME, and simultaneous waste processing of 3.23% of total EFB and 4.98% to total ash produced on site via anaerobic co-digestion with a total solids and volatile solids removal of 81 ± 22% and 89± 18% respectively. Future research on pre-treatment parameters optimization, ash addition benefits for microbial community in anaerobic systems, and EFB:POME ratio evaluation will maximize methane yield.

Keywords

Biogas, Methane Yield, Pre-treatment, Co-digestion, Palm Oil Mill Effluent (POME), Empty Fruit Bunches (EFB).

Resumo

A presente tese investigou a produção de biogás a partir de cachos vazios de frutas (EFB) como forma de valorização energética destes resíduos, usando um teste de potencial de geração de biometano (BMP) à escala laboratorial; foram consideradas como principais estratégias para aumentar a produção de metano o pré-tratamento e co-digestão com efluente de óleo de palma (POME). O pré-tratamento de EFB foi realizado utilisando NaOH 0.1 M a 80 °C durante 2 h tendo-se obtido uma recuperação de 66.6%. Uma mistura de $Ca(OH)_2$/Cinza 60:40 (% em peso) foi proposta como forma de ajustar o pH; a utilização de 4.82 ± 0.15 g por litro de POME permitiu atingir um pH de 6.6 e uma redução de 16.7% no $Ca(OH)_2$ necessário. Foram realizadas sete experiências com uma duração de 22 dias, em condições mesofílicas e à temperatura ambiente, usando o método de deslocamento de líquido para quantificar a produção de CH_4. O rendimento cumulativo de metano mais baixo foi de 7.3 ± 0.3 mL CH_4 / g VS para POME em condições facultativas, enquanto o rendimento cumulativo mais alto foi de 415 ± 34 mL de CH_4 / g VS para POME em condições anaeróbicas. O pré-tratamento alcalino não mostrou nenhum efeito positivo na produção de biogás a partir de EFB e as condições de pré-tratamento devem ser reconsideradas. O rendimento cumulativo de metano para co-digestão de POME e EFB não tratado com uma relação POME:EFB de 6:2 em base sólida volátil (VS) foi de 369 ± 31 mL CH_4 / g VS, equivalente a 46.5 m^3 CH_4 / ton de EFB misturado e POME, e processamento simultâneo de resíduos de 3,23% do EFB total e 4,98% do total de cinzas produzidas localmente via co-digestão anaeróbia. Investigação futura poderá incidir sobre a otimização de parâmetros de pré-tratamento, os benefícios da adição de cinzas para a comunidade microbiana em sistemas anaeróbicos e avaliação da relação EFB: POME para maximizar o rendimento de metano.

Palavras-chave

Biogás, Rendimento de Metano, Pré-tratamento, Co-digestão, Efluente de Fábrica de Óleo de Palma (POME), Cachos Vazios de Frutas (EFB).

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BMP	Biomethane Potential Test
C/N	Carbon to Nitrogen Ratio
CAPEX	Capital Expenses
COD	Chemical Oxygen Demand
CPO	Crude Palm Oil
DC	Palm Oil Decanter Cake
DM	Dry Matter
EFB	Empty Fruit Bunches
FFB	Fresh Fruit Bunches
FM	Fresh matter
HHV	High Heating Value
IRR	Internal Rate of Return
ISR	Inoculum to Substrate Ratio
LHV	Lower Heating Value
NA	Not Applicable
NR	Not Reported
POM	Palm Oil Mill
POME	Palm Oil Mill Effluent
RPM	Revolutions per Minute
SHF	Separate Hydrolysis and Fermentation
SSF	Simultaneous Saccharification and Fermentation
TS	Total Solids
VFA	Volatile Fatty Acids
VS	Volatile Solids

List of Symbols

No symbols

List of Software

MS Excel 365   Data processing and graphing tool

Chapter 1

Introduction

This chapter starts with an overview of the palm oil industry globally, particularly focused in Colombia. For the following section, motivation and content are described, focusing on waste production in palm oil mill and limited applications for empty fruit bunches (EFB). Anaerobic co-digestion for simultaneous waste processing is proposed as novelty during this thesis. At the end of the chapter, a brief content of following chapters is given.

1.1 Overview

World palm oil production has been increasing during the last 30 years starting at a value of 81.7 million tonnes for 1994 and reaching a value of 410.7 million tonnes for 2019, showing an increment in 403% during considered timespan (FAOSTAT statistical database, 1997b). Colombia production during the same period of time exhibited a similar behaviour for palm oil production, raising from 1.68 million tonnes in 1994 to 8.39 million tonnes in 2019, resulting in an 400% increment which is comparable to world palm oil production (FAOSTAT statistical database, 1997b). Colombia average palm oil production between 1994 and 2019 was 3.9 million tonnes per year, reaching 5th place in the world with Indonesia (104.8 million tonnes/year), Malaysia (74.4 million tonnes/year), Nigeria (8.3 million tonnes/year), and Thailand (7.6 million tonnes/year) as top four oil palm producers globally (FAOSTAT statistical database, 1997a). Regarding oil palm production area in the world for 2019, top five in thousands of hectares are: Indonesia 12780 (56.1%), Malaysia 5200 (22.8%), Thailand 920 (4.0%), Nigeria 525 (2.3%), and Colombia 486 (2.1%) (Fedepalma, 2020). As top five producer, Colombia has an important role in palm oil market.

1.2   Motivation and Contents

During palm oil production, several liquid and solid waste streams are produced. Figure 1.1. shows a schematic flow diagram of a palm oil mill process. During first step, fresh fruit bunches are sterilized and stripped obtaining fresh fruits and Palm Oil Mill Effluent (POME) and Empty Fruit Bunches (EFB) (22%) as waste streams. Fresh fruits are transformed into palm oil and press cake by means of digestion, clarification and pressing processes with POME as waste stream (Total: 67% combined with previous step). Then, press cake goes to depericarping step producing nut and fibre (13.5%) as solid waste stream. Last but not least, nuts are cracked to obtain kernel (6%) and shell (5.5%) as waste stream. To sum up, liquid waste stream produced are POME while EFB, fibre, and shell are solid waste streams.
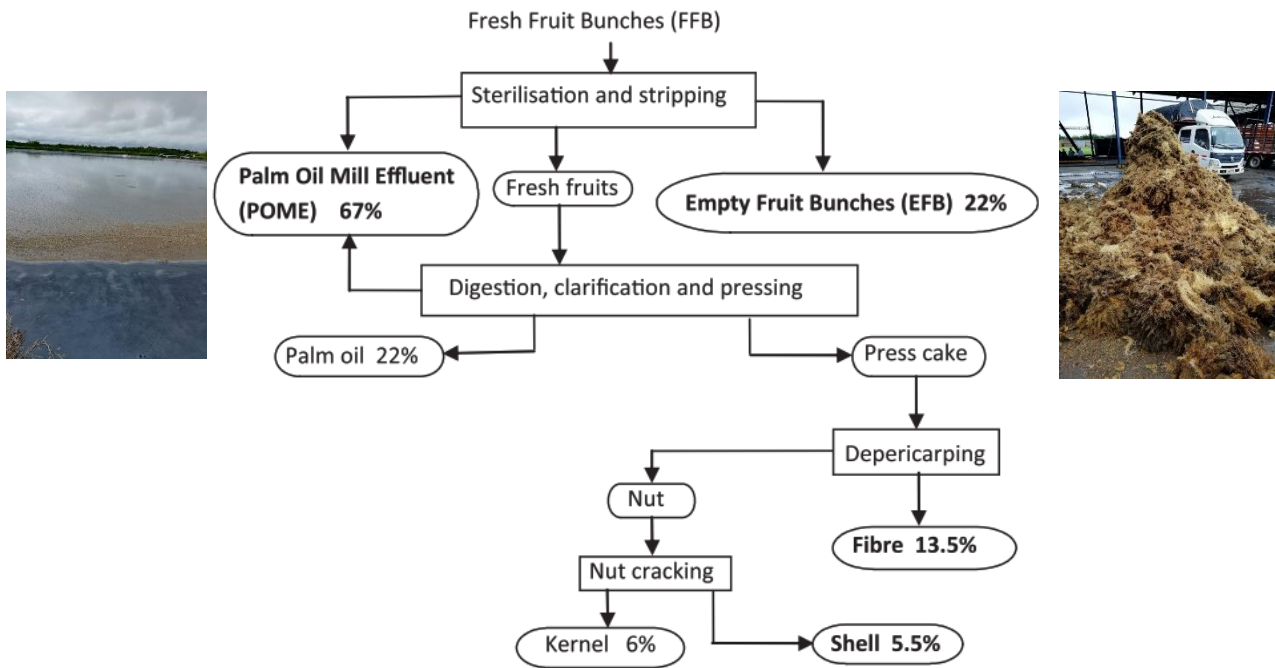
Figure 1.1. Simplified process flow diagram of an oil palm mill (main waste streams in bold, all percentages on wet fresh fruit bunch basis) (Sulaiman et al., 2011)

Other waste streams that could be considered are fronds, leaves, and trunks, which are produced on the field, and ash which is produced during fibre and shell combustion in the boiler (Rahayu et al., 2018).

Waste management for residues generated in palm oil mill (POM) are mostly focused on a waste-to-energy concept (Garcia-Nunez et al., 2016). For POME, a wastewater treatment system with biogas production is normally considered while for fibre and shell are usually employed as solid fuel for the boilers (Garcia-Nunez et al., 2016). However, EFB has not been considered in this approach mainly for its high moisture content which limits the application as solid fuel and high potassium content from EFB could lead to fouling and slagging problems in the boiler, limiting heat transfer in the boiler and increasing maintenance schedule (Garcia Nuñez et al., 2010; Tepsour et al., 2019). For these reasons, current uses in Colombia for EFB are mulching/soil amendment and composting (Ramírez et al., 2015) which are valorisation routes with no value-added products or energy production for a waste that reached 1.56 million ton EFB/year for 2019. Considering that Colombia's palm oil production was around 2% of world production for 2019 (FAOSTAT statistical database, 1997b), it is estimated that 78 million ton EFB per year were generated in 2019 globally.

The current thesis is precisely motivated by waste-to-energy valorisation route for EFB, which is non-existent in industrial scale, with an astonishing potential due to current uses in Colombia. In particular, the objective is to assess the biogas production as alternative use for EFB, considering the effect of alkaline pre-treatment and co-digestion with POME. The study aims at determining the conditions where the biogas production is maximized by means of laboratory-scale biomethane potential test (BMP).

Figure 1.2. summarizes current technology and proposed approach for this thesis, where three waste streams are processed simultaneously leading to value added products (digestate) and energy

generation via biogas production. No reports were found connected with biogas production utilizing these three waste types at the same time.
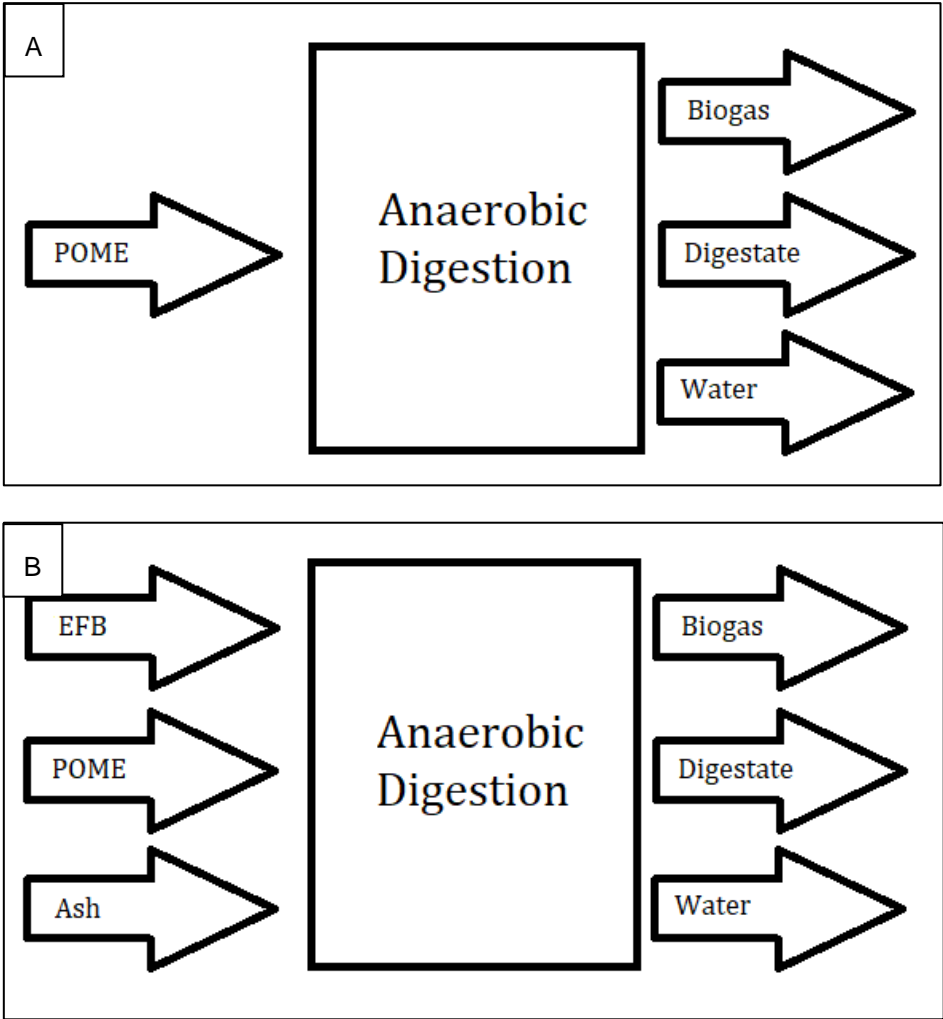
Figure 1.2. Waste-to energy valorisation routes via bigas production for A) current technology and B) thesis approach.

To perform this research, chapter 2 comprised a state-of the-art literature review with current and promising uses for EFB, biogas technology and biomethane potential test (BMP) description, and biogas production from POME and EFB.

Subsequently in chapter 3, materials and methods were described. Sampling for EFB, POME, ash, and inoculum as well as characterization employed for each starting material was included. Alkaline pretreatment for EFB and pH trials for ash procedures were described. Fixed and study variables (pre-treatment and co-digestion) were defined for biogas production experimental design (7 experiments) as well as experimental set-up details and methane yield calculations.

Results and discussion were collected in chapter 4. Data collected from material characterization, alkaline pre-treatment of EFB, and pH test for ash was compared to literature. Then, biomethane potential test (BMP) results were evaluated considering experimental set-up, biogas production from

POME and EFB and the influence of alkaline pre-treatment and co-digestion on enhancing methane yield from EFB.

Conclusions from this work and in connection with chapter 4 were outlined in chapter 5.

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Chapter 2

State of art literature review

Chapter 2 is a complete up-to-date summary of empty fruit bunches (EFB) uses and biogas technology at laboratory scale. This chapter provides in section 2.1 an overview of empty fruit bunches (EFB) properties, promising and current uses from literature and industry. For section 2.2, biogas production technology is introduced, considering main parameters for laboratory scale biomethane potential test (BMP), and effect of pre-treatment and co-digestion for enhancing methane yield. Last section is devoted to biogas production conditions and yields from palm oil mill effluent and (POME) and empty fruit bunches (EFB) including pre-treatment and co-digestion as alternatives in order to increase methane production.

2.1 Promising uses for EFB

2.1.1 Introduction

EFB (empty fruit bunches) is a non-wood lignocellulosic residue from palm oil processing and their average chemical composition is described in Table 2.1 (Garcia-Nunez et al., 2016). EFB is mainly composed of cellulose and hemicellulose with a low lignin content (ca.15%). In addition, EFB has a high water content (up to 70%) which should be taken into account for technologies where water is removed prior to processing. Its high content of potassium makes EFB a good nutrient source when fertilizing options (i.e., mulching, composting) are considered. Since it is estimated that the amount of crude palm Oil (CPO) (18 - 24% wt.% of fresh fruit bunches (FFB)) is almost as the amount of EFB produced (18 - 24% wt.% of FFB) (Garcia Nuñez et al., 2010), and the total production of CPO in Colombia is 1.56 million tonnes of CPO per year (Fedepalma, 2020), it is estimated that total production of EFB is 1.56 million ton EFB/year for 2019.

Table 2.1. EFB characterization (Garcia-Nunez et al., 2016).

Component	Mean	SD
Lignin (%)	15	8.9
Cellulose (%)	43	15.1
Hemicellulose (%)	21	6.3
Moisture (%)	36	28.8
Ash (%)	5.7	3.5
Volatiles (%)	80	5.8
C (%)	47	4.2
N (%)	0.6	0.4
S (%)	0.4	0.4
Mg (mg/kg)	913.5	-
P (mg/kg)	572.7	-
K (mg/kg)	5574.0	-

*SD: Standard deviation

2.1.2 Waste-to-Energy technologies for EFB processing

Several technologies have been evaluated to convert EFB into fuels, energy carriers, or as a direct source of energy such as direct incineration, pelletizing, bioethanol, bio-oil, biochar, and hydrogen/syngas production.

Direct incineration

The direct use of EFB in combustion processes is not carried out and even banned in countries such as Indonesia and Malaysia (Kaniapan et al., 2021) mainly due to heavy pollution effects. It is important to

note that high content of water significantly reduces its high heating value (8.2 kJ/kg) compared to kernel shell (21.4 kJ/kg) and fiber (19.2 kJ/kg), which are residues that feed the boilers in Palm Oil Mills (POM) (Garcia Nuñez et al., 2010). Additionally, high potassium content from EFB could lead to fouling and slagging problems in the boiler, limiting heat transfer in the boiler and increasing maintenance schedule (Tepsour et al., 2019).

Pellets production

The production of EFB pellets using sagu starch as agglutinant was evaluated (Rahman et al., 2013). The calorific value range from the resulting pellets was between 8160 kJ/kg to 17000 kJ/kg and the properties were similar to pinewood pellets. It is worth noting that drying was required prior to pelletization.

Pellets were produced from EFB and fiber mixtures obtaining briquettes with an average calorific value from 17,995 kJ/kg to 18,322 kJ/kg and briquette properties were comparable with commercial sawdust briquettes (Nasrin et al., 2011).

Steam explosion as used as pre-treatment for EFB pellets production (Lam et al., 2015), leading to a high heating value increase by 21% compared to unpretreated EFB. EFB was pre-treated at 220°C and 5 min and despite the fact that high energy compression was required, similar energy consumption is required as for wood pellets production. High heating value ranges from produced pellets was between 18.54 MJ/kg to 22.42 MJ/kg.

Main target of pelletization is to reduce moisture content, which is energy intensive for high water content starting material and produced EFB pellets showed high ash content (2-5%).

Bioethanol

EFB to bioethanol conversion steps are showed in Figure 2.1. It comprises three processes: pretreatment, hydrolysis, and fermentation, where pretreatment is considered the limiting step (Derman et al., 2018).
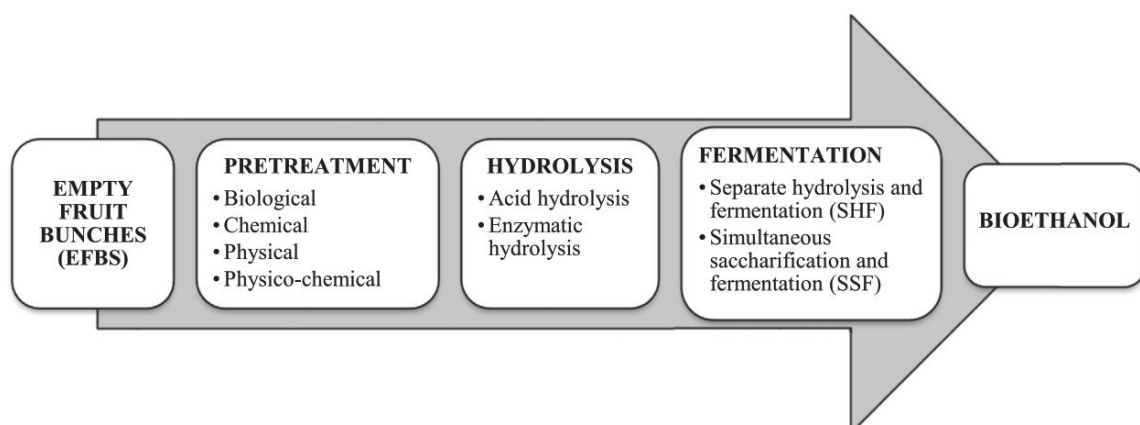

Figure 2.1. EFB to Bioethanol conversion process (Derman et al., 2018)

Bioethanol was produced using formiline as pre-treatment, enzymatic hydrolysis, and simultaneous saccharification and fermentation (SSF), leading to 71.9 g/L and 83.6 g/L glucose and ethanol yield

respectively, representing 85% of ethanol theoretical yield (Cui et al., 2014).

Different strategies for bioethanol production were implemented such as sequential acid/alkali pre-treatment strategy, enzymatic hydrolysis, and simultaneous saccharification and fermentation (SSF), with a result of 70.8 g/L and 37.8 g/L glucose and ethanol yield respectively, where 88% of sugars was used in ethanol fermentation process (S. Kim & Kim, 2013).

Ethanol production was investigated (Duangwang & Sangwichien, 2015) from EFB using alkali pre-treatment (15% w/v NaOH for 40 min at 130 °C), acid hydrolysis (7% v/v H_2SO_4 at 119 °C for 110 min), and separate hydrolysis and fermentation (SHF), resulting in 33.45 g/L and 6.23 g/L - 8.49 g/L glucose and ethanol yield respectively, where 88% of sugars was used in ethanol fermentation process.

Current drawbacks for bioethanol production from EFB are low product yield, high recovery cost, and high CAPEX and energy consumption mostly connected with pre-treatment step.

Bio-oil and biochar

During pyrolysis, a thermochemical process in absence of oxygen, three main products are obtained: high energy density liquid (bio-oil), high energy density solid (biochar) and low energy density gas (syngas), To maximize bio-oil production, fast pyrolysis is employed (short residence times and fast heat transfer) whereas slow pyrolysis (high residence times and low heat transfer) is conducted to maximize biochar yield (Laird et al., 2009).

Regarding bio-oil production, slow pyrolysis was used at 600°C and obtained a 13 wt.% yield and a High Heating Value (HHV) equal to 31.44 MJ/kg (Khor et al., 2009). The authors concluded that obtained bio-oil from EFB could be used as fuel oil feed for a boiler or furnace.

Fast pyrolysis was worked at 400-600°C temperature range and residence times between 0.79 s-1.32 s resulting in a maximum bio-oil yield of 55.1 wt.% and a HHV of 36.06 MJ/kg (Abdullah et al., 2010).

Solvolysis is a different technique which uses a solvent to reduce the temperature requirements for the pyrolysis (Fan et al., 2011). Conditions were 275°C for 60 minutes using ethylene glycol as solvent. Conversion reached 96.4% for bio-oil with a HHV of 29.42 MJ/kg.

Barriers for technology implementation are the wide variety of compounds present in the bio-oil, pilot scale research is limited, and high investment is required for pyrolysis process.

In the case of biochar, slow pyrolysis was employed at 500°C for 60 minutes, yielding 29 wt.% biochar with a HHV between 27.96 MJ/kg – 32.6MJ/kg. It is worth noting that ash content for EFB based biochar was close to 13 wt.% (Abnisa et al., 2013).

Microwave-assisted pyrolysis of EFB (Azni et al., 2019) is a novel technique with several advantages. Pyrolysis temperature (253 °C) was reduced compared to conventional pyrolysis using a microwave power of 2.6 kW for 90 minutes. Biochar conversion achieved 50 wt.% with a HHV of 26.43 MJ/kg, biochar derived from EFB showed similar properties compared to sub-bituminous coal, EFB biochar combustion test exhibited lower CO and NO_x emissions compared to sub-bituminous coal combustion.

There are still few reports for biochar production from EFB, drying step is required and overall process

is capital intensive.

Hydrogen and syngas

Hydrogen and syngas from biomass are produced by gasification. Pyrolysis is focused on solid and liquid phase. On the other hand, gasification is a thermochemical route for high production of gaseous products under specific oxygen concentration ranges (Demirbaş & Arin, 2002). Equation 2.1. describes the reactants and products from gasification, while conditions are defined to maximize H2 and/or CO production:

$$Biomass + O_2 + Heat \rightarrow H_2 + CO + CO_2 + CH_4 + Hydrocarbon + Char \ (2.1.)$$
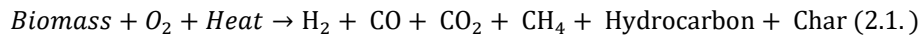
Syngas is a mixture of H_2 and CO which is used in petrochemical industry for fuel synthesis mainly via Fischer-Tropsch Synthesis (FTS) or Higher Alcohol Synthesis (HAS) (Laohalidanond et al., 2006). Resulting products from FTS are long chain hydrocarbons such as gasoline, diesel, naphtha, and wax whereas HAS main output are methanol and ethanol.

Air gasification of EFB (Mohammed et al., 2011) in the temperature range of 700°C -1000°C produced mainly H_2, CO, CO_2 and CH_4, reaching a maximum Lower Heating Value (LHV) of 15.55 MJ/m^3 at 1000°C. Maximum hydrogen production (27.31 vol.%) was achieved at 850°C. Cost analysis showed that H_2 production cost is \$2.11/kg EFB which was 5 times lower than production cost from conventional electrolyzed hydrogen (\$10/kg).

EFB gasification was studied in a bubbling fluidized bed within temperature range from 650°C –1050°C reaching maximum HHV of 5.37 MJ/Nm^3 and carbon conversion of 93% at 1050°C, however, at higher temperature agglomeration was observed for EFB leading to reduction or even abrupt stop of the fluidization process in the bed. To overcome this effect, temperature was lowered to 770°C with a maximum HHV of 4.53 MJ/Nm^3 (Lahijani & Zainal, 2011).

For gasification, low moisture content (<10 wt.%) is required for the starting material as well as particle size reduction (between 0.3 mm and 1.0 mm). High initial investment is also mandatory for gasifier which could be considered as the main barrier for the process and further study is required to determine optimal conditions for maximizing hydrogen and syngas from EFB.

2.1.3 Current and promising uses for EFB

Current uses – Colombian case

EFB in Colombia is mostly returned to the agricultural field as mulch/soil amendment (63.8%), transformed into compost (24.8%) or other uses such landfill disposal (11.4%)(Ramírez et al., 2015). Agronomic use requires no pre-treatment for EFB and it is an inexpensive alternative for EFB disposal and use, providing nutrient recycling via slow decomposing of material on the field. However, phytosanitary issues connected with fly *Stomoxys calcitrans* multiplication in EFB disposed on field were reported in specific regions in Colombia, this implied additional solutions to this problem such as use of Sphalangia sp as parasite for fly control, fly traps, and plastic coverage to avoid fly multiplication, leading to cost increment due to materials and workforce employed for this purpose (Rodrigo B., 2007), as well

as transportation cost for a material with high moisture content.

Composting

Composting is an aerobic decomposition process where usually EFB and POME are simultaneously transformed into compost with CO_2, H_2O, and heat as subproducts (Gandahi & Hanafi, 2014). Key parameters for the process are oxygen content, moisture, feedstock, and heat transfer. It is estimated that from 40 ton EFB is produced 10 ton compost (Galindo & Romero, 2012).

Miranda et al (Miranda et al., 2007) reported co-composting of EFB and POME for a 8-10 weeks period. The produced compost could represent 1.6 M EUR / year revenue for a single plant when biogas generation, composting, and transportation savings are considered.

A zero-waste concept with nutrient recycling was reported from EFB and POME co-composting (Ling-Hoak et al., 2007). The pilot scale research showed that the system could replace existent ponds for POME treatment, and it is expected an internal rate of return (IRR) between 5% and 39%.

Co-composting of EFB and POME reached a compost maturity in 8 weeks, and it could represent an important transportation cost compared to EFB mulching. In addition, nutrient concentration in EFB was increased after composting for elements such as K, P, and Mg (Hoe et al., 2016).

The use of heavy machinery on a regular basis for aeration during composting and lack of market opportunities for final low-cost product are considered the main barriers for this alternative.

Other promising uses

Research reports showed different products derived from EFB: bio-composites, cellulose pulp and paper, bio-plastics, food for ruminants, enzyme production, chemicals via catalytic routes, among others (Garcia-Nunez et al., 2016). Most of these products are still in early stages of development to be considered for industrial scale.

2.2   Biogas technology

2.2.1   Introduction

Biogas is the main product from anaerobic degradation of organic matter, and it is composed mainly of methane (45-70%), carbon dioxide (24-40%), and small amounts of other compounds (N_2, H_2, O_2, H_2S), where hydrogen sulfide concentration is relevant considering an upgrading step or further use (Shirzad et al., 2019). The composition of biogas depends on the technological process and substrates used. Table 2.2. shows the typical content of individual components in biogas.

Table 2.2. Biogas composition and concentration of main components (Rodero et al., 2018)

Component	Content
Methane (CH$_4$)	50-75 %
Carbon dioxide (CO$_2$)	25-45 %
Hydrogen sulfide (H$_2$S)	20-20000 ppm
Hydrogen (H$_2$)	< 1 %
Carbon monoxide (CO)	0-2,1 %
Nitrogen (N$_2$)	< 2 %
Oxygen (O$_2$)	< 2 %
Other	Traces

Biogas and biomethane world production in 2018 was around 35 million tonnes of oil equivalent (Mtoe), around 6% of the estimated overall potential (IEA, 2020). The feedstocks that can be used for biogas production are crop residues, animal manure, municipal solid waste, wastewater, and forestry residues (via gasification). The aforementioned feedstocks are considered since they do not compete with food or agriculture land and, additionally, could play an important role in waste management in different scenarios and locations. Regarding locations, at least one of these feedstocks can be found in every part of the world, showing that biogas potential is remarkable with a projected increment of 40% of the availability of sustainable feedstocks by 2040 (IEA, 2020). Figure 2.2. exhibits the biogas production potential by region and feedstock considered (IEA, 2020). Each region, regardless of the feedstock type, has a remarkable potential for energy production, where Asia Pacific and North America regions have the larger opportunities. The potential would grow during the next years by improving collection rates and waste management in developing countries, therefore management of organic waste in all countries could be enhanced by the use of biogas digesters since more than 50% in all regions correspond to animal manure and crop residues. Last but not least, around 50% of biogas potential in Central and South America corresponds to crop residues (e. g. EFB).
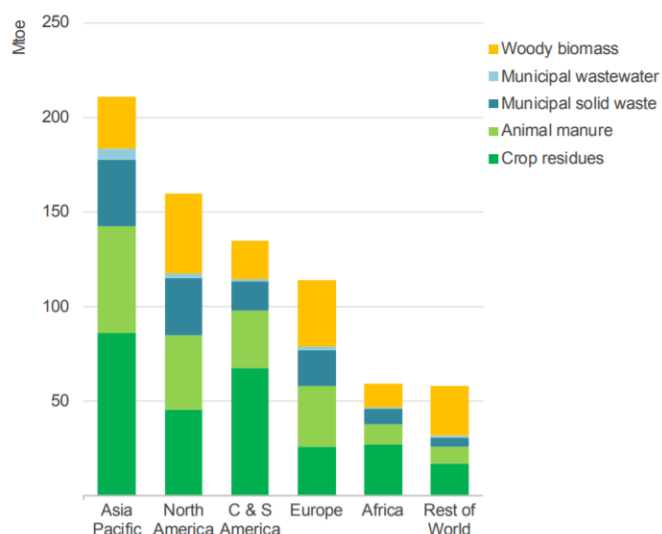
Figure 2.2. Production potential for biogas by region and feedstock source (IEA, 2020)

Digestate is the solid and liquid product obtained from anaerobic digestion of organic matter (Nkoa, 2014). Most of the elements different from carbon, nitrogen, oxygen, and sulphur from the original feedstock are concentrated and mineralized from the organically-bound nutrients in this by-product, making it a suitable fertilizer. The composition of the digestate is variable and it depends on the type of feedstock used since the chemical properties of the feedstock will be preserved in the resulting digestate, and the design of the digester. The recommendation is the evaluation of this organic fertilizer for each feedstock and biodigester case. Table 2.3. shows the main characteristics of a digestate.

Table 2.3. Typical composition of digestate from cattle manure (Nkoa, 2014)

Parameter	Unit	Value range
Total Solids	%	1.5 - 45.7
Volatile Solids	%	38.6 - 75.4
Total N	% of DM	3.1 – 14
Total N	% of FM	0.12 - 1.5
Total NH_4^+	% Total N	35 – 81
Total P	% of DM	0.2 - 0.35
Total P	% of FM	0.04 - 0.26
Total K	% of DM	0.19 - 4.3
Total K	% of FM	0.12 - 1.15
pH	-	7.3 - 9.0

*DM: Dry matter, *FM: Fresh matter

The positive effects of using digestate as a fertilizer is the partial of total replacement of regular fertilizer. In the case of phosphorus, the digestate would provide the P requirements for most crops, and for nitrogen could fulfil 60-80% of the requirement for several crops. Moreover, the use of feedstock with high content of potassium (i.e. EFB from palm oil crops) would increase the percentage of this nutrient in the final fertilizer and digester's performance as a whole lies between manure/compost and regular fertilizers (Nkoa, 2014). Another outcome is the reduction of costs and emissions by using the fertilizer that is produced locally. It is estimated that the use of digestate in coffee and corn crops could reduce the cost by 40% (Nkoa, 2014). A study conducted in Germany for organic farms evaluated the yield from different crops that uses digestate as main fertilizer (Gerlach et al., 2013) and the main findings are shown in Figure 2.3. The use of digestate led to an increase in yield percentage in all 8 considered crops in the range from 12.0% to 29.4% with an average of 15.0%, therefore the benefit for a farmer using the organic fertilizer is evident. It is worth to mention that also farmers reported a quality improvement in crops (i.e., protein content in grain is increased) which is transformed into high market value of the final product.
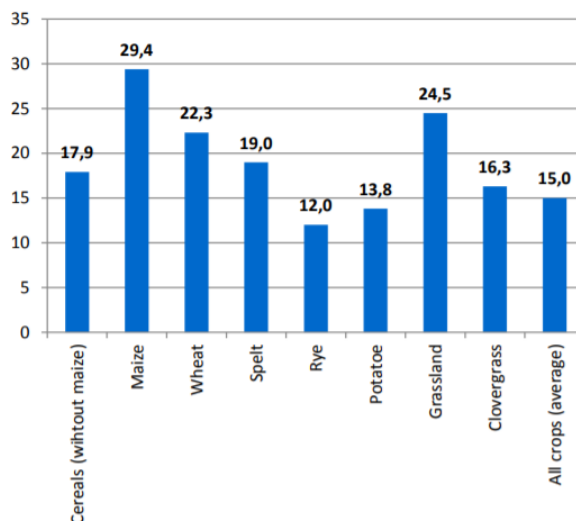
Figure 2.3. Yield percent increase using digestate in 51 organic farms (Gerlach et al., 2013)

The following are the main threats and challenges for the use of digestate (Gerlach et al., 2013; Nkoa, 2014):

- Short retention times leads to incomplete digestion and the resulting digestate may have problems with toxic organic compounds, phytotoxicity, pathogens, and odour emissions.
- Emissions of gaseous nitrogen compounds (NH_3, N_2O) is greater compared to regular manure.
- Presence of trace metals in high concentration (Mn, Cu, Zn) could lead to toxicity for agricultural soils and affect different type of crops.
- Lack of information regarding use and advantages of digestate could lead to inappropriate management of the biodigester and disposal of the digester.

2.2.2 Biogas production and biomethane potential test (BMP)

Biogas production is carried out in four steps which are described in Figure 2.4. (Mirmohamadsadeghi et al., 2021). In the first step, long-chain polymers are hydrolyzed to sugars, amino-acids, and long-chain fatty acids. Hydrolysis is the limiting step for the process since most of the lignocellulosic material is comprised of cellulose, hemicellulose, and lignin, which has a very complex structure and is not suitable for anaerobic fermentation (Mirmohamadsadeghi et al., 2021). The second step is acidogenesis where sugars are transformed mainly in volatile fatty acids (VFA), acetic acid, H_2 and CO_2. It is considered the fastest step of whole process and VFA are used by methanogenic bacteria as substrate. Then, in acetogenesis stage, VFA, and short-chain alcohols are transformed into acetic acid, H_2 and CO_2. This conversion is required since methanogens only transform acetic acid, H_2 and CO_2 into methane. In the last step, acetic acid, hydrogen and carbon dioxide are transformed into methane, CO_2, and water. Acetophilic methanogens converts acetic acid into methane following the reactions (Demirel & Scherer, 2008):

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (2.2.)$$

$$CH_3COOH + 4H_2 \rightarrow 2CH_4 + H_2O \quad (2.3.)$$
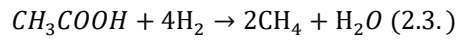
while a secondary route uses hydrogen and CO_2 by hydrogenophilic methanogens to produce methane and water (Demirel & Scherer, 2008):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2.4.)$$
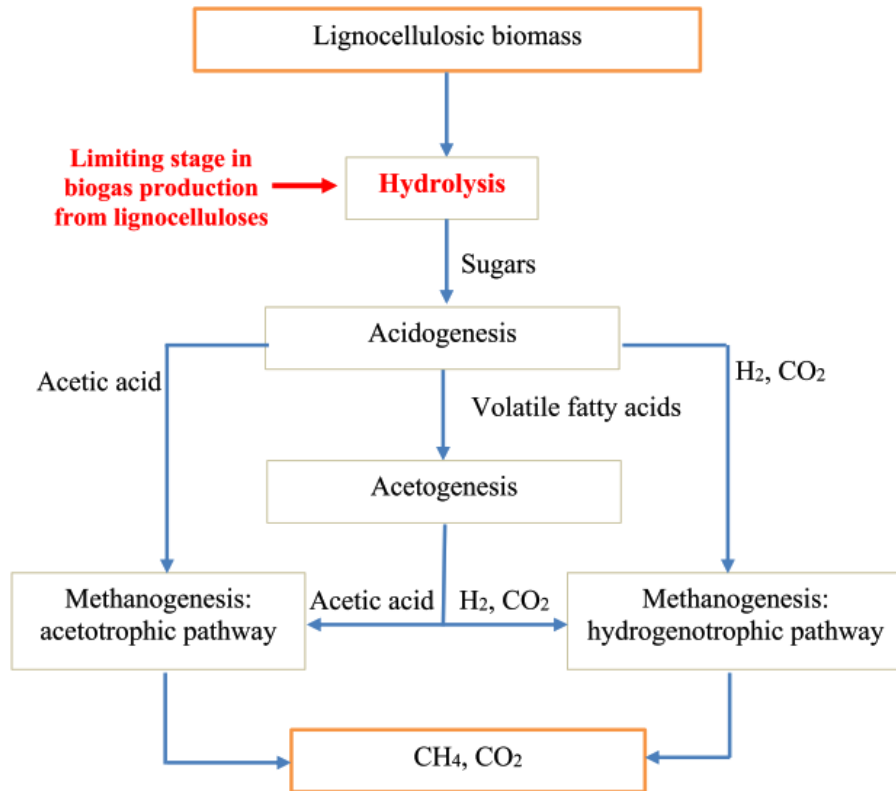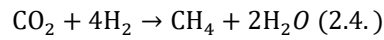
Figure 2.4. Biogas production steps from lignocellulosic material (Mirmohamadsadeghi et al., 2021)

Biomethane potential test (BMP) is a simple procedure that involves adding a defined amount of organic feedstock to an active inoculum (e.g. sludge from an anaerobic lagoon) in a sealed serum bottle assuring absence of oxygen. The amount of biogas produced is measured and methane content is evaluated (Esposito et al., 2012).

Since there is no official standard for BMP (Ohemeng-Ntiamoah & Datta, 2019), variability in results among studies reported in literature is important and, at the same time, it is difficult to make comparisons between similar experiments. This is mainly due to lack of reported information, wider range of variables, and even reported results in different units of measurement (Angelidaki & Sanders, 2004). To determine critical parameters and working ranges for operating conditions in BMP test, Ohemeng-Ntiamoah and Datta (Ohemeng-Ntiamoah & Datta, 2019) reviewed 78 BMP studies from 2007 and 2018 covering a broad range of substrates. For the upcoming critical experimental parameters, which are inoculum to substrate ratio (ISR), substrate concentration, temperature, blank control, reactor size, headspace, mode of mixing, and pH, recommended ranges are based on this study.

Inoculum to substrate ratio (ISR)

One of the most critical operation parameters expressed as volatile content ratio (g VS), a low ISR could lead to organic overloading of the system, increasing production of volatile fatty acids (VFA) and lowering pH, even inhibiting the process completely (Angelidaki & Sanders, 2004). It is recommended:

* a minimum value of 2 for highly degradable feedstock (e.g., food waste), and

* a ISR value of 1 for less degradable substrates (e.g., EFB, lignocellulosic material) but not lower than 1 to avoid overloading.

Substrate concentration

Similarly to ISR, a high concentration of substrate expressed in g VS/L could lead to overloading and VFA accumulation, therefore concentration should be carefully defined prior experimentation. Among 78 studies, a maximum of 10 g VS/L was employed in most studies and concentration ranged from 2 g VS/L to 10 g VS/L.

Temperature

Most frequent temperature regime for BMP are either mesophilic (35 ± 2 °C) or thermophilic (55 ± 2 °C) conditions and water bath, incubator, or thermally controlled chamber are employed for this purpose (Y. Chen et al., 2008). Mesophilic conditions improved stability while thermophilic conditions promoted faster degradation (Krause et al., 2016). The recommendation is to work closer to the temperature regime for inoculum.

Blank control

Inclusion of blank control, which is not always reported in literature, allows accountability for endogenous methane production from inoculum and remaining organic compounds degradation. In addition, blank controls avoid preincubation period to reduce background methane production.

Reactor size and headspace

Reactor volume reported for BMP ranged from 118 mL to 2300 mL. Small reactors (100 mL) are suitable for homogeneous samples and could lead to difficulties to obtain a representative substrate sample. On the other hand, big reactors (500 to 2000 mL) are suitable for heterogeneous substrates and could exhibit mixing issues affecting degradation rates (Holliger et al., 2016). Reactor size range recommended for BMP is 100 mL to 2000 mL. Regarding headspace, inappropriate headspace volume selection could lead to underestimation or overestimation of produced biogas. Main outcome of a high headspace volume is to make it difficult to measure low gas production, whereas a low headspace volume (<20% of total volume) is proposed for expected low gas volumes but could lead to overpressure the system (Valero et al., 2016). The recommended maximum headspace is 40%.

Mode of mixing

Mixing is required for an appropriate heat transfer and contact between substrate and microorganisms that allows degradation. In consequence, insufficient mixing could result in lower methane production connected with non-uniform contact between organic source and inoculum while high intensity mixing

could promote VFA formation (with the same outcome as expressed for ISR) via syntrophic interaction breaking of microbial consortia(Amani et al., 2010). Most of studies reviewed (48%) employed manual shaking once per day (Ohemeng-Ntiamoah & Datta, 2019). It is recommended to use a reproducible procedure for shaking and to keep mixing frequency close to once per day since a small reactor size does not require a constant mixing system to ensure proper mixing (Holliger et al., 2016).

pH

For promoting appropriate growth of methanogenic microorganisms, pH range should be near neutral 6.5-7.5), therefore pH adjustment could not only provide the required pH but also enhance buffering capacity to prevent VFA accumulation (Wu et al., 2015). In the particular case of biogas production from POME, pH adjustment is required since measured pH for POME ranges from 3.3 to 4.6 and low pH condition resulted in increased specific decay rate of methanogenic archaea 10 times more in a low pH environment (e.g. pH 5.1) compared to neutral pH (pH 7.0) (Singkhala et al., 2021).

To define experimental conditions for this research, operational parameters recommendations in this section will be combined with reported experimental parameters for similar studies in section 2.3.

2.2.3 Pre-treatment and co-digestion effects on biogas generation

Pre-treatment

As mentioned in the previous section, hydrolysis is the limiting step in biogas production from lignocellulosic substrates, associated with recalcitrant structure which pose a barrier for hydrolysis to sugars (Gao et al., 2019). For this reason, pre-treatment is considered a key process to overcome this limitation and enhance biogas production. Table 2.4. exhibits different pre-treatment methods reported in literature for lignocellulosic materials (Jönsson & Martín, 2016).

Table 2.4. Pretreatment methods for lignocellulosic feedstock (Jönsson & Martín, 2016)

Pre-treatment methods	Main effect	Used chemicals	By-product formation
Acid-based methods	Hydrolysis of hemicelluloses to monosaccharides	Involve catalysts such as H_2SO_4, SO_2, HCl, H_3PO_4	Aliphatic carboxylic acids, phenylic compounds, furans, etc.
Hydrothermal processing	Solubilization of hemicelluloses without complete hydrolysis	No additives	Acetic acid, minor amounts of furan aldehydes
Mild alkaline methods	Removal of lignin and a minor part of hemicelluloses	Involve alkali such as NaOH, $Ca(OH)_2$,NH_3	Acetic acid, hydroxy acids, dicarboxylic acids, phenolic compounds
Oxidative methods	Removal of lignin and part of hemicelluloses	Involve oxidants such as H_2O_2 and O_2 (alkaline conditions), and O_3	Aldonic and aldaric acids, furoic acid, phenolic acids, acetic acid
Chemical pulping processes	Methods that target lignin and to some extent hemicelluloses	Kraft pulping, sulfite pulping, soda pulping, organosolv pulping	Aliphatic acids
Alternative solvents	Dissolution of specific lignocellulosic components or the whole biomass	Ionic liquids	Dependent on solvent and conditions

In lignocellulosic substrates, cellulose, hemicellulose, and lignin comprises 80% of this material with composition variation depending mainly on feedstock type (Aghbashlo et al., 2019). Therefore, pre-treatment action mechanisms are focused on different changes in these particular components. Pre-treatment could lead to one or more of the following results in aforementioned compounds: changes in chemical composition, lignin removal, changes in cellulose crystallinity, decrease in degree of polymerization and deacetylation (Mirmohamadsadeghi et al., 2021). At the same time, subproducts of pre-treatment such as aliphatic carboxylic acids (acetic acid, formic acid, levulinic acid), phenolic compounds, and furans leading to inhibition of enzyme activity and microbial metabolism and further research is required to reduce the inhibition consequences of pre-treatment (Jönsson & Martín, 2016).

Biogas was produced using sunflowers residues as feedstock (Zhurka M et al., 2019). Pretreatment conditions were NaOH alkaline solution (4 g NaOH/g total solid) at 55°C for 24h. For sunflower heads, the biogas production from raw feedstock to pretreated residue changed from 210.56 to 268.47 mL CH_4/ g VS, showing 27.5% more methane production for the pretreated feedstock.

Using steam explosion as pretreatment, biogas was produced from Birch (Vivekanand et al., 2013). The researchers explored 13 different conditions within 170 to 230 °C temperature range and 5 -15 min residence time range with the aim of xylan degradation and formation of pseudo-lignin. Maximum methane yield achieved was 369 mL CH_4/ g VS which was 1.8 times higher compared to raw birch.

Biogas production from wheat straw with ammonia as pretreatment was studied (Li et al., 2015). Optimal conditions for maximizing biogas production were 51.0 °C, 14.8% NH_3 concentration and 27 h residence time focusing on lignin removal and cellulose/hemicellulose retention. Comparing biogas yields, unpretreated EFB biogas yield and highest biogas yield from treated EFB were 400 mL /g VS and 625 mL/ g VS respectively, concluding that pre-treatment enhances biogas production yield in 56%.

Co-digestion

Combining different types of organic waste can increase the biodegradability and therefore, the production of biogas. This is known as co-digestion. It allows the adjustment of the substrate depending on the characteristics of the system. Using a co-substrate can improve the biogas yield of the system, as one substrate can supply the missing nutrients in another and vice-versa. It is also observed that the combination of substrates results in synergy for the process, balancing C/N ratio (e.g. low carbon content feedstock such as protein rich waste and high carbon content material such as lignocellulosic crop residues) to an optimal range between 20 and 30 (Hagos et al., 2017), improving buffer capacity, or reducing negative effects of toxic or inhibitory compounds (Esposito, Frunzo, Giordano, et al., 2012; Robles et al., 2018).

Table 2.5. illustrates different co-digestion examples from different feedstocks. The main outcome of co-digestion were enhanced biogas production rates and increase in biogas yield up to from 57% to 337% (Khalid et al., 2011).

Table 2.5. Co-digestion yields from different feedstock (Khalid et al., 2011)

Substrate	Co-substrate	Methane yield (L/kg VS*)	Comments	References
Cattle excreta	Olive mill waste	179	The co-digestion system produced 337% higher biogas than that of excreta alone	(Goberna et al., 2010)
Cattle manure	Agricultural waste and energy crops	620	Significant increase in biogas production from the co-digestion was observed	(Cavinato et al., 2010)
Fruit and vetable waste	Abattoir wastewater	611	The addition of abbattoir wastewater to the feedstock incresed biogas yield up to 51.5%	(Bouallagui et al., 2009)
Municipal solid waste	Fly ash	222	Application of fly ash significantly enhanced biogas production rates of the municipal solid waste	(Lo et al., 2010)
Municipal solid waste	Fat,oil and grease waste from sewage treatment plants	350	Co-digestion resulted in an increase of 72% in biogas production and 46% methane yield in comparison with municipal solid waste	(Martín-González et al., 2010)
Pig manure	Fish and bio-diesel	680	Highest biogas production rates were obtained by the mixture	(Álvarez et al., 2010)
Potato waste	Sugar beet waste	680	Co-digestion improved methane yield up to 62% compared to the digestion of potato waste alone	(Parawira et al., 2004)
Primary sludge	Fruit and vegetable waste	600	Co-digestion produced more biogas as compared to primary sludge alone	(Gómez et al., 2006)
Sewage sludge	Municipal solid waste	532	Biogas production of the mixtures increased when increasing proportions of the municipal solid waste	(Sosnowski et al., 2003)
Slaughter house waste	Municipal solid waste	500	Biogas yield of the co-digestion systems doubled that of the slaughter house waste digestion system	(Cuetos et al., 2008)

*VS: Volatile solids

2.3 Biogas production from empty fruit bunches (EFB) and palm oil mill effluent (POME)

2.3.1 Introduction

POME could produce potentially 20-30 m^3 biogas/m^3 POME at industrial scale level (O-Thong et al.,

2012). For POME, it is reported that biogas production is equal to 562 m^3 CH_4/ton VS, 483 m^3 CH_4/ton TS, and 15 m^3 CH_4/ m^3 effluent (Langeveld JWA & Quist-Wessel PMF, 2014). Considering the previous figures, POME is classified as high biogas production feedstock on VS basis (>500 m^3 biogas/ ton VS), however, it is classified as low biogas production on fresh matter (FM) basis (< 15 m^3 biogas/ton FM) (Langeveld & Peterson, 2018), meaning that despite the fact the biogas production is quite high, organic concentration is low, leading to large space requirements (i.e. ponds or large reactors) for effluent processing via anaerobic digestion.

Biogas production from EFB as alternative method of its utilisation exhibits several advantages when compared to the use and technologies described in section 2.1.:

- Mild temperature (35-55°C) and pressure (ambient pressure) conditions.
- Moisture removal not required to process EFB via anaerobic digestion.
- Low capital investment compared to other technologies that require expensive reactors to handle extreme temperature and pressure.
- Mature technology with presence in 7 out of 69 palm oil mill plants in Colombia in the form of methanogenic covered lagoons to process POME (Fedepalma, 2020).
- Self-sufficiency for energy consumption and energy excess production sold to the grid or near-by towns by 2 palm oil mill plants in Colombia (Fedepalma, 2020), helping rural economy since most of these plants are located in regions with no connection to the national grid.
- Production of digestate as by-product, promoting circular economy and nutrient recycling since anaerobic sludge could be used as fertilizer in the palm oil plantation or other farms.

The main drawbacks for the process are low biogas production from EFB (0.20 m^3 CH_4/ kg VS) (Nieves et al., 2011) due to its lignocellulosic nature and large space/reactor requirements for biogas production. To overcome low biogas production from EFB, promising solutions such as pre-treatment, co-digestion, and a combination of both have been reported and are discussed in the following section.

2.3.2 Literature information on production of biogas from EFB and POME

Several studies regarding biogas production from EFB and/or POME are described in this section. Some of these experiments included pre-treatment and/or co-digestion as strategies to enhance methane yield.

Biogas production from EFB and POME using co-digestion was evaluated (S. H. Kim et al., 2013). Experimental conditions were mesophilic temperature (35°C) and EFB:POME ratio ranging from 0:1 to 1:1 in COD basis. For 40 days experiment, methane yield for EFB and POME solely were 221 mL CH_4/g COD and 301 mL CH_4/g COD respectively while the highest methane yield was 450 mL CH_4/g COD for EFB:POME ratio of 1:1 in COD basis leading to 1.5 times more methane produced compared to POME production and 2 times more compared to EFB production.

Co-digestion of EFB and POME under thermophilic conditions (55°C) was tested (O-Thong et al., 2012).

Three different pre-treatment for EFB were analyzed: chemical (NaOH 1 wt %), hydrothermal (steam 230°C), and a combination of chemical and hydrothermal treatment. The best methane yields after 45 days for POME and EFB separately were 503 mL CH_4/g VS and 202 mL CH_4/g VS respectively. When EFB:POME ratio (in g VS basis) was evaluated in the range (0.4:1 to 11:1), the best methane production was 340 mL CH_4/g VS for 0.4:1 ratio. The authors evaluated EFB:POME ratio of 6.8:1 for pre-treatment experiments due to biomass availability in real conditions, obtaining a maximum of 392 mL CH_4/g VS methane yield using chemical and hydrothermal combination as pretreatment, high organic load (46 g VS/L) compared to similar studies, and 91% biodegradability. From this result, it was estimated a methane production of 82.7 m^3/ton mixed EFB and POME.

Co-digestion of EFB and POME was analyzed under facultative conditions (no inoculum added and air medium in the reactor) (Nurliyana et al., 2015). After 14 days and ambient temperature close to mesophilic conditions (27-30 °C), methane production from POME with a starting pH of 4.8 was 0.3668 mL CH_4/g VS while maximum methane yield was 0.5932 mL CH_4/g VS for a combination of 24 %w/w EFB and 76 %w/w POME (C/N ratio of 45) and starting pH of 5.7. Co-digestion resulted in 1.6 times more methane production compared to POME, however, when compared to methane production under anaerobic conditions, 392 mL CH_4/g VS (O-Thong et al., 2012) , methane yield was 660 times lower for facultative production.

Biogas production from EFB and POME via co-digestion was evaluated (Liew et al., 2021). Alkaline pretreatment of EFB, mesophilic (35°C) and thermophilic (55°C) temperature conditions, and co-digestion in 35-day experiments were analyze in this research. Considering pretreatment effect on co-digestion with POME, it was observed that methane production was higher for untreated EFB compared to treated POME at EFB:POME ratio of 0.3:1 and 0.45:1 on COD (chemical oxygen demand) basis, regardless of the temperature. The authors concluded that pre-treatment employed should be reconsidered since no significant effect on biogas production was obtained. For mesophilic temperature and thermophilic temperature, maximum methane yields were 60.00 and 74.02 mL CH_4/g VS respectively (2.36 times more than methane production from POME), leading to a COD removal of 77% for both cases after anaerobic digestion. Maximum methane production was obtained for a EFB:POME ratio of 0.6:1 in COD basis or a C/N ratio of 10.72.

Co-digestion of EFB and POME was evaluated taking into consideration EFB particle size and EFB:POME ratio as main variables for the study at mesophilic conditions (37 °C) (Saelor et al., 2017). Particle size and EFB/POME VS concentration were evaluated between 0.5-6 cm and 2-10 g VS/L respectively. Highest methane production achieved was 52 m^3 /ton biomass, corresponding to a cumulative methane production of 282 mL CH_4/g VS and 40% biodegradability for 6:2 EFB mixing ratio and 3.3 cm EFB particle size.

Solid-state co-digestion of EFB and palm oil decanter cake (DC) was investigated (Tepsour et al., 2019). Oil palm ash generated from combusting fiber and shell residues in a boiler was added to adjust pH, making the process suitable to include three different solid waste streams (EFB, DC, and ash). In mesophilic conditions (35°C), dried EFB produced 353.0 mL CH_4/g VS while co-digestion with DC at EFB:DC ratio of 1:1 (VS basis) and 5% ash addition produced 414.4 mL CH_4/g VS, showing a 17.4%

biogas production rise for co-digestion.

An increment of 63% in biogas production was reported when POME is co-digested with EFB changing from 152 L cumulative biogas for POME to 248 L cumulative biogas for EFB after 15 days in 50 L batch reactor at mesophilic conditions. However, relevant data such as volatile solids concentration, mixing frequency, starting pH, and EFB:POME ratio were missing in this research (Ali et al., 2012).

Biogas production from POME considering pH adjustment by means of effluent recycling or oil palm ash addition derived from shell and kernel fed boiler was evaluated (Singkhala et al., 2021). Using ash provided additional benefits such as savings in typically employed alkali chemicals for pH adjustment (i.e. slaked lime, lime, and sodium bicarbonate) and addition of alkali and trace metals (i.e. Fe and Co) that were relevant for increased number of methanogenic microorganisms and enzyme activity for biogas production (Mamimin et al., 2019). Methane yield after 45 days at thermophilic conditions (55°C) for raw POME (starting pH 4.3) was 132 mL CH_4/g VS. The best results achieved for methane production considering biogas effluent (20% v/v, starting pH of 6.5) and ash (%5 w/w, starting pH 6.6) addition separately were 351 mL CH_4/g VS and 440 mL CH_4/g VS respectively, reaching 3.3 times more methane production with the ash addition compared to raw POME. Furthermore, highest removal chemical oxygen demand (COD) was 94% for 5% w/w ash addition.

Alkaline pretreatment of EFB with high concentration of NaOH and acid pretreatment with H_3PO_4 was studied in order to improve biogas production (Nieves et al., 2011). Due to alkaline pretreatment, a reduction of cellulose crystallinity and partial solubilization of hemicellulose and lignin were found. After 30 days at thermophilic conditions (55°C), biogas production increased from 0.20 m^3 CH_4/ kg VS for untreated EFB to 0.28 m^3 CH_4/ kg VS for acid treated EFB. The best results were obtained for NaOH pretreatment during 60 min, 0.404 m^3 CH_4/ kg VS, which means 100% improvement in terms of methane yield and 97% of theoretical yield based on carbohydrate content. The authors estimated that energy production from pretreated EFB could reach 11700 MJ/ ton EFB.

Table 2.6. summarizes the main experimental conditions for the best result obtained by the articles considered in this section. This information combined with the discussion in section 2.2.2. are used to set the experimental conditions and design in this MSc thesis.

Table 2.6. Experimental conditions for biogas production from POME and EFB reported in literature

Reference	Kim, 2013	O-thong, 2012	Nurliyana, 2015	Liew, 2021
Co-digestion study	yes	yes	yes	yes
Dried EFB	no	no	yes	yes
EFB concentration (g VS/L)	-	-	-	-
POME concentration (g VS/L)	-	-	-	-
EFB:POME ratio (g VS/L)	1:1 COD basis	6.8:1	24 %w/w EFB 76 %w/w POME	0.6:1 COD basis
pH adjustment	yes 7 to 7.7	NR	NR	NR
Inoculum to substrate ratio (VS basis)	1.1	1.1	NA	1.92
EFB Pretreatment	-	0.1% NaOH 1 day Steam 230°C 15 min	-	8% NaOH 120°C 30 min 3.9 bar
Maximum particle size EFB (mm)	1	5	10-20	1-3
Susbtrate concentration (g VS/L)	3.0	46	4.63	11
Temperature condition	Mesophilic	Thermophilic	Mesophilic	Mesophilic
Mixing frequency	150 rpm	NR	NR	110 rpm
C/N ratio	NR	NR	45	10.72
Total volume (mL)	250	320	20000	250
Working volume (mL)	150	100	100	NR
Methane production (mL CH_4/g VS)	450 (g COD)	392	0.593	74.02

*NR: Not reported

Reference	Saelor, 2017	Tepsour, 2017	Ali, 2012	Singkhala, 2017	Nieves, 2011
Co-digestion study	yes	yes	yes	no	no
Dried EFB	yes	yes	yes	-	yes
EFB concentration (g VS/L)	-	solid state	-	-	20
POME concentration (g VS/L)	-	-	-	7.5	-
EFB:POME ratio (g VS/L)	6:2	1:1	-	-	-
pH adjustment	yes 7	yes 6.5 to 7.8	NR	yes 6.6 (ash)	NR
Inoculum to substrate ratio (VS basis)	NR	0.33	NR	0.5	2
EFB Pretreatment	-	Steam145°C 90 min 3 bar	-	-	8% NaOH 60 min 100°C
Maximum particle size EFB (mm)	33	2	2	-	0.420
Substrate concentration (g VS/L)	8	NR	NR	7.5	20
Temperature condition	Mesophilic	Mesophilic	Mesophilic	Thermophilic	Thermophilic
Mixing frequency	NR	NR	NR	NR	NR
C/N ratio	NR	89	NR	NR	NR
Total volume (mL)	NR	500	50000	500	118
Working volume (mL)	NR	NR	NR	300	25
Methane production (mL CH_4/g VS)	282	414.4	248 L	440	404

Chapter 3

Experimental methods

This chapter outlines detailed experimental procedures in order to carry out the investigation. Section 3.1 collects sampling techniques for each starting material and characterization methods. Section 3.2 describes alkaline pre-treatment for EFB and section 3.3 shows complete steps for pH adjustment tests. Last but not least, section 3.4. gives a description of biomethane potential test (BMP) considering experimental design, set-up, and methane quantification.

3.1 Material sampling and characterization

3.1.1 Sampling

EFB sampling

5 kg of pressed EFB was taken from Alianza del Humea SA, Cabuyaro. The average production from this plant is 6.5 ton EFB/h.

Figure 3.1. Sampling point for pressed EFB

EFB physical pre-treatment

The EFB was cut using scissors and dried at 105°C in the oven for one day to avoid fungi growth and microbial degradation. The dried EFB was sieved using a 19 mm mesh size test sieve. The sieved EFB was stored in plastic bags at ambient temperature until use.

POME, inoculum, and ash sampling

6L of POME, 8L of inoculum (sludge from methanogenic lagoon), and 1 kg of ash were taken from Unipalma SA, Veracruz. The methanogenic system comprises two parallel covered lagoons with a 20,000 m^3 capacity each and 4.5 m depth.

POME was collected before entering the methanogenic lagoon with a flow rate average of 4 L/s, 50°C, and COD between 40,000 and 60,000 mg/L. Inoculum was collected as sludge pumped from the methanogenic lagoon at 35°C. POME and inoculum were stored in sterilized containers at 4°C before use. Wetted ash was collected from the main boiler which is fed with mesocarp fiber and palm kernel shell with an average production of 400 ton ash/month. Water was added to ash for safety reasons and ease handling on site. Wetted ash was dried at 105°C in the oven for one day. Dried ash was stored in plastic bags at ambient temperature until use. The inoculum was stored at ambient temperature for seven days before the experiment to reduce background methane production from remaining organic matter in the sludge. Figure 3.2. shows sampling points for each material described above.
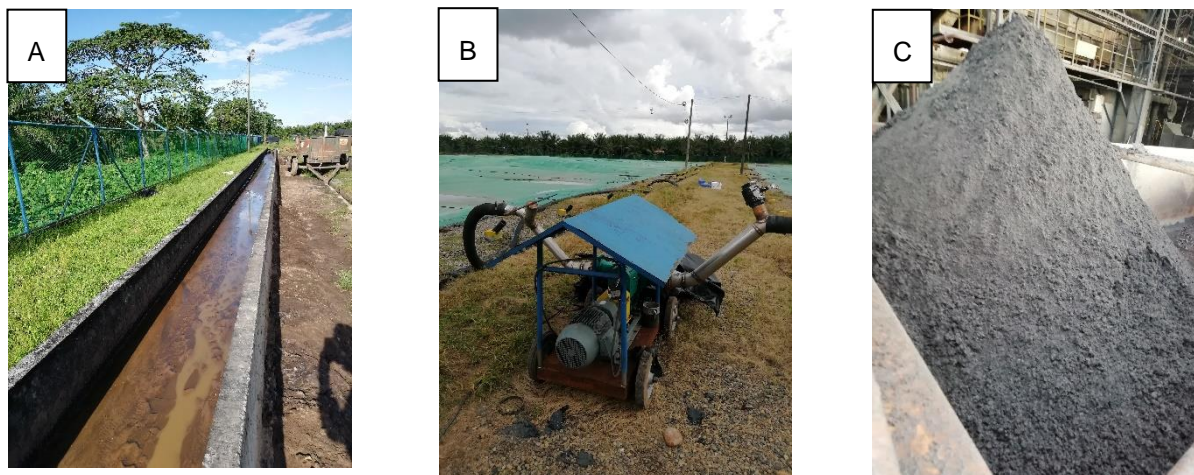
Figure 3.2. Sampling point for A) POME, B) inoculum, and C) ash

3.1.2 Characterization

Table 3.1 summarizes analytical methods employed for characterization of starting materials. In addition, total solids, volatile solids, and pH were measured before and after anaerobic digestion in order to evaluate organic load removal. All parameters were measured in triplicate.

Table 3.1. Characterization methods and parameters for collected materials.

Parameter	Method used*	EFB	POME	Inoculum	Ash
Total solids (TS)	APHA 2540B	x	x	x	
Volatile solids (VS)	APHA 2540E	x	x	x	
pH	APHA 4500H		x	x	x

*(APHA, 2017)

3.2 Alkaline pre-treatment for EFB

Considering pre-treatment suggested in literature (X. Chen et al., 2016), 17.2 g EFB (16 g EFB dry basis) were mixed with 182 g NaOH 0.1 M solution. The mixture was heated at 80°C for two hours at ambient pressure. After this time, the mixture was filtered and solid fraction was blended with distilled water for 30 seconds to ease washing. The previous step was repeated until pH 7 was reached. Pretreated EFB was then sun dried and stored in plastic bags before use. Figure 3.3. illustrates all pretreatment steps.

Figure 3.3. Alkaline pretreatment steps for EFB

3.3 pH tests for ash

In addition to pH determination for ash, it was determined the amount of ash required to increase the pH of POME. To do so, 40 mL or 50 mL POME were combined with ash with constant pH reading until the pH was 6.6, as it was shown in literature that biogas production using 6.6 as starting pH maximizes biogas production (Singkhala et al., 2021). The ash mass added for this purpose was obtained by subtracting initial and final mass of ash container. The result is reported in g ash/L and carried out in duplicate.

3.4 Biomethane potential test (BMP)

3.4.1 Biogas production experimental design

Based on key parameters described in section 2.2.2. and 2.2.3. for biogas production, all fixed variables for all experiments are tabulated in Table 3.2.

Table 3.2. Fixed variables for biogas production from EFB and/or POME

Fixed variable	Value	Notes
Temperature (°C)	Ambient	Max. and min. temperature is recorded
Inoculum:substrate ratio (ISR) (g VS)	1	
Substrate concentration (g VS/L)	8	
Working volume (mL)	300	
Headspace (%)	40	
Mixing (rpm)	500 for 2 minutes every two days	Vortex is employed
Starting pH	6.6	For POME and co-digestion experiments
EFB:POME ratio (g VS)	2:6	For co-digestion experiments

*g VS: Volatile solids mass expressed in grams

Two parameters were studied in the experiment: The effect of EFB pre-treatment and codigestión with POME. A total of seven experiments were proposed and described in Table 3.3. For experiment 1, blank experiment is considered combining inoculum and water. Experiment 2 is with POME only without the addition of inoculum. In the case of experiment 3, POME and inoculum are evaluated. For experiment 4 and 6, untreated EFB biogas production is assessed using EFB alone and codigestión with POME respectively. Similarly, in experiments 5 and 7, pre-treated EFB is employed without and with addition of POME respectively. All experiments were carried out in triplicate.

Table 3.3. Experiment design for pre-treatment and co-digestion evaluation

Experiment	Substrate			
	Water	EFB		POME
		Unpretreated	Pre-treated	
M1(blank)	x			
M2				x(no inoculum)
M3				x
M4		x		
M5			x	
M6		x		x
M7			x	x

3.4.2   Experimental set-up

A total of 21 batch experiments were carried out under ambient conditions near mesophilic temperature (24°C to 35°C) using the following set of elements per set-up: two 500 mL glass bottles, one for 2% NaOH alkaline solution with phenolphthalein as basic indicator and the other for biogas production, one

intravenous catheter 14G x 45 mm, one intravenous catheter 24G x 19 mm, one 3-way stopcock, two butyl rubber stopper, one solution administration set, and one 250 mL graduated cylinder. All elements are assembled as shown in Figure 3.4.
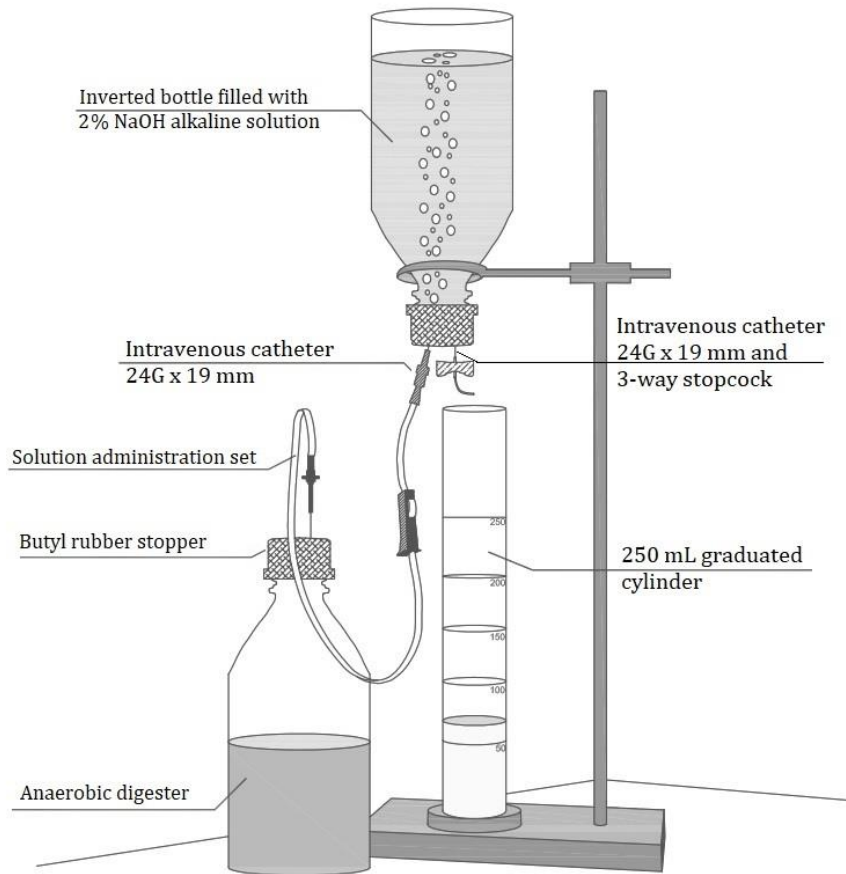
Figure 3.4. Experimental equipment for biogas production using liquid displacement method (Adapted from (Esposito, Frunzo, Liotta, et al., 2012a)

To each digester were added substrate (EFB, POME, or both), water and inoculum, to reach a concentration of 8 g VS/L and an ISR of 1 expressed in g VS. After mixing, pH was adjusted to 6.6. To ensure anaerobic conditions, reactor was purged with N_2 for 5 minutes. The reactor was then sealed with a butyl rubber stopper and connected to the gas collection system using the solution administration set and intravenous catheter 24G x 19 mm.

3.4.3 Biogas production measurement

The methodology employed for methane quantification is liquid displacement method, where the biogas produced is collected in an inverted bottle with 2% NaOH alkaline solution where CO_2 and H_2S reacts completely to remove these gases from the biogas (Lasocki et al., 2015) and the amount of solution displaced to the graduated cylinder is the volume of CH_4 produced. For 30 days, the volume collected was checked daily and anaerobic digester was stirred at 500 rpm for 2 minutes using vortex every two

days to ensure proper mixing and ease gas release from the medium. Gas and liquid leakage were evaluated twice per day and maximum and minimum temperature were recorded on a daily basis.

Cumulative volume is expressed at standard and pressure (STP) conditions (P = 1 atm, T = 273.15K) using the equation 3.1.:

$$V(STP, mL) = \frac{V_1 P_1 T_2}{P_2 T_1} \quad (3.1.)$$

Where P_2 and T_2 were STP conditions and P_1, T_1, and V_1 were local atmospheric pressure (0.995 atm), average experimental temperature for biogas production (273.15 + average T K), and methane volume at local conditions (mL) respectively (Singkhala et al., 2021).

The methane yield is the calculated using equation 3.2. to be comparable to different literature reports:

$$Methane\ yield\ \left(mL\frac{CH_4}{gVS} \right) = \frac{Cumulative\ volume\ CH_4(mL)}{Starting\ volatile\ solids\ mass\ (g\ VS)} \quad (3.2.)$$

Chapter 4

Results and discussion

In this chapter, results from experimental part described in chapter 3 are discussed and compared to similar investigations. Section 4.1 compares characterization results with literature, section 4.2. outlines more experimental details connected with alkaline pre-treatment of empty fruit bunches (EFB), and section 4.3 is devoted for discussion associated with pH adjustment alternatives and their evaluation. Lastly, section 4.4 is focused on biomethane potential test (BMP) results considering modified experimental set-up, baseline methane production for EFB and palm oil mill effluent (POME), and the effect of temperature, EFB pre-treatment, and co-digestion on methane yield.

4.1   Material characterization

Total solids (TS), volatile solids (VS), and pH were measured for different starting materials and collected in Table 4.1.

Table 4.1. Characterization parameters for the collected materials

Parameter	POME	Inoculum	EFB	Pre-treated EFB	Ash
Total solids (TS) (%)	3.20 ± 0.07	6.36 ± 0.12	93.11 ± 0.20	95.02 ± 0.36	-
Volatile solids (VS) (%)	2.67 ± 0.05	3.33 ± 0.05	90.20 ± 0.24	93.94 ± 0.40	-
pH	4.04 ± 0.04	7.54 ± 0.01	-	-	10.67 ± 0.03

For ash, pH value was basic and it was close to the literature reports for similar ash (11.2) (Singkhala et al., 2021). The main differences are justified by the fact that ash collected in literature included bottom ash and fly ash, whereas the one collected in this thesis was bottom ash solely. Regarding pH values for POME and inoculum, the values were comparable to the following results: 4.1 (Liew et al., 2021) and 8.32 (Saelor et al., 2017).

TS and VS content in EFB was similar to the values reported by Liew et al (Liew et al., 2021), obtaining a TS content and VS content for dried EFB of 94.94% and 91.25%, respectively. Usually, differences were observed when EFB was not dried, as in case of the article of O-thong et al (O-Thong et al., 2012) who reported TS 43.60% and VS 39.20% for EFB with no drying step. On the other hand, TS and VS content in POME showed high variability among studies ranging from 4.62% to 6.70% for TS and 5.70% to 3.70% for VS (S. H. Kim et al., 2013; Liew et al., 2021; O-Thong et al., 2012). This variation was explained by organic load concentration differences on effluent due to operational conditions, processing capacity, and equipment employed. High variation was also noticed for TS and VS content in inoculum (TS 10.50% and VS 8.10% (Saelor et al., 2017)) connected with similar reasons as for POME differences and it was also observed that TS and VS content in inoculum was higher than TS and V content in POME (Saelor et al., 2017).

VS concentration for POME, EFB (untreated and pre-treated), and inoculum were employed to calculate the amount of each component to be added to a respective biogas experiment based on substrate concentration and inoculum to substrate ratio (ISR).

4.2   Alkaline pre-treatment

During alkaline pretreatment, an additional analysis for losses and water use was performed taking into consideration mainly the washing step. The results collected are found in Table 4.2. Water consumption during washing step was about 2 liters of water for the starting mass of 16 g EFB. The concentration of total solids in this water was 2.43 g/L, representing 4.72 g of total solids in the resulting water, which is the main source of losses during the whole process, leading to a 66.6% recovery for the total process and a 5.34 g loss during the complete pre-treatment.

Table 4.2. Losses estimation during alkaline pre-treatment for EFB

Parameter	Value
Initial EFB mass (g, dry basis)	16.0014
Water consumed (mL)	1944
Total solids in water (g/L)	2.43
Amount of solids in water (g)	4.72
Final EFB mass (g)	10.6604
Recovery (%)	66.6

This finding was similar to that of Nieves et al (Nieves et al., 2011). When comparing unpretreated EFB and alkaline pretreated EFB with NaOH 8% for 60 min, total solids in both lignocellulosic materials were 942 g TS/kg EFB and 102 g TS/kg EFB, showing an important reduction in TS concentration after pre-treatment. These losses could be associated with lignin and hemicellulose partial solubilization as well as solids that are below the filter pore size and should be considered for future solids recovery from water stream and decision-making regarding suitable wastewater treatment for this effluent.

4.3   pH tests for ash

The incorporation of ash for pH adjustment was considered critical since it could be possible to include a third waste stream in the process and consumption of traditional chemical agents could be reduced. Furthermore, ash could provide other elements that are key for methanogenic bacteria as substrates for the biological activity (Mamimin et al., 2019).

Preliminary tests were carried out to determine the amount of ash required to increase pH in POME to reach a value of 6.6, which showed the best performance for biogas production based on literature (Singkhala et al., 2021) The results are collected in Table 4.3 and Table 4.4. It is required 94.80 ± 0.19 g ash per liter of POME. Considering that for a real palm oil mill (e.g., Unipalma), average flow rate of POME is 4 L/s and since it is required 95 g ash/L POME, calculations showed that the ash requirement on site for pH adjustment is 985 ton ash/month which clearly exceeds the produced amount of 400 ton/month, i.e. only 40% of this amount is covered with current ash production.

Table 4.3. pH determination in water for different samples employed in pH adjustment.

Sample	pH (5% w/w)
Ash	10.67 ± 0.03
$Ca(OH)_2$	12.63 ± 0.13
$Ca(OH)_2$/Ash 60:40 (% wt.)	12.68 ± 0.06

Table 4.4. pH adjustment for POME using different samples.

Sample	Initial pH	Final pH	sample concentration (g/L)
Ash	4.10 ± 0.06	6.59 ± 0.19	94.80 ± 0.19
Ca(OH)$_2$	4.03 ± 0.13	6.66 ± 0.06	3.47 ± 0.12
Ca(OH)$_2$/Ash 60:40 (% wt.)	4.04 ± 0.19	6.65 ± 0.38	4.82 ± 0.15

To overcome this issue, it was proposed to combine slaked lime (Ca(OH)$_2$) with ash in a proportion of 60 %wt. for Ca(OH)$_2$ and 40 %wt. for ash. An additional benefit is to promote a simpler transition from traditional chemicals, such as lime or slaked lime, for pH adjustment to an environmental-friendly and inexpensive option such as ash. Table 4.3. shows that pH measurement in water is higher for the proposed mixture (12.68 ± 0.06) compared to ash (10.67 ± 0.03) and it is almost the same pH value for slaked lime solely (12.63 ± 0.13). For pH adjustment of POME using mixture (Table 4.4.), it was required 4.82 ± 0.15 g mixture /L POME to increase pH over 6.6, whereas for Ca(OH)$_2$ the amount required is 3.47 ± 0.12 g/L POME. The mixture amount was 19.7 times lower compared to ash (94.80 ± 0.19 g/L POME) and 16.7% slaked lime consumption was diminished considering slaked lime alone (3.47 g/L POME). For these reasons, slaked lime/ash 60:40 mixture was employed for pH adjustment for biogas production in this thesis. Additional research should be carried out to evaluate the positive effect of ash addition on microbial community for biogas production from EFB and POME.

4.4   Biomethane potential test (BMP)

4.4.1   Experimental set-up

During preliminary tests, it was determined that the experimental set up proposed in literature (see Figure 3.4) showed a limited space for mixing, instability to support glass bottles containing alkaline solution, and longer times to refill these bottles. In order to improve these issues a different set up was proposed where alkaline solution was hanged using a plastic net. Figure 4.1. showed initial and modified set up. After testing the set-up modification, mixing, and refilling operation were simplified, and better stability for the bottles was observed.

Figure 4.1. Experiment set up A) Initial and B) modified

Table 4.5. summarized initial conditions for each proposed biogas production experiment. For those experiments where POME was not included (M1, M3, and M4), pH adjustment was not carried out. Inoculum concentration was always 8 g VS/L except for M2 experiment.

Table 4.5. Summary of the starting conditions for each biogas production experiment

Experiment	EFB concentration (g VS/L)	POME concentration (g VS/L)	Initial pH	pH after adjustment	Ash/Ca(OH)$_2$ concentration (g/L)
M1	0	0	7.54 ± 0.01	7.54 ± 0.01	NA
M2	0	27	4.06 ± 0.15	6.60 ± 0.04	13.15 ± 3.52
M3	0	8	5.88 ± 0.30	6.62 ± 0.02	3.75 ± 2.55
M4	8	0	7.47 ± 0.01	7.47 ± 0.01	NA
M5	8	0	7.61 ± 0.03	7.61 ± 0.03	NA
M6	2	6	6.26 ± 0.02	6.60 ± 0.07	0.92 ± 0.26
M7	2	6	6.25 ± 0.35	6.61 ± 0.04	1.13 ± 0.67

*NA: Not applicable, pH adjustment is not required

4.4.2 Biogas production from EFB and POME

For 22 days, cumulative methane production and cumulative methane yield were collected in Table 4.6

Table 4.6. Summary of biogas production

Experiment	Brief description	Cumulative methane production (mL CH$_4$)	Cumulative methane yield (mL CH$_4$/g VS)
M2	POME, no inoculum	58 ± 2	7.3 ± 0.3
M3	POME	997 ± 81	415 ± 34
M4	Untreated EFB	310 ± 23	129 ± 9
M5	Pre-treated EFB	179 ± 23	74 ± 10
M6	Untreated EFB:POME	885 ± 75	369 ± 31
M7	Pre-treated EFB:POME	807 ± 69	336 ± 29

Cumulative methane yield for POME in absence of inoculum is the lowest among all experiments. Different researchers reported a maximum value for methane yield equal to 0.5932 mL CH_4/g VS which is 12.3 times lower than the methane yield in this research (Nurliyana et al., 2015). The main difference between both procedures is starting pH since in literature the starting pH value was equal to 5.6 while starting pH for this experiment was 6.6 and working in the pH between 6.5-7.5 is recommended for appropriate methanogenic process (Wu et al., 2015).

For biogas production in experiment M3 (POME), the obtained result (415 mL ± 34 CH_4/g VS) was comparable to cumulative methane yield for adjusted POME in similar conditions (440 mL CH_4/g VS) (Singkhala et al., 2021). Regarding methane yield for untreated EFB (experiment M4), the experimental value (129 ± 9 mL CH_4/g VS) was close to the untreated EFB methane yield range reported in literature (130 – 200 mL CH_4/g VS) (Nieves et al., 2011).

Figure 4.2. and 4.3. show cumulative methane production and cumulative methane yield evolution as a function of time, respectively. Cumulative methane yield from day 8 to day 22 in descending order is: M3 (POME) > M6 (Untreated EFB:POME) > M7 (Pre-treated EFB:POME) > M4 (Untreated EFB) > M5 (Pre-treated EFB) > M2 (POME, no inoculum). Effect of temperature, pre-treatment, and co-digestion on EFB biogas production are discussed in next sections.
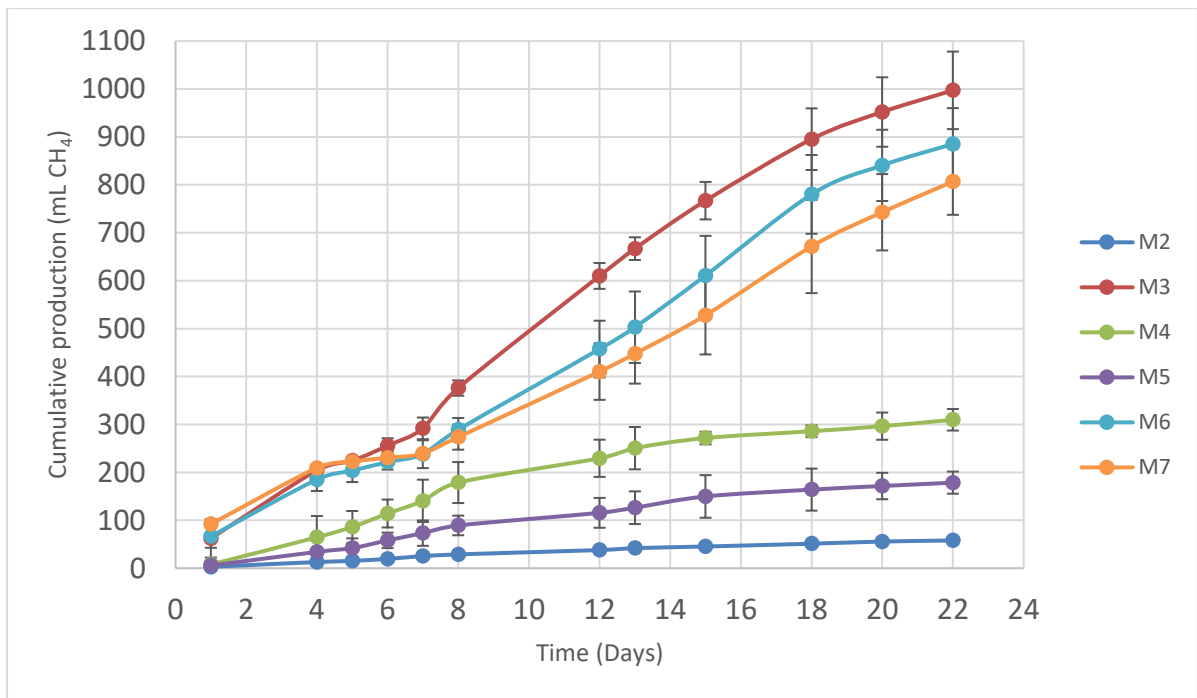

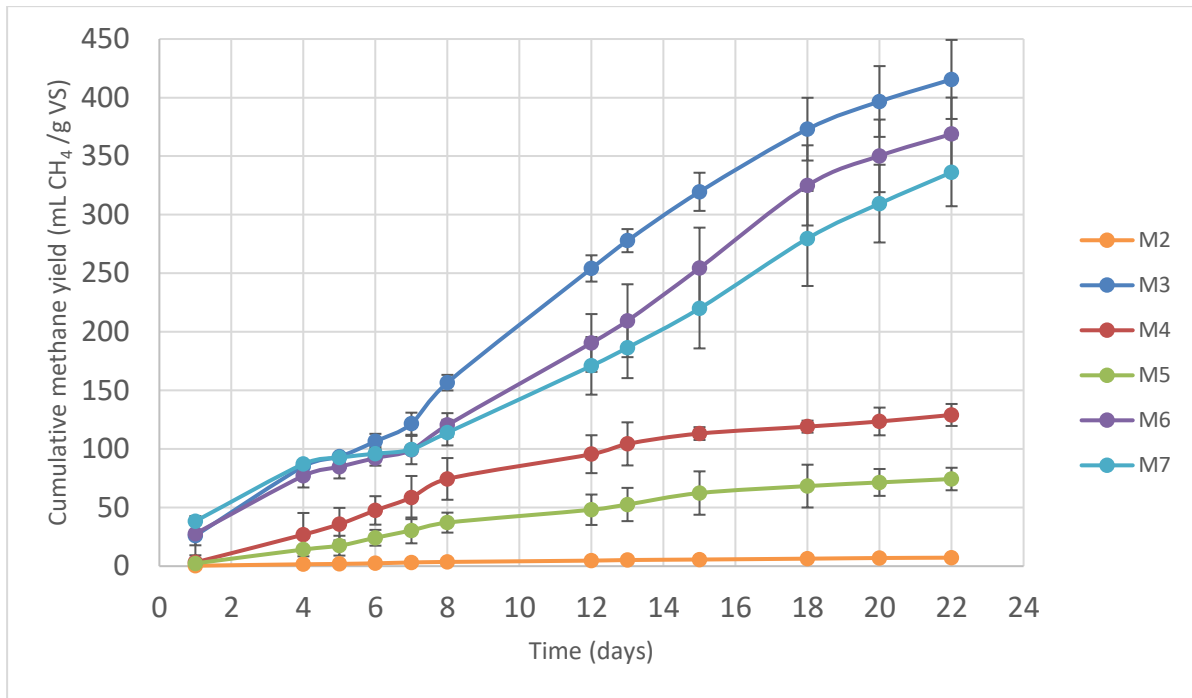Figure 4.2. Cumulative methane production from POME and/or EFB

Figure 4.3. Cumulative methane yield from POME and/or EFB

Changes in total solids, volatile solids, and pH before and after biogas production are summarized in Table 4.7. The removal of total solids ranged from 63 to 83% and for volatile solids the removal ranged from 74 to 90%, showing high removal efficiencies during anaerobic digestion and additional benefits when considering organic load reduction as wastewater treatment. Final pH was between the optimal pH range for biogas production which is between 6.5 and 7.5 (Wu et al., 2015).

Table 4.7 Total solids, volatile solids, and pH changes before and after anaerobic digestion

Experiment	TS removal (%)	VS removal (%)	Initial pH	Final pH
M3 (POME)	83 ± 15	90 ± 13	6.62 ± 0.02	7.30 ± 0.06
M4 (unp EFB)	63 ± 28	74 ± 30	7.47 ± 0.01	6.67 ± 0.09
M6 (Unp EFB:POME)	81 ± 22	89 ± 18	6.60 ± 0.07	7.06 ± 0.06
M7 (Pre EFB: POME)	77 ± 23	87 ± 22	6.61 ± 0.04	7.04 ± 0.19

*Unp: Unpretreated, Pre: Pretreated

4.4.3   Temperature effect on anaerobic digestion

Daily methane production and temperature as a function of time are included in Figure 4.4. and Figure 4.5., respectively.
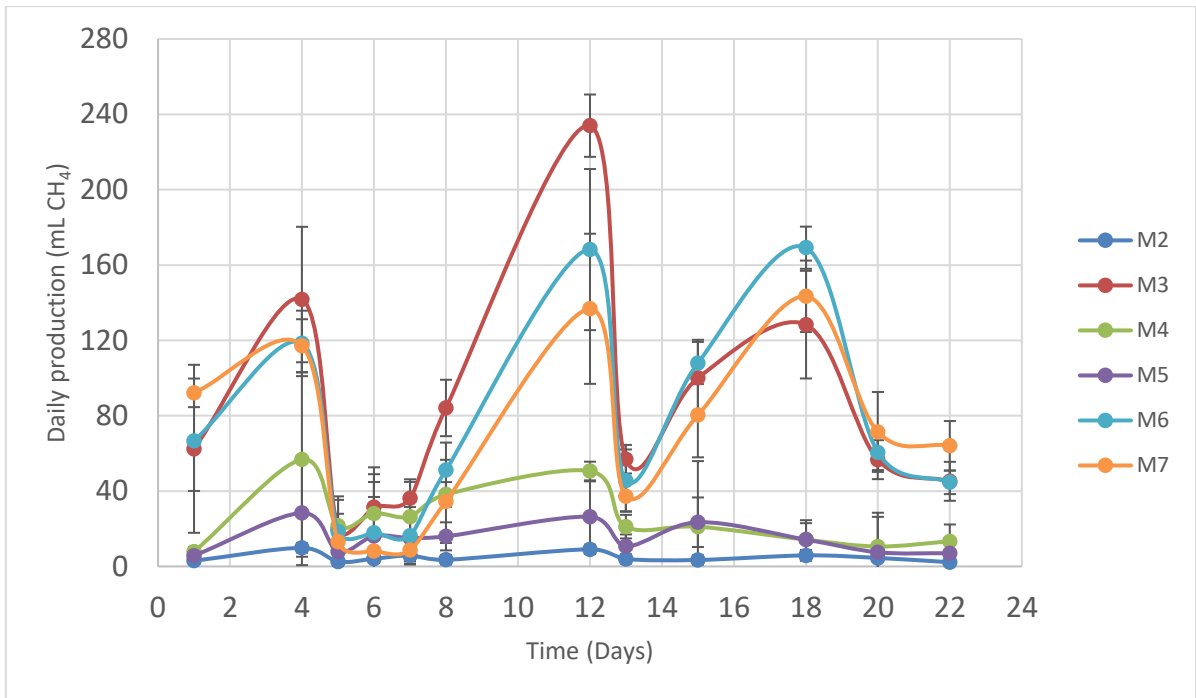
Figure 4.4. Daily methane production from POME and/or EFB
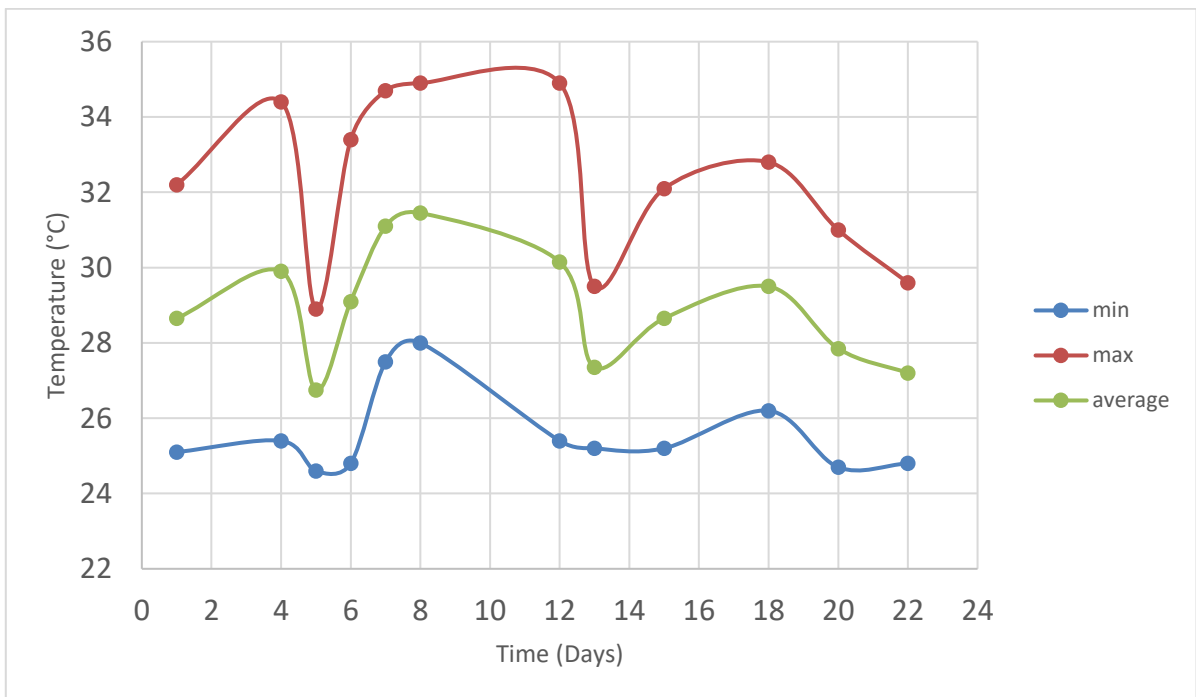
Figure 4.5. Maximum, minimum, and average temperature for biogas production

Temperature variation, especially maximum temperature, showed an effect on biogas production. For days 5 and 13, where the maximum temperature exhibited low values compared to other days, biogas production was also reduced for most of the experiments. However, biogas production was also influenced by the duration of experiments. It was estimated that 90% of biogas production was achieved the first 12-14 days (O-Thong et al., 2012) and methane production rate under thermophilic conditions

was 5 times higher than methane production at mesophilic conditions (Tepsour et al., 2019), therefore it was expected the methane production reduction for the second week which was also affected by temperature which is the case for lower production during day 20 and 22.

4.4.4 Pre-treatment effect on EFB anerobic digestion

The cumulative methane yield for untreated EFB and pre-treated EFB were 129 ± 9 mL CH_4/g VS and 74 ± 10 mL CH_4/g VS, respectively, showing that methane yield for pre-treated EFB was 42.6 % lower. This behavior was also detected for co-digestion experiments where cumulative methane yield for untreated EFB was 369 ± 31 mL CH_4/g VS while for pre-treated EFB was lower (336 ± 29 mL CH_4/g VS). This result was similar to the biogas production from EFB under mesophilic conditions (Liew et al., 2021), where methane yield for untreated EFB was always higher compared to pre-treated EFB. Both results could relate to pre-treatment conditions that were not suitable for biogas production due to mild conditions (e.g., 80°C). Another study (Nieves et al., 2011) used a more concentrated NaOH solution (8%), higher temperature (100°C), and lower EFB particle size (<0.420 mm) reaching a methane production two times higher when compared with untreated EFB. Therefore, proposed alkaline pre-treatment conditions should be redefined to enhance biogas production and, at the same time, balancing costs regarding the use of more concentrated NaOH solution, higher temperature, or reduced particle size.

4.4.5 Co-digestion effect on EFB anaerobic digestion

For co-digestion experiments, cumulative methane yield for untreated EFB and pre-treated EFB were 369 ± 31 mL CH_4/g VS and 336 ± 29 mL CH_4/g VS, respectively, and were comparable to the highest methane yield 415 ± 34 mL CH_4/g VS obtained for POME anaerobic digestion, showing a synergic effect for simultaneous digestion of EFB and POME. Methane yield in this experiment was higher than that reported in literature for mesophilic conditions at the same EFB:POME ratio which is 271 mL CH_4/g VS (Saelor et al., 2017) and closer to EFB and POME co-digestion reported at thermophilic conditions (392 mL CH_4/g VS) (O-Thong et al., 2012). When comparing pre-treatment and co-digestion as strategies for enhancing biogas production, co-digestion exhibited better performance and pre-treatment conditions in this experiment should be reviewed and additional improvement opportunities on methane yield could be considered for EFB:POME ratio optimization.

Since the maximum methane yield for co-digestion was 369 mL CH_4/g VS and taking into consideration a EFB:POME ratio of 2:6 in g VS basis, it was calculated that methane yield in terms of mass of POME and EFB was equal to 46.5 mL CH_4/g of mixed EFB and POME, which would be equal to 46.5 m^3 CH_4 /ton of mixed EFB and POME. Considering an energy content of 36 MJ/m^3 CH_4 (O-Thong et al., 2012), it was estimated that an energy content in produced methane would be 1674 MJ/ ton of mixed EFB and POME.

Considering a flow rate of 4 L POME/s and the EFB:POME ratio of 2:6 expressed in g VS, it was calculated that EFB could be processed at a rate of 0.21 ton/h via anaerobic co-digestion, leading to

3.23% consumption of EFB generated. Similarly, assuming that 4.82 g ash/slaked lime mixture per one liter of POME were used to pH adjustment (6.6), it was estimated that ash consumption for biogas production is 19.9 ton/month, which was equal to 4.98% of total ash produced per month. Besides biogas production, nutrients stored in ash from biomass boiler and EFB could be returned to the field in the water for irrigation and digestate for partial fertilization replacement, following nutrient recycling and circular economy approach, and reaching a zero-waste concept for anaerobic digestion process. Ash is commonly used as nutrient source in palm oil cultivation due to its high content of Ca, K, Mg, and P and, similarly, digestate (also known as sludge from anaerobic lagoon) is added in palm oil plantation as fertilization complement due to its high content of macro and micronutrients, contributing to an increase fruit production (Ramírez et al., 2011). Additionally, the fertilizer values of liquid digestates lie between those of livestock manures and inorganic fertilizers (Nkoa, 2014).

Chapter 5

Conclusions

This chapter finalises this work, summarising conclusions based on result discussion and pointing out aspects to be developed in future work.

The current thesis intended to analyse biogas production from empty fruit bunches (EFB) as waste-to-energy valorization route using laboratory scale biomethane potential test (BMP). Two approaches have been considered for this purpose: EFB pre-treatment and co-digestion.

Regarding material characterization, total solids (TS), volatile solids (VS), and pH measurements for EFB, palm oil mill effluent (POME), and ash were in the same ranges compared to literature. Alkaline pre-treatment was considered as EFB pre-treatment using NaOH 0.1M at 80°C for 2 h with a recovery of 66.6% with main losses during washing step, requiring additional steps to recover solids and discharge wastewater under local regulations.

Adjustment of pH was evaluated using $Ca(OH)_2$/Ash 60:40 (% wt.) leading to 4.82 ± 0.15 g per litre of POME to reach a pH of 6.6 which was 19.7 times lower compared to ash solely, $Ca(OH)_2$ consumption was reduced by 16.7% considering $Ca(OH)_2$ alone (3.47 g/L POME), and allowing a simpler transition from traditional pH chemical agents employed or pH adjustment.

Seven experiments were carried out during 22 days at mesophilic conditions using laboratory scale biomethane potential test (BMP) in order to determine biogas production. Fixed variables were inoculum to substrate ratio (ISR) equal to 1 g VS basis, ambient temperature, substrate concentration equal to 8 g VS/L, working volume equal to 300 mL, headspace (%) equal to 40, mixing equal to 500 rpm for 2 minutes every two days, starting pH of 6.6, and EFB:POME ratio of 2:6 in g VS basis. A simpler experimental set-up based on liquid displacement method was proposed, showing simplification of the regular tasks such as mixing and alkaline solution refilling.

Lowest cumulative methane yield was 7.3 ± 0.3 mL CH_4/g VS for POME under facultative conditions (M2) while highest cumulative methane yield was 415 ± 34 mL CH_4/g VS for POME under anaerobic conditions (M3). Methane daily production is influenced simultaneously by temperature and methane production rate, which is time-dependant.

Untreated EFB (M4) and pre-treated EFB (M5) methane yields were 129 ± 9 mL CH_4/g VS for POME and 74 ± 10 mL CH_4/g VS for POME respectively. Pre-treatment was not suitable as strategy for enhancing biogas production from EFB and pre-treatment parameters used in this research should be evaluated for improvement.

Co-digestion of untreated EFB (M6) and pre-treated EFB (M7) with POME resulted in methane yields of 369 ± 31 mL CH_4/g VS and 336 ± 29 mL CH_4/g VS respectively, showing co-digestion as alternative for biogas production using EFB as feedstock. Methane production of 369 mL CH_4/g VS was equivalent to 46.5 m^3 CH_4 /ton of mixed EFB and POME and represented an energy content of 1674 MJ/ ton of mixed EFB and POME, allowing waste processing of 3.23% EFB and 4.98% ash produced on site and nutrient recycling via water for irrigation and digestate for partial fertilizer replacement, leading to a future zero-waste concept with a total solids and volatile solids removal of 81 ± 22% and 89 ± 18% respectively.

Future research should be carried out to optimize pre-treatment conditions to enhance biogas production, including ash addition benefits for microbial community in anaerobic systems, and EFB:POME ratio evaluation to determine its optimal value maximizing biogas production from EFB and POME co-digestion.

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