5-2021

Biomethanation and Alkaline Wet Air Oxidation of Water Hyacinth (*Pontederia crassipes*) from Ozama River, Dominican Republic

Yessica A. Castro
Utah State University

BIOMETHANATION AND ALKALINE WET AIR OXIDATION OF WATER HYACINTH (*PONTEDERIA CRASSIPES*) FROM OZAMA RIVER, DOMINICAN REPUBLIC

by

Yessica A. Castro

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Biological Engineering

Approved:

_____ Foster A. Agblevor, PhD Major Professor	_____ Ronald C. Sims, PhD Committee Member
_____ Jixun Zhan, PhD Committee Member	_____ Conly Hansen, PhD Committee Member
_____ Carlos Rodríguez, PhD Committee Member	_____ D. Richard Cutler, Ph.D. Interim Vice Provost of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2021

ABSTRACT

Biomethanation and Alkaline Wet Air Oxidation of Water Hyacinth (*Pontederia crassipes*) from Ozama River, Dominican Republic

by

Yessica A. Castro, Doctor of Philosophy

Utah State University, 2021

Major Professor: Dr. Foster A. Agblevor
Department: Biological Engineering

Water hyacinth (*Pontederia crassipes* Mart.), is an invasive aquatic plant that could be considered as a third-generation feedstock for bioconversion processes due to its rapid growth and phytoremediation properties when cultivated in contaminated water. The anaerobic digestion of water hyacinth could be a sustainable approach for the remediation of contaminated waters and the production of bioenergy. The pretreatment of this lignocellulosic biomass and the use of process aids increase the performance of the bioconversion processes.

In this work, the physicochemical characteristics and biomethanation potential of water hyacinth from the Ozama River (Dominican Republic) were determined. Also, the energy consumed in harvesting was estimated. Furthermore, the optimal conditions for the process scaling up were determined including the feed to inoculum ratio (F/I), mesophilic temperature, and supplementation. To improve the biomethanation of water

hyacinth, the effects of wet air oxidation (WAO) and alkaline wet air oxidation (AWAO) on the feedstock's structure and biomethanation were compared. Also, the use of solid residues from thermochemical processing, i.e. biochar, as an aid for the biomethanation of unpretreated and pretreated water hyacinth was studied.

The biochemical methane potential of water hyacinth from Ozama River was 399.2 ± 32.2 N. mL CH_4/g VS_{added}. The estimated energy produced per tonne of fresh biomass was 846.5 MJ, more than 10 times the estimated energy required for harvesting. The estimated higher net energy for a 5 m^3 batch digester occurred at the highest F/I (30) and 40°C. The AWAO was most suitable pretreatment for the biomethanation of water hyacinth than WAO. The AWAO using 0.14 g Na_2CO_3/ g feed at 170°C increased the maximum methane potential of water hyacinth by 24%, and the methane production rate from 4.1 ± 0.2 to 7.8 ± 1.6 N. mL CH_4/g feed · day. The AWAO of water hyacinth at lower temperature and alkali concentration during (0.07 g Na_2CO_3/ g feed at 80°C) increased the methane yield by almost 45% after 21 days of digestion. The effect of poultry litter biochar on the biomethanation kinetics of water hyacinth from the Ozama river was negligible. However, the addition of 10% poultry litter biochar to pretreated water hyacinth (0.07 g Na_2CO_3/ g feed at 170°C), prevented the system from acidification. The AWAO is a promising pretreatment process for the biomethanation of water hyacinth from contaminated water bodies like Ozama river.

(174 pages)

PUBLIC ABSTRACT

Biomethanation and Alkaline Wet Air Oxidation (AWAO) of Water Hyacinth (*Pontederia crassipes*) from Ozama River, Dominican Republic

Yessica A. Castro

Obtaining valuable products from environmental remediation waste is a sustainable approach that contributes to the ecological well-being of developing countries. In the present work, the feasibility of the water hyacinth anaerobic digestion as a post-weed management practice in the Ozama River (Dominican Republic) was demonstrated. The estimated energy required for harvesting was lower than that produced during digestion. The biomethanation of water hyacinth was improved by Alkaline Wet Air Oxidation (AWAO), a thermochemical pretreatment process that almost doubled the methane production rate and increased the yield by 24% when conducted at high temperatures. At lower temperatures, the methane yield of the AWAO water hyacinth was more than 40% higher than the unpretreated biomass. After subjecting water hyacinth to high temperature and low alkali AWAO, the addition of poultry litter biochar, a residue from thermochemical processing, improved the biomethanation kinetics of the system. This dissertation not only contains valuable information for the scale-up of the water hyacinth's biomethanation as a biorefinery process in developed countries but also contributes to the development of sustainable 'from waste to product' technologies in developing countries like the Dominican Republic.

To God almighty, Father, Son, and Holy Spirit:

That your perfect will on my life be accomplished to glorify your Name through my work.

To my parents, Julio César Castro and Altagracia Estevez:

Thanks for your love, trust, and encouragement.

To my siblings, Julissa, Jennifer, Julio Francisco, and Stephany:

Thanks for being my unconditional friends.

To my nieces and nephew, Yulianna, Gloria, Thiago, and Julissbeth:

That I may be an example of integrity and dedication to follow.

To Adrian Johnston:

Thanks for believing in my ability to succeed and for supporting me in this journey.

To my beloved country, Dominican Republic:

That my life and work might contribute to your development.

ACKNOWLEDGMENTS

This research was financially supported by the National Research Fund for Science, Technology, and Innovation [FONDOCYT 2015-2A3-123] of the Dominican Republic Ministry of Higher Education, Science, and Technology (MESCYT).

I would like to thank Dr. John Morales former Research Head of Instituto Especializado de Estudios Superiores Loyola (IEESL) and Willy Maurer, Research Project Coordinator of IEESL for facilitating the submission of the proposal through that institution. I would like to especially thank my committee members, Drs. Foster Agblevor, Ronald Sims, Jixuan Zhan, Conly Hansen, and Carlos Rodriguez, for their support and assistance throughout the entire process.

I give special thanks to my family, friends, and colleagues, for their encouragement, moral support, and patience as I worked my way from the initial proposal writing to this final document. I am also grateful for the support given by Jeevan Kumar on the suggestion of journals during the publication process.

Yessica A. Castro

CONTENTS

Abstract iii

Public Abstract v

Acknowledgments vii

List of Tables xvi

List of Figures xviii

Chapter I Introduction 1

1.1 Dissertation Format 1

1.2 Overview 2

From a Fossil-based to a Bio-based Economy 2

Feedstock for Bio-based Products 3

Water Hyacinth as a Feedstock for Bio-based Production 4

Biomethanation of Water Hyacinth from Ozama River 7

Pretreatment of Water Hyacinth 9

1.3 Research Objectives 10

1.4 Engineering Significance 10

Chapter II Characterization and Biomethanation of Water Hyacinth 12

2.1 Abstract 12

2.2 Introduction 13

2.3 Materials and Methods 17

Study Sites and Water Quality 17

Biomass Harvesting and Preparation 18

Photosynthetic Pigments 18

Density 19

Proximate Analysis 19

Ultimate Analysis 20

Summative Analysis 20

Extractable Salts 21

Inorganic Elemental Analysis 21

Anaerobic Digestion 21

Gas Measurement 22

Modified Gompertz Equation 23

Energy Assessment 23

Statistical Analysis 24

2.4 Results 24

Water Quality 24

Photosynthetic Pigments 25

Density 25

Proximate Analysis 25

Ultimate Analysis (CHNSO) 27

Summative Analysis 28

Extractable Salts 29

Inorganic Elemental Analysis 29

Anaerobic Biodegradation 32

Energy Assessment 32

2.5 Discussion 32

Eutrophication of the Ozama River 32

Chemical Composition of Water Hyacinth 34

Productivity Indicators 35

Biomethanation of Water Hyacinth 36

Potential Inhibitions from Feedstock 37

Energy Assessment 38

2.6 Conclusion 39

Chapter III Effect of High Feed to Inoculum Ratio (F/I) and Temperature on the Biomethanation Kinetics of Water Hyacinth 40

3.1 Abstract 40

3.2 Introduction 41

3.3 Materials and Methods 45

Biomass 45

Inoculum 45

Experimental Conditions 45

Biomethane Production 46

Kinetic Models 46

Energy Analysis 47

Statistical Analysis 48

3.4 Results and Discussion 49

Media Supplementation 49

Feed to Inoculum Ratio (F/I) 49

Inoculum Acclimatization 52

Temperature 53

Kinetic Models 54

Energy Analysis 58

3.5 Conclusion 60

Chapter IV Effect of Wet Air Oxidation on the Composition and Biomethanation of Water Hyacinth 61

4.1Abstract 61

4.2 Introduction 62

4.3 Material and Methods 66

Biomass 66

Pretreatment 66

Proximate and Ultimate Analyses 67

FT-IR Spectra 67

Chemical Oxygen Demand (COD) 67

Anaerobic Digestion 68

Gas Measurement 68

Modified Gompertz Model 69

Statistical Analysis 69

4.4 Results and Discussion 69

Operational Profiles 69

Thermal Degradation 70

Proximate Analysis 73

Ultimate Analysis 73

FT-IR Spectra 75

Chemical Oxygen Demand 76

Anaerobic Digestion 77

Biomethanation Kinetics 81

4.5 Conclusion 82

Chapter V Parametric Studies and Biochar Effect on the Biomethanation of Wet Air Oxidized Water Hyacinth 84

5.1 Abstract 84

5.2 Introduction 85

5.3 Materials and methods 88

Biomass 88

Biochar 88

Surface Area 88

Proximate and Ultimate Analyses 88

Inorganic Elemental Analysis 89

Alkaline Wet Air Oxidation (AWAO) 89

Anaerobic Digestion (AD) 89

Kinetic Models 90

Characterization of Residues 90

Thermogravimetric Analysis 90

Lignocellulose Composition 90

Energy Analysis 91

Statistical Analysis 91

5.4 Results and Discussion 93

Biochar Composition 93

AWAO Operational Conditions 93

Biomethanation Kinetics 94

Effect of Biochar on the Biomethanation of AWAO Water Hyacinth 94

Effect of AWAO on Water Hyacinth 100

Matter Reduction in the Biomethanation of Water Hyacinth 103

Biosolids Elemental Composition 104

Energy Analysis 106

5.5 Conclusion 107

Chapter VI Summary and Conclusion 108

6.1 Variation in Biomass Composition and Biomethane Potential in Ozama River 108

6.2 Energy Produced from Mechanically Harvested Water Hyacinth 109

6.3 Optimization of Water Hyacinth's Anaerobic Digestion 109

6.4 Alkaline Wet Air Oxidation of Water Hyacinth 110

6.5 Optimization of Alkaline Wet Air Oxidation for the Biomethanation 111

6.6 Effect of Biochar on the Biomethanation of Wet Air Oxidized 111

6.7 Characteristics of the Bio solids from Water Hyacinth 111

6.8 Future Prospects 112

References 113

Appendices 143

Appendix A. Map of Sampling Points 144

Appendix B. Energy Analysis for F/I and Temperature Effects on Batch System 145

Appendix C. ANOVA for the Biochar, Alkali and Temperature Effects on the Biomethanation Kinetics of AWAO Water Hyacinth 149

Appendix D. Energy Analysis for the Biomethanation of Low Temperature AWAO Water Hyacinth 153

Curriculum Vitae 154

LIST OF TABLES

Table 2-1 Mean ± SD values of proximate and ultimate analyses, and composition of water hyacinth from the Ozama river.. 26

Table 2-2 Inorganic elements in water hyacinth from Ozama river 30

Table 2-3 Kinetic parameters from the modified Gompertz model for the biomethanation of water hyacinth from the Ozama river. 33

Table 2-4 Estimated energy consumed in the mechanical harvesting, and energy produced by the anaerobic digestion of water hyacinth..... 34

Table 3-1 Methane yield and kinetic parameters at different feed to inoculum ratios (F/I) and temperature (T)..... 55

Table 3-2 Energy analysis for the anaerobic digestion of water hyacinth at 30° and 40°C using different F/I for a 5 m^3 biodigestor..... 59

Table 4-1 Proximate analysis of unpretreated water hyacinth and solid residues from pretreated biomass 72

Table 4-2 Ultimate analysis of unpretreated water hyacinth biomass and solid residues of pretreated water hyacinth..... 74

Table 4-3 Kinetic parameters (mean ± SD) from the modified Gompertz model for the biomethanation of water hyacinth before and after wet air oxidation (WAO) and alkaline wet air oxidation (AWAO). 81

Table 5-1 Methane yield and kinetics after digesting unpretreated and Alkaline Wet Air Oxidized (AWAO) water hyacinth under different pretreatment temperature and alkali concentration. 95

Table 5-2 Methane yield [N. mL CH_4 /g feed] and kinetics after digesting unpretreated and Alkaline Wet Air Oxidized (AWAO) water hyacinth under different biochar concentrations. 98

Table 5-3 Proximate analysis and structural composition of water hyacinth before (biomass) and after (biosolids) anaerobic digestion 102

Table 5-4 Inorganic elements in biosolids from raw and pretreated water hyacinth from Ozama river..... 105

LIST OF FIGURES

Figure 2-1 SEM-EDX images of Na, Cl, K, and Mg in ethanol extractives of water hyacinth from La Ciénaga (brackish water) and El Naranjo (freshwater). 27

Figure 2-2 Biochemical methane potential of water hyacinth from La Ciénaga (brackish waters) and El Naranjo (fresh water) within Ozama River..... 31

Figure 3-1 Biochemical methane potential of water hyacinth from Ozama River) at different feed to inoculum (F/I) ratios when digested at 40°C using non-acclimatized and acclimatized inoculum. 51

Figure 3-2 Biochemical methane potential of water hyacinth from Ozama River at different feed to inoculum (F/I) ratios when digested at 30°C. 52

Figure 3-3 Anaerobic digestion of water hyacinth at 30°C and F/I = 30. 56

Figure 3-4 Periodic biogas production (N.mL/g feed) and methane percentage during the anaerobic digestion of water hyacinth at 30°C and F/I = 30. 57

Figure 4-1 Curves of the differential thermogravimetric analysis of unpretreated and pretreated water hyacinth.. 71

Figure 4-2 FT-IR spectra from unpretreated water hyacinth, and from Wet Air Oxidation (WAO) and Alkaline Wet Air Oxidation (AWAO) solid residues. 75

Figure 4-3 Biogas yield during the anaerobic digestion of unpretreated, wet air oxidized (WAO), and alkaline wet air oxidized (AWAO) water hyacinth. 77

Figure 4-4 Methane production and modified Gompetz models for the unpretreated, Wet Air Oxidized (WAO), and Alkaline Wet Air Oxidized (AWAO) water hyacinth 79

Figure 4-5 Percentage of methane in the biogas during the anaerobic digestion of water hyacinth before pretreatment and after Wet Air Oxidation (WAO), and Alkaline Wet Air Oxidation (AWAO). 80

Figure 5-1 Operative curves of temperature and pressure during the Alkaline Wet Air Oxidation (AWAO) of water hyacinth. 92

Figure 5-2 Interaction plot between alkali concentration] and biochar] on the biomethanation of water hyacint..... 97

Figure 5-3 Curves of the differential thermogravimetric analysis of unpretreated and pretreated water hyacinth. 99

Figure 5-4 Curves of the differential thermogravimetric analysis of the biosolids from the unpretreated and pretreated biomass..... 101

CHAPTER I

INTRODUCTION

1.1 Dissertation Format

The Chapter I of this dissertation provides an overview of the effect of a fossil-based economy in the environment including the water pollution in rivers and other water sources, which manifests in the excessive growth of water hyacinth. The influence of this invasive weed on eutrophic rivers in the Dominican Republic and its impact on the society is discussed. The potential uses of water hyacinth as biomass feedstock, conversion to energy using thermochemical methods and biomethanation were examined. In addition, the research objectives and engineering significance of the project are stated in this chapter. Chapter II is an article published in *Environmental Science and Pollution Research* (Castro and Agblevor 2020a) and deals with the characterization and biomethanation of water hyacinth as a weed management practice in developing countries like Dominican Republic. Chapter III is an article published in *Springer Nature Applied Sciences* (Castro and Agblevor 2020b) that covers the effects of important process control parameters such as thermophilic temperature and feed to inoculum ratio on the biomethanation of water hyacinth. Chapter IV is an article published in *Biomass Conversion and Biorefinery* (Castro and Agblevor 2020c) and focuses on the effect of aqueous oxidative pretreatment on the characterization and biomethanation of water hyacinth. Chapter V is an article in preparation that deals with the effect of lower temperature pretreatment and the addition of biochar as an aid on the biomethanation of

water hyacinth. Chapter VI is a summary of the project findings and states future prospects and recommendation related to the work conducted.,

1.2 Overview

From a Fossil-based to a Bio-based Economy

Since the industrial revolution (1750 AD), fossil fuels have been essential to the energy supply of modern societies. These fuels (coal, oil, natural gas) are comparatively cheap and convenient energy carriers for heating, cooling, lighting, power production (mechanical and electric), transportation, and the manufacturing of fine and bulk chemicals and other materials (de Jong and Van Ommen 2015). However, according to the BP Energy Outlook (P.l.c. 2019), the rise of the global energy demand, triggered by the increasing prosperity in fast-growing developing economies, is expected to cause stress on the limited conventional sources (i.e. fossil fuels) and promote the growth of the renewable ones by 2040. As a preventive approach, Europe has adopted strategies for the application of a bio-based economy. According to the European Commission, *Bioeconomy is Europe's response to key environmental challenges the world is facing already today. It is meant to reduce the dependence on natural resources, transform manufacturing, promote sustainable production of renewable resources from land, fisheries and aquaculture and their conversion into food, feed, fiber, bio-based products and bioenergy, while growing new jobs and industries*. The effective transition from a fossil-based to a bio-based economy requires community actions related to market development, technology, research, science, and policy (Vandermeulen et al. 2012). The implementation of bio-based economies could contribute to the sustainability of developing countries, but the support of the scientific community is required.

The population growth, climate change, reduction of waste, energy, and food security are some of the factors that trigger the application of a bio-based economy. The world's population is expected to grow from 7 to 9 billion by 2050, which would increase greenhouse gas (GHG) emissions, e energy, and food demand (Lewandowski 2017). Since 1750 AD, the combustion of fossil fuels, deforestation, and soil-borne emissions have triggered an increase in the atmospheric concentrations of the major GHG such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) by 40%, 150%, and 20%, respectively (ICCP, 2014). The increasing atmospheric concentration of GHG that leads to global warming could be mitigated by the use of bio-based instead of fossil resources. The utilization of waste from bio-based agricultural practices is not only environmentally friendly but also contributes to food security by increasing the total biomass supply for non-food biomass applications such as the production of biofuels or chemicals (Lewandowski, 2017; Bennich and Belyazid, 2018; Lokesh et al. 2018). Bio-based economies should rely on the use of feedstocks that do not affect food security worldwide.

Feedstock for Bio-based Products

The selection of the right feedstock determines the sustainability of a bio-based economy. The most important factors to consider during the feedstock selection are biomass composition, yield, and sustainability (Wyman 2013). On that basis, the feedstocks used for the production of bio-based products are classified as first- (food crops), second- (energy crops or agricultural residues), and third- (seaweed) generation feedstocks (Allen et al. 2016; Gerbens-Leenes 2017). Even though the first-generation feedstocks are more valuable at the compositional level, they compete with food and feed

production leading to low sustainability. Thus, second and third-generation feedstocks are the most desirable for a bio-based economy. Among second-generation feedstocks, energy crops have a larger water footprint (m^3/GJ) than crop residues (Gerbens-Leenes 2017). Therefore, residual biomass, invasive energy crops that grow in scarce conditions or aquatic plants that can grow in wastewater are ideal.

Water Hyacinth as a Feedstock for Bio-based Production

Water hyacinth (*Pontederia crassipes* Mart.) formerly known as *Eichhornia crassipes* (Mart.) Solms is a free-floating flowering perennial aquatic plant native to the Amazon river basin and present in tropical and subtropical areas in the world. When water bodies are invaded by this macrophyte, there are changes in the water chemistry, reduction in the penetration of dissolved oxygen, increase in evapotranspiration, and flora disruption (Hossain et al. 2015). Water hyacinth is considered as a potential feedstock for bio-based production because of its high growth rate, minimum requirements for cultivation, and no competition with food and feed production. Water hyacinth productivity is up to 100-200 MT/ha / yr (Duke 1983). Also, water hyacinth can be cultivated under stress, including temperatures as low as 14°C, and water with salinity up to 2%, and very high or limited nutrient (N, P) content (Wilson et al. 2001). Furthermore, water hyacinth has been successfully used in cleaning up municipal and agricultural wastewaters for the removal of algae, fecal coliform bacteria, suspended particles, trace toxic metals, organic compounds, and other impurities (Gupta 1980). Water hyacinth is a promising feedstock for bio-based conversion processes.

Uses of Water Hyacinth

In geographic areas where water hyacinth is present, this lignocellulosic biomass has been used to satisfy societal needs such as feed, heat, transportation, and chemicals through physical and biochemical processing. Water hyacinth has been reported to be useful for paper production, fertilizer, animal feed, composting, bioethanol, biogas, and furniture (Rezania et al. 2015a). Water hyacinth fiber was characterized for potential use in the textile industry (Bhuvaneshwari and Sangeetha 2016). The roots of water hyacinth have been used as a matrix to immobilize iron oxyhydroxide (FeOOH) to be used as arsenic adsorbent (Lin et al. 2018). Similarly, water hyacinth pellets immobilized with *Chlorella sp.* was used for the bioremediation of cadmium (Shen et al. 2018). Carboxymethyl cellulose from water hyacinth has been used as a binder material for lithium-ion battery electrodes (Hidayat et al. 2018). Water hyacinth is a good potential feedstock for biogas production due to its high nitrogen content and C/N ratio of around 15 (Koutika and Rainey 2015). Studies show that the anaerobic digestion of water hyacinth and cow dung mixture (4:1) is estimated to yield 370 L of biogas per kg of dry biomass (Rezania et al. 2015b). Anaerobic fermentation of water hyacinth has also been conducted using *Clostridium diolis*, and *Clostridium beijerinckii* for biohydrogen and biobutanol production, respectively. Some of the value-added products that have been experimentally obtained from water hyacinth include enzymes (i.e. cellulase, β-glucosidase, and xylanase) as well as organic acids such as levulinic acid, and shikimic acid (Sindhu et al. 2017). Furthermore, two antioxidant peptides from water hyacinth leaf protein hydrolysates were isolated, purified, and identified for potential use as supplements of human diet (Zhang et al. 2018). The variety of potential applications for

the use of water hyacinth as feedstock requires the evaluation of the characteristics of the biomass to determine the feasibility of the conversion approaches.

Thermochemical Conversion of Water Hyacinth to Biofuels

Combustion and thermochemical processing such as pyrolysis and gasification are some of the thermal applications that have been conducted using water hyacinth as feedstock. Slow pyrolysis of water hyacinth was studied and showed 24.6 wt. % of oil production (Biswas et al. 2017). Two-stage pyrolysis of fresh, putrefied, and microbe-treated water hyacinth yielded 34.34%, 58.31%, and 43.21% by mass of highly upgraded oil, respectively (Hussain et al. 2017). Also, microscale pyrolysis of dried (~8% moisture) water hyacinth was performed at 500°C resulting in a bio-oil mainly composed of glycerol, *o*-benzenediol, *p*-benzenediol, arabinoic acid, levoglucosan, and hexadecanoic acid (Santos et al. 2017). Likewise, water hyacinth modified with the addition of $Fe_2(SO_4)_3$ has been used for co-gasification with coal to reduce the ash fusion temperature of the process (Liu et al. 2013). Similarly, water hyacinth has been used for the production of charcoal briquettes for combustion in communities from Thailand (Suttibak and Loengbudnark 2018). Even though water hyacinth has been used as feedstock for thermochemical processing, the feasibility of this feedstock for this type of conversion process is questionable.

The use of water hyacinth for thermochemical processes is economically unfeasible due to the high amount of energy required not only for the biomass conversion but also for the conditioning before processing. The sustainability assessment of water hyacinth for fast pyrolysis showed that drying and grinding are required steps for this application due to the very high moisture content (i.e. 92.2 ± 3.5%) and low HHV (i.e.

14.1 MJ/kg) of the plant on fresh conditions (Buller et al. 2015). Besides, studies showed that decomposition of cellulose in water hyacinth at temperatures below 280°C was not possible under pyrolytic conditions but was attained through hydrothermal treatment (Luo et al. 2011). Similarly, feedstocks with more than 15% of water content are not suitable for conventional gasification systems but are considered to be suitable for supercritical water gasification (SCWG). However, SCWG is bound to high installation costs due to elevated temperature-pressure and rust-resistant materials, and high energy requirements (Sikarwar et al. 2017). To achieve 95% of efficiency on SCWG of water hyacinth, temperatures over 500°C, and reaction times longer than 60 min are needed (QiuLing et al. 2017). Despite the thermochemical conversion processing that has been experimentally conducted on water hyacinth, more economically feasible routes for obtaining valuable products from this feedstock should be studied.

Biomethanation of Water Hyacinth from Ozama River

The Dominican Republic is a developing country located in the Caribbean Sea, within the American continent. The services industry, mainly tourism-related activities, dominates the Dominican economy (Pozo et al. 2013). The tributary rivers Ozama and Isabela, located in Santo Domingo, the capital city of the Dominican Republic, are affected by water hyacinth. The contamination of these water bodies leads to further eutrophication due to the presence of water hyacinth (Salas and Martino 1988). This condition is socio-economically detrimental for Santo Domingo due to the resulting bad odor and the inability to use these water bodies for urban, recreational, and agricultural activities. The main areas of the rivers affected by the presence of water hyacinth are highlighted in Appendix A. In addition to water hyacinth, *Pontederia Azurea* (Swartz)

Kunth also known as anchored water hyacinth was identified at a lower density in some of the sampling points (e.g. El Naranjo). Currently, the mechanical harvesting of water hyacinth is conducted periodically at the high-density areas within the Ozama and Isabela rivers (Gavilán 2018). The use of the residual biomass for the production of biobased goods is an alternative that could contribute to the transition from fossil-based to the bio-based economy in the Dominican Republic.

The use of water hyacinth from Ozama and Isabela rivers for bioenergy production could mitigate the costs associated with weed harvesting and increase the sustainability of this process. Aquatic plants like water hyacinth are considered to be promising feedstocks for anaerobic digestion due to their high water content and high digestible organic matter (Wellinger et al. 2013). The anaerobic digestion is a process where hundreds to thousands of microbial species convert complex organic matter into biogas (CH_4 and CO_2) through hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Pavlostathis and Giraldo-Gomez 1991; Wellinger et al. 2013). The feasibility of the anaerobic digestion of water hyacinth as a post weed management practice in the Ozama river is explored in Chapter II (Castro and Agblevor 2020a). The water quality from two distinct areas of the Ozama river and the characteristics and biomethanation kinetics of the water hyacinth from those sites are compared. For the feasibility analysis, the energy required for harvesting and that produced from the water hyacinth bioconversion process were compared. Similarly, a parametric study on the anaerobic digestion of water hyacinth based on kinetics and energy analyses is presented in Chapter III. The main and interaction effects of different feed to inoculum (F/I) ratios, mesophilic temperatures, media supplementation on the kinetics of the water hyacinth

biomethanation, and their alteration by inoculum acclimatization were studied through factorial experiments. The differences in kinetics and energy balance between the anaerobic digestion of water hyacinth at different F/I and low and high mesophilic temperatures are also presented in Chapter III. The potential viability of water hyacinth from Ozama River as a biogas feedstock is established in the following two chapters.

Pretreatment of Water Hyacinth

The productivity of the bioconversion processes from lignocellulosic feedstocks, e.g. water hyacinth, is limited by the recalcitrance of the biomass. Pretreating lignocellulose before fermentation increases the bioavailability of the targeted macromolecules resulting in faster digestion (Tian et al. 2005; Xu et al. 2019; Zoghlami and Paës 2019; Sankaran et al. 2020). The water hyacinth from the Ozama river was subjected to wet air oxidation (WAO) and alkaline wet air oxidation (AWAO) under lower pressure conditions. The effect of these pretreatments on the structure and biomethanation kinetics of water hyacinth feedstock is presented in Chapter IV (Castro and Agblevor 2020c). The chapter also shows the feasibility of WAO and AWAO for the biomethanation of this feedstock by comparing the pretreatment heating energy and the produced energy from unpretreated and pretreated water hyacinth. Finally, parametric studies on the AWAO of water hyacinth for anaerobic digestion are presented in Chapter V. The study considers the temperature and the alkali load as control parameters for optimization. The effect of poultry litter biochar as an aid on the biomethanation of pretreated and unpretreated water hyacinth is also discussed in Chapter V.

1.3 Research Objectives

The purpose of this dissertation is to provide insight on the biomethanation of the invasive water hyacinth as a post weed management practice in eutrophic water bodies, and to improve the biochemical methane potential of this feedstock via aqueous oxidative pretreatment.

- Objective 1. Determine the physicochemical characteristics and composition of water hyacinth from Ozama River.
- Objective 2. Determine the biochemical methane potential of water hyacinth from Ozama river.
- Objective 3. Determine the effect of high feed to inoculum ratio (F/I), temperature, and inoculum acclimatization on the biomethanation of water hyacinth.
- Objective 4. Determine the effect of oxidative pretreatment on the structure and biomethanation of water hyacinth
- Objective 5. Determine the effect of low pretreatment temperatures on the biomethanation of water hyacinth
- Objective 6. Determine the effect of biochar on the biomethanation of pretreated water hyacinth.

1.4 Engineering Significance

The biomethanation of water hyacinth provides an environmentally friendly solution for the use of this invasive plant that affects 50 countries around the globe. Since water hyacinth is generally mechanically removed from eutrophic water bodies to reduce the impact of this species on aquatic ecosystems, the use of this feedstock for bioenergy

production would mitigate the costs related to harvesting. Similarly, the optimization of the biomethanation of water hyacinth could be useful during the scaling up of batch systems to increase the process performance by controlling the mesophilic temperature and high feed to inoculum ratio. The pretreatment of water hyacinth increases the digestibility of the feedstock reducing the bioprocessing time, improving the efficiency of the process. This research is intended to benefit developing countries which are affected by water hyacinth such as the Dominican Republic. However, the findings on the pretreatment of water hyacinth are of importance to any bioconversion process using this weed as feedstock. The effect of aqueous oxidative pretreatment and on the biomethanation of water hyacinth is very significant for constructed systems where water hyacinth is cultivated for phytoremediation of wastewaters (i.e., wetlands). The present work contributes to the elimination of waste and continual use of resources, activities that define a circular economy.

CHAPTER II

CHARACTERIZATION AND BIOMETHANATION OF WATER HYACINTH AS A POST WEED MANAGEMENT PRACTICE

2.1 Abstract

Anaerobic digestion of water hyacinth (*Pontederia crassipes* Mart.) from eutrophic water bodies could be a sustainable post-weed management practice to generate bioenergy. Comparative analyses of the water quality, physicochemical characteristics, and biomethanation kinetics of water hyacinth from two sites with different water types (brackish versus freshwater) in the Ozama river, Dominican Republic, were conducted. Also, the energy produced from the anaerobic digestion and that consumed in harvesting was estimated. The highest non-structural components in the form of protein (18.8 ± 1.9%) and extractives (26.4 ± 0.1%) were found in brackish water hyacinth, whereas that from freshwater had the highest amount of holocellulose (41.2 ± 2.8%). Indicators of plant productivity, i.e., chlorophyll b and bulk density, were more than 30% higher in brackish than in freshwater hyacinth. The methane production rate in the digestion of water hyacinth from brackish water (22.5 N. L/kg VS_{added}· day) was twice that from freshwater (10.0 N. L/kg VS_{added}· day). The higher nutrient content in the brackish water could have influenced the superior performance of water hyacinth from that source compared with that from freshwater. Overall, the maximum methane potential of the Ozama river water hyacinth was 399.2 ± 32.2 N. L CH_4/kg VS_{added}. The estimated energy produced per ton of fresh biomass was 846.5 MJ, but only 57.9 MJ would be required for mechanical harvesting. The biomethanation of water hyacinth can mitigate weed management costs in developing countries.

2.2 Introduction

Water hyacinth (*Pontederia crassipes* Mart.), formerly *Eichhornia crassipes* (Mart.) Solms (Pellegrini et al. 2018) is one of the most noxious and invasive aquatic plants threatening the water quality of tropical and subtropical ecosystems. The capacity of this plant to reproduce sexually and asexually leads to high growth rates and formation of large floating mats. As a result, water bodies affected by water hyacinth have lower oxygen and high organic debris contents. Decaying biomass has detrimental effects on rivers such as acceleration of eutrophication, unpleasant taste of water and odor due to oxygen depletion (Jones 2001; Hronich et al. 2008; Gettys et al. 2009). Increased eutrophication and reduced light penetration due to the dense mats can be lethal to fish and other plant species. Invasions by aquatic weeds have also been linked to increases in human water-related diseases (Jones 2001; Chamier et al. 2012). The proliferation of water hyacinth in rivers and its detrimental impact on the ecosystems require sustainable weed management practices.

The reduction of costs associated with weed management has the potential to contribute to the sustainability of environmental protection practices. In high-income countries, millions of dollars are expended annually to prevent harbors from aquatic weed invasions. California Bay-Delta paid $46.852 million on herbicidal treatments to control invasive weeds between 2013 and 2016 (Jetter and Nes 2018). In developing countries, high costs can limit the application of environmental management practices. Therefore, sustainable and cost-effective methods for weed control are needed. Herbicides (e.g. diquat, ioxynil + 2,4-D-isooctyl) can be as effective as manual and mechanical harvesting but are linked to higher operational costs (Alimi and Akinyemiju 1990). The use of

chemical methods to eliminate water hyacinth from water bodies is five times less cost-effective than biological, mechanical, and integrated methods (Wyk and Wilgen 2002). However, the mechanical removal of weeds is connected to high disposal costs. Some methods that have been considered for facilitating and reducing disposal expenses are energy-consuming such as fluidizing, dewatering, and combustion (Livermore et al. 1971). Integrating the mechanical harvesting of water hyacinth with the bioprocessing of the biomass could reduce the harvesting and weed disposal costs by generating valuable products.

Ozama river, an important water body in the Dominican Republic that is used for fishing, urban, industrial, recreational, and agricultural activities, has been invaded by water hyacinth. Previous reports on the water condition of the river along Santo Domingo showed turbidity ranging from 5.0 to 12.0 NTU; 10-35 μg/L of chlorophyll-a; 0.4 - 4.0 mg/L dissolved oxygen (DO); and salinity levels ranging from 0.1 to 2.5 PSU (Miño et al. 2011). Water hyacinth has been identified as the main macrophyte associated with the high nutrient contamination of the river due to plant debris sedimentation (Salas and Martino 1988). Corrective measures were applied recently to mitigate the eutrophication of the water through the mechanical harvesting of the weed (Gavilán 2018). After removal, the plant biomass could serve as a feedstock for the generation of valuable products, which would potentially contribute to the sustainability of environmental protection practices by reducing the costs associated with weed management, a key factor in developing countries.

The biomethanation of water hyacinth from contaminated rivers in developing countries could be a sustainable weed management practice since the pollutants

accumulated in the biomass can be digested or immobilized during anaerobic digestion while generating bioenergy. Water hyacinth has phytoremediation properties targeting heavy metals, and organic and inorganic compounds such as sulfates, phosphates, nitrates, nitrites, ammonia, phenols, and formaldehyde (Wolverton and McKown 1976; Mahmood et al. 2010; Moyo et al. 2013; Gong et al. 2018; Ting et al. 2018; Melignani 2019; Shirinpur-valadi et al. 2019). Cultivation of water hyacinth in contaminated waters and subsequent harvesting of the biomass increased DO, and decreased total dissolved solids (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD), phosphorous, and nitrogen in the water (Saha et al. 2017; Edwige et al. 2018; Sekar and Ansari 2018; Zhang et al. 2019). Anaerobic digestion could be a sustainable process for the treatment of water hyacinth after phytoremediation of contaminated waters. Many xenobiotics including monoaromatic and polyaromatic substances with or without chloro substitutes can be degraded or dechlorinated by anaerobic mixed cultures (Gallert and Winter 2005). Aquatic plants have also been identified as one of the most promising feedstocks for anaerobic digestion due to their high water content and low indigestible organic matter (Wellinger et al. 2013). The implementation of this technology in rural areas has potential dual benefits for producing renewable energy and treating organic wastes (Radu et al. 2017). In addition, biogas could one day be used as fuel for aquatic harvesters (Angelidaki et al. 2018).

The success of integrating the management of water hyacinth using physical removal and biomethanation methods require understanding the impact of the up-taken compounds on the bioconversion process. Monitoring chlorophyll levels helps to estimate the effect these compounds (e.g. formaldehyde) have on photosynthesis efficiency and

macrophyte bioproductivity, which are necessary for phytoremediation proficiency (Lage-pinto et al. 2008; Pavlović et al. 2014; Gong et al. 2018). Progressive drought and nutrient stress decreased chlorophyll content in water hyacinth and consequently compromised the photosynthetic activity of the plants (Venter et al. 2017). TDS are organic solutes and salt ions that can act as stress agents for water hyacinth and be detrimental for anaerobic digestion when they accumulate in the plant biomass. Within six days, water hyacinth is able to remove up to 55% of TDS from waters containing 4500 mg/L TDS (Sekar and Ansari 2018). However, high concentrations of chloride salts (i.e. 4-10g/L) in feedstock for anaerobic digestion have an inhibitory effect on biomethane production (Mccarty and Mckinney 1961; Feijoo and Soto 1995). Reports of the effect of TDS on water hyacinth growth are variable. When plants were cultivated in high TDS waters (i.e. sewage), larger leaves were observed than when cultivated in distilled, tap, and lake waters (Daddy et al. 2002). In contrast, other authors (Sekar and Ansari 2018) reported a reduction in plant size and chlorophyll production due to high TDS.

The water quality and composition of the water hyacinth from areas with different characteristics need to be accounted for when considering anaerobic digestion as post weed management practice. The performance of the bioconversion processes such as anaerobic digestion depends on the feedstock composition, which is influenced by growth conditions (Angelidaki and Sanders 2004; Agblevor and Pereira 2013). In the Dominican Republic, water hyacinth from two sites (La Ciénaga and El Naranjo), with different water types, TDS loads, and demographic characteristics within the Ozama river are being affected by water hyacinth growth. La Ciénaga (brackish water) and El Naranjo

(freshwater) are 1.5 km and 23.14 km north of the Caribbean Sea, respectively. The TDS of freshwater like that from El Naranjo is below 1000 ppm, whereas estuaries or brackish water like that from La Ciénaga have between 1000 and 35,000 ppm of TDS (Swenson and Baldwin 1965). La Ciénaga is a dense low-income area of Santo Domingo city characterized by numerous informal settlements on the riverbank while El Naranjo is a low populated rural area located in the peripheries of Santo Domingo. The anthropogenic contamination at La Ciénaga is higher than at El Naranjo. The Ozama river carries solid waste, raw sewage, industrial discharges, and pestilential odor along La Ciénaga (Chantada 1991; Edelman 2019). These differences between La Ciénaga and El Naranjo could impact the water hyacinth characteristics and biomethanation performance.

The energy generated through the anaerobic digestion of water hyacinth from eutrophic rivers can mitigate the costs associated with weed harvesting, making this process more sustainable in developing countries such as the Dominican Republic. In the present work, the water quality of the Ozama river at La Ciénaga and El Naranjo were evaluated. The physicochemical characteristics including bioproductivity indicators (chlorophyll, and density), and the biomethanation kinetics of the water hyacinth from La Ciénaga and El Naranjo were compared. Additionally, the energy produced by the anaerobic digestion of water hyacinth from the Ozama river was compared to the energy required to mechanically harvest the plant from eutrophic rivers.

2.3 Materials and methods

Study Sites and Water Quality

Samples of water hyacinth were collected from two sites: El Naranjo (18°34'27.2"N 69°47'09.9"W) and La Ciénaga (18°29'21.8"N 69°52'57.4"W) within

Ozama River (Appendix A). The sampling sites were 21.64 km apart along the river. The water type at El Naranjo is freshwater, whereas the water at La Ciénaga is brackish. The water quality (temperature, pH, DO, salinity, nitrates, and TDS) were measured in situ during harvesting using YSI DSSPro (YSI Incorporated, Yellow Springs OH, USA). TDS and nitrate measurements were repeated the following year after harvesting. Because only one site per water type was sampled, caution must be used when interpreting the data.

Biomass Harvesting and Preparation

About 10 kg of freshwater hyacinth biomass was manually harvested from each site and knives were used to discard the roots. The leafy biomass was washed with tap water, ground using Power Pro 2 Model FP 1510 (Black and Decker, Towson, MD, USA), and placed on shelves to dry at ambient conditions for 3 weeks at the Specialized Institute of Higher Studies Loyola (San Cristobal, Dominican Republic). The air-dried ground biomass was stored and shipped to Utah State University. The rest of the preparation was conducted as described by ASTM E 1757-01. The biomass was milled with a Thomas-Wiley Laboratory Mill Model 4 (Thomas Scientific, Swedesboro, NJ, USA) equipped with a 2 mm mesh. Ro-Tap model E test shaker (W.S. Tyler, Mentor, OH, USA) was used for sieving.

Photosynthetic Pigments

For the determination of chlorophyll-*a* (Ca) and chlorophyll-*b* (Cb), 0.5 g of prepared biomass was placed in test tubes with 80% acetone (10 mL) and vortexed for 5 min. The absorbance of the supernatant was taken at 470, 646, and 663 nm using a DR5000 Hach UV-Vis spectrophotometer (Hach Company, Loveland, CO, USA).

Pigment content was calculated using Lichtenthaler (1987) equations. Based on previous research, chlorophyll content measurements using air-dried biomass do not differ from those using fresh biomass (Roshanak et al. 2016). The procedure was conducted in triplicates for each biomass type.

Density

Bulk volume (VB) of air-dried biomass (180 μm-850 μm) was determined using three graduated cylinders according to the methods outlined by Mani et al. (2008). The biomass was poured to the containers from a 300 mm height measured from the bottom of the container. The procedure was conducted four times for each biomass type.

Proximate Analysis

The analyses were conducted in triplicate using a TGA-Q500 (TA Instruments, New Castle, DE, USA) according to previous works (García et al. 2013; de Jong and Van Ommen 2015). The alumina pan containing 20 mg of biomass was heated at a rate of 10 °C/min to reach a maximum temperature of 800 °C. Nitrogen at flow rates of 40 mL/min and 60 mL/min was used as reference gas, and inert gas, respectively. At 600 °C, the carrier gas was changed to air instead of nitrogen, at the same flow rate (60 mL/min) to allow fixed carbon combustion.

Equations 2-1 to 2-3 were used for the determination of volatile solids (VS), fixed carbon (FC), and total ash content (ASH).

$$\%VS = ((W_{T=190°C} - W_{T=550°}) * 100\%)/W_{T=190°C} \quad \text{(Eq. 2-1)}$$

$$\%FC = ((W_{T=600°C} - W_{T=700°}) * 100\%)/W_{T=190°C} \quad \text{(Eq. 2-2)}$$

$$\%ASH = (W_{T=700°C} * 100\%)/ W_{T=190°C} \quad \text{(Eq. 2-3)}$$

Ultimate Analysis

The organic elemental analysis (CHNSO) was conducted using FLASH 2000 Organic Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The oxygen content was calculated as the residual mass after accounting for CHNS and ash content. The experiment was performed with four replicates per site.

Summative Analysis

The moisture content was determined using the IR-60 infrared moisture analyzer (Denver Instruments, Bohemia, NY, USA) as described in ASTM E-1756-08, Test Method B. The total extractives were determined via sequential extraction using ethanol/toluene mixture (1:2), 95% ethanol, and deionized water. For the extractions, ASTM E1690-08 was followed and the BUCHI 011 rotavapor equipped with a BUCHI 461 water bath used (BUCHI AG, Fawil, Switzerland). The ash content was determined using a Thermo Scientific Lindberg/Blue M furnace (Thermo Fisher Scientific, Waltham, MA, USA), following ASTM E 1755-01. The non-extractable ash was the inorganic material in the biomass after extractives removal. The extractable ash was the difference between the total ash on a whole dry basis and the non-extractable ash. The protein content was estimated using the nitrogen conversion factor (NF = 6.25).

The carbohydrates and acid-insoluble lignin were determined in six replicates following ASTM E 1758-01 and in triplicate using ASTM E1721 methods, respectively. For lignin combustion, 475°C instead of 575°C was used, for a 20h period. The monosaccharides were measured using LC-10AT, equipped with a RID-10A (Shimadzu Corp., Kyoto, Japan). The sample was injected at 0.40 mL/min and passed through a BP-800Pb column (Benson Polymeric, Reno, NV, USA) at 80°C for separation.

Monosaccharides were determined for six replicates per site. Cellulose was calculated from glucose, assuming that 90% of the monomer came from the digested polymer and 10% from hemicellulose (Deka et al. 2018). The rest of the sugar monomers derived from hemicellulose.

Extractable Salts

To assess the type of chloride salts accumulated in the biomass, the water hyacinth extractives were analyzed with a FEI Quanta FEG 650 Scanning Electron Microscopy (SEM) (FEI Company Oregon, USA). The instrument was equipped with an Oxford energy dispersive X-ray spectrometer (EDS) with X-Max detector (Oxford Instruments, Abingdon, UK).

Inorganic Elemental Analysis

For the total inorganic elemental composition, 2.0 g of water hyacinth ash from each site was acid digested according to EPA 3050 and analyzed using ICP-AES by Utah State University Analytical lab (USUAL), Logan, UT, USA. The results of the duplicate samples were reported on dry ash basis.

Anaerobic Digestion

The biochemical methane potential (BMP) of water hyacinth was determined following the guidelines in Holliger et al. (2016). The inoculum used was mesophilic anaerobic sludge from North Davis Sewer District (Syracuse, UT, USA), provided by the Plant Superintendent, Mr. Myron Bachman, in March 2019. The sludge had 2.3 ± 0.08 % total solids, 62.4 ± 1.9 VS% (1.4 ± 1.12% VS on a dry basis), and pH 7.8 ± 0.07. The standard anaerobic medium was prepared as reported by Angelidaki et al. (2009) but without the addition of resazurin. Since there was no a priori evidence of the presence of

nutrients on the feedstock or inoculum, anaerobic media was added to the reactors. The biodegradation reactions took place in 200 mL amber serum bottles containing 1.2 g of water hyacinth mixed with 50 mL of anaerobic medium and 50 mL of sludge. The negative control contained the anaerobic medium and sludge without the biomass. The experimental units had 2.365% total solids and the feed to inoculum ratio (F/I) was 1.0. The triplicated samples and negative control had 1.445 g and 0.725 g of total VS, respectively. The bottles were incubated inside a reciprocal shaking water bath, Precision Model 50 (American Laboratory Trading, East Lyme, CT, USA) at 38.0 ± 1.0 °C.

The original assay (Group 1) was reproduced (Group 2) in duplicate for both water hyacinth types using the residual anaerobic sludge from Group 1 as inoculum.

Gas Measurement

The produced gas was measured via volume displacement using a lubricated glass syringe every 48 h-72 h and analyzed using an Agilent 490 Micro (Group 1) and Agilent 7890B (Group 2) Gas Chromatographs (Agilent Technologies, Santa Clara, CA, USA). The measured volume (V) was converted to normal volume (V_0) through Eq. 2-4, where T_0 = 273.15 K and P_0 = 101,325 Pa. The barometric pressure (P) and temperature (T) during the gas measurements were 86,400 ± 6.6 Pa and 294.3 ± 0.4 K, on average.

The accumulated methane volume was reported per mass of VS added to the systems. The normalized volume of methane produced by the negative control, which is the inoculum without VS added, was subtracted from all the experimental units to eliminate the methane due to inoculum substrate residues. When using the present method (Group 1), the biochemical methane potential of amorphous cellulose was 395.3

N.L CH_4/Kg VS added, which is 95.4% of the theoretical value (i.e. 414 N.L CH_4/Kg VS).

$V_0 = V * P * T_0 / P_0 * T$ (Eq. 2-4)

Modified Gompertz Equation

The modified Gompertz model for the batch anaerobic digestion assumes that methane production follows the microbial growth pattern, and is appropriate for batch systems (Kafle and Chen 2016). In the model (Eq. 2-5), W [N.L CH_4/kg VS added] is the accumulated methane produced as a function of time, A [N. L CH_4/kg VS added] is the maximum methane produced, K_z [N. L CH_4/Kg VS added * day] is the absolute growth rate, and T_{lag} [days] is the lag time. The doubling time (T_d) was calculated from the model. The W (t) curves of each replicate were fitted using the data analysis add on "Solver" in Microsoft Excel 2010.

$$W(t) = A * EXP\left(-EXP\left((e * k_z / A) * (T_{lag} - t) + 1\right)\right) \quad \text{(Eq. 2-5)}$$

Energy Assessment

The operational characteristics associated with harvesting water hyacinth were calculated from previous studies with harvesting rates up to 9.3 t/h, (Bryant 1969). However, rates up to 34.55 t/h have been recorded for mixed aquatic plants using similar equipment (Smith 1984). The operative costs considered in this study were due to diesel fuel consumption (10- 15 L/h) of aquatic harvesters with middle load capacity, i.e. 2.5 t/load (Julong 2018). Eq. 2-6 and Eq. 2-7 were used to estimate the energy consumed (E_c [MJ/$t_{biomass}$]) in harvesting and energy produced (E_p [MJ/$t_{biomass}$]) from anaerobic digestion of fresh biomass. FC [L/h] is the fuel consumption per machine operation time, assumed to be 15, and HR [$t_{biomass}$/h] is the harvesting rate, assumed to be 10. The higher

heating values (HHV) are 38.6 MJ/L diesel and 0.0398 MJ/L CH_4. BMP [L CH_4/Kg VS] is expressed on a fresh biomass basis under the assumption that the water content of the harvested biomass is 91% (Akendo et al. 2008). The BMP value is the models' mean on the anaerobic digestion of water hyacinth from the Ozama river.

$$E_c = (FC/HR) * HHV_{fuel} \quad \text{(Eq. 2-6)}$$

$$E_p = BMP * (1000kg/t) * (VS/100) * (TS/100) * HHV_{CH_4} \quad \text{(Eq. 2-7)}$$

Statistical Analysis

The comparison between the characteristics (photosynthetic pigments, density, extractable salts, proximate analysis, ultimate analysis, inorganic element, and summative analysis) of water hyacinth from La Ciénaga and El Naranjo, and the methane percentage in the produced biogas (%CH_4) were made using the Welch's unpaired *t*-test (www.graphpad.com). The two populations were assumed to be independent, normally distributed and unequal variances. The variability of the data was reported as the standard deviation of the mean (mean ± SD).

The kinetics from the fitted modified Gompertz model was compared using analysis of variance (ANOVA) in R Studio (version 3.6.1). The factors and levels considered for the analysis were: i) water source (El Naranjo, La Ciénaga) as treatment factor and ii) Group (1, 2) as a blocking factor. The responses analyzed in ANOVA were the kinetic parameters (A, K_d, T_{lag}, T_d).

2.4 Results

Water Quality

At the time of harvesting, the water temperature and pH at El Naranjo (freshwater) were 26.4°C and 7.13, and 28.1°C and 7.11 at La Ciénaga (brackish water).

The salinity was 0.09 ppT and 1.23 ppT at El Naranjo and La Ciénaga, respectively. DO in El Naranjo was 2.50 mg/L and1.37 mg/L at La Ciénaga. The nitrate content in La Ciénaga ranged from 11.76 to 17.33 mg/L NO3-, and from 2.6 to 4.5 mg/L NO3- in El Naranjo one year between harvestings. Similarly, the TDS was between 122 mg/L and 640 mg/L in El Naranjo, and between 1550 mg/L and 3028 mg/L in La Ciénaga.

Photosynthetic Pigments

The chlorophyll-a (Ca) and chlorophyll-b (Cb) contents in water hyacinth from El Naranjo was 0.48 ± 0.01 mg Ca /g and 0.68 ± 0.02 mg Cb /g (1.16 ± 0.02 mg Ca+b /g), while those from La Ciénaga were 0.46 ± 0.01 mg Ca/g and 0.89 ± 0.03 mg Cb/g (1.35 ± 0.04 mg/g Ca+b). The chlorophyll a/b ratios were 0.5 and 0.7 for the water hyacinth from La Ciénaga and El Naranjo, respectively. The total chlorophyll (Ca+b) was higher (p = 0.018) in the biomass from La Ciénaga due to a higher (p = 0.002) chlorophyll-b content. However, the chlorophyll a/b ratio was lower (p = 0.008) in the water hyacinth from La Ciénaga than in that from El Naranjo.

Density

The bulk density of the biomass from La Ciénaga (0.219 ± 0.03 g/L) was higher (p = 0.004) than that from El Naranjo (0.114 ± 0.003 g/L).

Proximate Analysis

The values of proximate analysis of water hyacinth (VS, FC, ASH) showed no difference (p > 0.057; Table 2-1) between La Ciénaga and El Naranjo. The water hyacinth from the Ozama river had 57.9% to 60.6 % VS, 19.3% to 20.5% FC, and around 20% ASH on a dry weight basis.

Table 2-1 Mean ± SD values of proximate and ultimate analyses, and composition of water hyacinth from the Ozama river. Results are reported on a dry weight basis.

		El Naranjo (Freshwater)	**La Ciénaga (Brackish)**
Proximate Analysis (% w/w)	Volatile Solids (VS)	59.9 ± 0.7[a]	58.4 ± 0.5[a]
	Fixed Carbon (FC)	19.9 ± 0.2[a]	19.9 ± 0.6[a]
	Total Ash [1] (ASH)	20.3 ± 0.6[a]	21.7 ± 0.1[a]
Ultimate Analysis (% w/w)	C	38.5 ± 1.0[a]	39.4 ± 0.4[a]
	H	3.9 ± 0.2[a]	4.0 ± 0.2[a]
	N	1.8 ± 0.2[a]	3.7 ± 0.1[b]
	O	35.6 ± 2.0[a]	31.3± 0.8[b]
	C/N	21.4	10.5
Composition (% w/w)	Cellulose	24.5 ± 1.2[a]	19.5 ± 0.5[b]
	Hemicellulose	16.8 ± 1.5[a]	12.6 ± 1.2[b]
	Lignin	4.0 ± 0.1[a]	3.6 ± 0.1[b]
	Ash[2]	10.5 ± 0.1[a]	8.1 ± 0.2[b]
	Protein	9.8 ± 0.7[a]	18.8 ± 1.9[b]
	Extractives	17.3 ± 0.2[a]	26.4 ± 0.1[b]

Ash: [1] Determined from total biomass; [2] is the non-extractable ash, determined after extractives removal.
[a,b] Different letters within each row indicate a significant difference between sites for Welch's unpaired *t*-test (alpha =0.05).

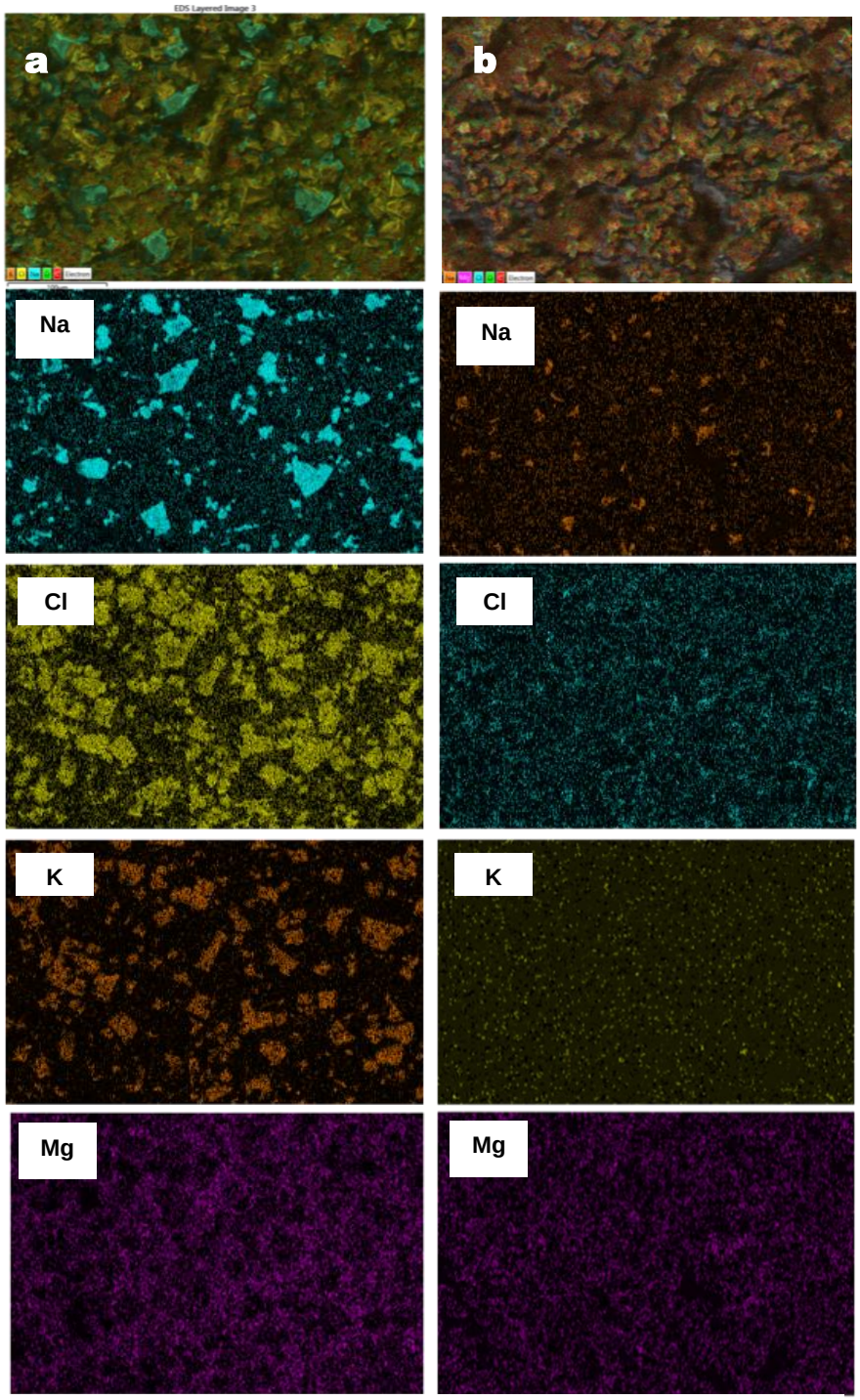

Fig. 2-1 SEM-EDX images of Na, Cl, K, and Mg in ethanol extractives of water hyacinth from a) La Ciénaga (brackish water) and b) El Naranjo (freshwater).

Ultimate Analysis (CHNSO)

There was no difference ($p > 0.1840$; Table 2-1) in the carbon, hydrogen, and sulfur content of the water hyacinth from La Ciénaga and El Naranjo. In contrast, the nitrogen and oxygen contents in the biomass from the two sites were different ($p < 0.0001$, and $p = 0.03$, respectively). The sulfur content for all samples was below the detection limit (i.e 100 ppm).

Summative Analysis

The percentages of structural components in the biomass from El Naranjo (45.3 ± 2.38 % w/w) was higher ($p = 0.03$) than that from La Ciénaga (34.7 ± 5.3% w/w). The amounts of protein and extractives in the biomass from La Ciénaga were higher ($p = 0.02$, and $p = 0.002$, respectively; Table 2-1) than those from El Naranjo. Similarly, the extractable ash in the biomass from La Ciénaga (13.6 ± 0.3 % w/w) was higher ($p = 0.01$) than in that from El Naranjo (9.8 ± 0.7% w/w).

The amount of holocellulose in the water hyacinth from El Naranjo (41.3 ± 1.18% w/w) was higher ($p = 0.046$, Table 2-1) than in that from La Ciénaga (32.1 ± 1.7 % w/w). All the monosaccharides were higher ($p < 0.01$) in the biomass from El Naranjo compared to that from La Ciénaga. However, the percentage of pentoses within the total monosaccharide content was not different ($p = 0.31$) between the water hyacinth from El Naranjo (28.6 ± 2.2%) and La Ciénaga (27.3 ± 2.0 %). The main monosaccharides in La Ciénaga and El Naranjo's water hyacinth were glucose (21.6 ± 0.5 % and 27.0 ± 1.4 %), arabinose (5.3 ± 0.2 % and 7.5 ± 0.5 %), xylose (3.5 ± 0.5 % and 4.3 ± 0.4 %), and galactose (1.8 ± 0.1 % and 2.5 ± 0.2%), in that order. Mannose was under the detection

limit. The content of acid-insoluble lignin in the water hyacinth from El Naranjo was higher ($p = 0.03$, Table 2-1) than in that from La Ciénaga.

Extractable Salts

The salt clusters in the extractives from La Ciénaga were larger than in those from El Naranjo (Fig. 2-1). The map sum spectrum for the salt ions in the biomass from the water at La Ciénaga was 18.6 ± 0.1 wt % Cl, 9.7 ± 0.1 wt% K, 4.1 ± 0.0 wt% Na, and 1.4 ± 0.0 wt% Mg; and from El Naranjo was 6.6 ± 0.1 wt % Cl, 1.7 ± 0.0 wt% Mg, 1.1± 0.0 wt% Na, and 0.7 ± 0.1 wt% K. The total chloride ion (wt %) in the extractives from La Ciénaga (33.8 ± 0.2 wt %) water hyacinth was higher ($p = 0.001$) than that from El Naranjo (10.7 ± 0.2 wt %). The results suggest that the main extractable salts from La Ciénaga and El Naranjo biomass were KCl, and $MgCl_2$, respectively. However, the spectrum for Mg (Fig. 2-1) shows that most of the element was not tied to Cl, which indicates that the element might be present as Mg^{+2} or $MgCO_3$.

Inorganic Elemental Analysis

The total content of Na and Mg in the water hyacinth from La Ciénaga is higher ($p < 0.013$, Table 2-2) than that from El Naranjo. Similarly, phosphorus in water hyacinth from La Ciénaga was twice ($p = 0.009$) that from El Naranjo. However, the biomass from El Naranjo had higher ($p < 0.02$) content of metals (i.e. Fe, Al, Co, As, Cr, Co) than that from La Ciénaga.

Table 2-2 Inorganic elements in water hyacinth from Ozama river. The values are on a dry ash basis.

		El Naranjo (Freshwater)	**La Ciénaga (Brackish)**
Macronutrients (% w/w)	Ca	11.3 ± 0.6[a]	7.2 ± 0.5[b]
	K	17.9 ± 2.0[a]	21.9 ± 1.1[a]
	Mg	1.3 ± 0.1[a]	3.1 ± 0.2[b]
	P	0.9 ± 0.06[a]	3.1 ± 0.3[b]
	S	0.3 ± 0.09[a]	1.0 ± 0.04[b]
Micronutrients (% w/w)	Fe	1.2 ± 0.04[a]	0.2 ± 0.02[b]
	Mn	0.3 ± 0.01[a]	0.2 ± 0.01[b]
	Al	1.73 ± 0.06[a]	0.18 ± 0.01[b]
	Na	0.65 ± 0.2[a]	2.2 ± 0.03[b]
	Si	1.3 ± 0.3[a]	0.79 ± 0.04[a]
Trace Minerals (mg/Kg)	Cu	54.3 ± 5.2[a]	41.0 ± 2.6[a]
	Ni	37.8 ± 19.1[a]	23.9 ± 12.7[b]
	Mo	5.5 ± 3.0[a]	2.8 ± 1.0[a]
	Co	7.6 ± 0.1[a]	2.2 ± 0.04[b]
	Zn	114.3 ± 7.5[a]	142.5 ± 22.0[a]
	As	1.9 ± 0.03[a]	0.19 ± 0.2[b]
	Cd	0.4 ± 0.1[a]	< 0.05[a]
	Cr	26.1 ± 0.1[a]	7.3 ± 0.3[b]

[a,b] Different letters within each row indicate a significant difference between sites for Welch's unpaired *t*-test (alpha =0.05).

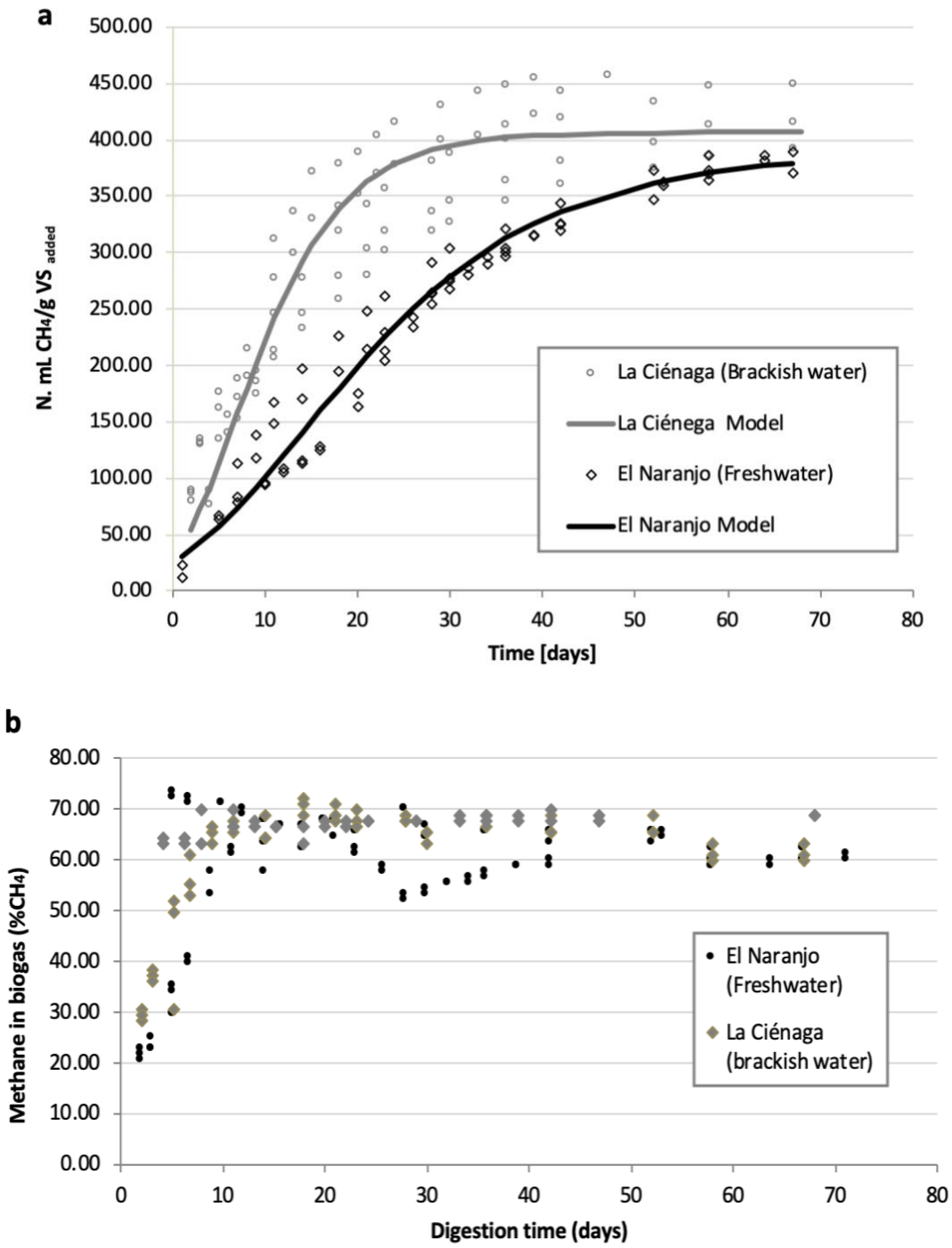

Fig. 2-2 Biochemical methane potential of water hyacinth from La Ciénaga (brackish waters) and El Naranjo (fresh water) within Ozama River, Dominican Republic: a) Methane production curves and the fitted modified Gompertz models, and b) Percentage of methane in the biogas.

Anaerobic Biodegradation

The methane yield from the water hyacinth at La Ciénaga (452.2 ± 51.5 N. L CH_4/Kg VS $_{added}$) was higher (p = 0.044; Fig. 2-2a) and El Naranjo (387.2 ± 10.9 N. L CH_4/Kg VS added). Similarly, the methane production rate (K_z) of water hyacinth from La Ciénaga was higher (p = 0.0004, Table 2-3) than that from El Naranjo. However, there was no difference (p = 0.134, Table 2-3) between the estimated maximum methane potential (A) of the biomass from both sites (399.2 ± 32.2 N. L CH_4/Kg VS $_{added}$). In general, the estimated lag phase of the anaerobic digestion from the Ozama river biomass was below 1 day (Table 2-3). The doubling time (T_d) was two times higher for the anaerobic digestion of water hyacinth from El Naranjo than that from La Ciénaga.

During the first 10 days of digestion, the CH_4 in Group 2 (68.2 ± 4.1% CH_4), which was set up using adapted inoculum, was higher (p =0.0001) than in Group 1 (40.0 ± 14.9% CH_4). After 10 days of digestion, the % CH_4 was higher (p = 0.0001, Fig. 2-2b) for the water hyacinth from la Ciénaga (67.0 ± 2.5 % CH_4) than for El Naranjo (61.9 ± 4.7% CH_4).

Energy Assessment

The amount of energy (MJ/t fresh biomass) produced via anaerobic digestion of water hyacinth from the Ozama river was more than 10 times that required for harvesting (Table 2-4).

2.5 Discussion

Eutrophication of the Ozama River

Dissolved oxygen, phosphorus, and total nitrogen are the most effective parameters in the determination of the water quality index and eutrophication level of

estuaries (Wang et al. 2019). The nitrate content at La Ciénaga was three times higher than at El Naranjo during harvesting and a year after. Also, water hyacinth from La Ciénaga (Table 2-2) contained higher phosphorus than the water hyacinth from El Naranjo, which suggests higher available phosphorus in La Ciénaga water. Thus, the water from La Ciénaga is more eutrophic than the water from El Naranjo, which might be due to the anthropogenic activities surrounding that site. Similarly, the higher heavy metal content in the water hyacinth from El Naranjo (Table 2-2) suggests a higher content of metals in the water that is attributed to the salinity barrier that is present near the site (Parayil et al. 2006).

Table 2-3 Kinetic parameters from the modified Gompertz model for the biomethanation of water hyacinth from the Ozama river.

Parameters [1]	La Ciénaga (Brackish water)	El Naranjo (Freshwater)
A [N. L CH_4/Kg VS $_{added}$]	408.5	389.8
K_z [N. L CH_4/Kg VS $_{added} \cdot$ day]	22.5	10.0
T_{lag} [day]	0	0.0
T_d [day]	9.1	19.5
RMSE [N. L CH_4/Kg VS $_{added}$]	4.6	4.03
R^2	0.886	0.901

[1] A is the maximum methane produced, Kz is the absolute growth rate, T_{lag} is the lag time, and T_d is the doubling time. RMSE is the root mean square error, and R^2 is the variation of the measurements explained by the model.

Table 2-4 Estimated energy consumed in the mechanical harvesting, and energy produced by the anaerobic digestion of water hyacinth.

	Parameters [1]	**Value**	**Energy (MJ/t biomass)**
Consumption	FC [L/h]	15	**E_c = 57.9**
	HR [$t_{biomass}$/h]	10	
	HHV_{Diesel} [MJ/L]	38.6	
Production	BMP_{Mean} [L CH_4/kg VS]	399.2	**E_p** = 846.5
	$HHV_{Methane}$ [MJ/L]	0.0398	
	VS_{Mean} [%]	59.2	

[1] FC is the fuel consumption per machine operation time, HR is the harvesting rate, and BMP is the average methane yield.

Chemical Composition of Water Hyacinth

Results from the organic elemental analysis of water hyacinth from the Ozama river are comparable to those from previous studies on tropical water bodies with similar water conditions. For instance, the organic elemental composition of water hyacinth from Indian fresh eutrophic waterbodies was 40.3% carbon, 34.0% oxygen, 1.51% nitrogen, 4.6% hydrogen, and non-detected sulfur (Vaz 2016). Similarly, the monosaccharides content is in concordance with previous works in water hyacinth (Ahn et al. 2012; Xia et al. 2013; Cheng and Zhong 2014), where arabinose was the dominant hemicellulose monomer. However, our results differ from most herbaceous biomass feedstocks and from the water hyacinth found in other tropical regions where xylose has been reported as the main hemicellulose sugar (Nigam 2002; Lin et al. 2015).

The higher amount of lignocellulose in the biomass from El Naranjo (freshwater) than that from La Ciénaga (brackish water) is related to the salinity content in the biomass. The larger salt clusters in the extractives (Fig. 2-1) and the higher Na content (Table 2-2) in the water hyacinth from La Ciénaga suggest higher salt content in the biomass. The increase of water salinity during plant irrigation decreases the content of lignocellulosic components in *Salicornia sp* (Cybulska et al. 2014). Also, the higher amount of nitrogen available during growth is related to lower cellulose content in plants (Etter 1972). The protein content in biomass from La Ciénaga is almost two times higher than in biomass from El Naranjo due to the higher content of nitrogen available in the more eutrophic waters.

Productivity Indicators

The indicators of productivity (e.g., photosynthetic activity, density) in water hyacinth did not suggest lower performance in the growth of the species from brackish waters. The photosynthetic activity (i.e. Chlorophyll levels) of water hyacinth was not compromised because of accumulated NaCl and KCl ions (Fig. 2-1) after growing in water containing TDS levels up to 3,000 mg/L. The amount of total chlorophyll was 15% higher in the biomass from brackish than in that from freshwaters. The value of chlorophyll a/b ratio for the water hyacinth from both sites was very low, which indicates that the specimens from El Naranjo and La Ciénaga exposed and adapted to low light environments (Givnish 1988). Thus, the concentration of TDS in the biomass did not affect the survival mechanism of the species. Similarly, biomass from the brackish waters showed greater bulk density than that from freshwaters, resulting in higher biomass yield (wt %) per growth area. In anaerobic digestion, denser feedstock has been linked to better

degradation performance (Wang et al. 2016). The suggested higher performance in the productivity of water hyacinth from the brackish water at La Ciénaga could be due to the higher eutrophication compared to the freshwater.

Biomethanation of Water Hyacinth

The higher salt content in the biomass when compared to that from El Naranjo did not compromise anaerobic digestion of water hyacinth from La Ciénaga. Studies have shown that low levels of NaCl promote the hydrolysis and acidification steps of anaerobic digestion, but inhibit the methanogens (Zhao et al. 2017). The Gompertz model for the anaerobic digestion of water hyacinth from La Ciénaga estimated a biomethane potential that was not significantly different from that from El Naranjo, but the production rate was higher. Similarly, the methane yield of water hyacinth from La Ciénaga was higher and the stationary phase was reached sooner than that from El Naranjo (Fig. 2-2a). Thus, water hyacinth from La Ciénaga brackish water was as effective as or superior to that from El Naranjo freshwater.

During the first 10 days of digestion, the methane percentage in the biogas was higher when adapted anaerobic sludge was used as inoculum. After 10 days, the percentage of methane in the biogas from La Ciénaga biomass was higher than that from El Naranjo. The higher methane in the biogas from La Ciénaga water hyacinth can be attributed to the buffering capacity of high nitrogen levels in the biomass. The higher biomethanation rate of water hyacinth from La Ciénaga can be attributed to the low content of structural components in this biomass compared to that from El Naranjo since biopolymers are more difficult to digest than non-structural compounds.

Potential Inhibitions from Feedstock

The high nitrogen content of water hyacinth from the Ozama river can have beneficial or inhibitory effects on anaerobic digestion. When nitrogen is converted into ammonia, it acts as an alkaline agent that neutralizes the volatile acids produced by fermentative bacteria and hence reduces inhibition of methanogens. However, excessive ammonia can be toxic to the microbial community when enough acid is not produced to neutralize it. The recommended C/N ratio in feedstocks for steady anaerobic digestion is between 10 and 45 in the hydrolysis step and between 20 to 30 during methanogenesis (Wellinger et al. 2013). However, water hyacinth from La Ciénaga had a theoretical methanogenic hindrance (i.e. C/N 10.5) that was not observed in our study. This could be explained by the higher content of phosphorus in the water hyacinth (Table 2-2). Gil et al. (2019) reported that the highest proportion of methane in the biogas occurred when both nitrogen and phosphorus in the feedstock were high.

Phosphates or precipitates of cations such as magnesium and calcium also contribute to the buffer capacity of anaerobic digestion (de Jong and Van Ommen 2015). However, calcium might also act as a microbiological inhibitor when present in quantities higher than 2.5 g/L (Ahn et al. 2006). The sulfur in biomass for biochemical conversion processes is unfavorable. The inorganic content of sulfur in the ash of water hyacinth from the Ozama river ranged from 0.28% to 1.00% on dry biomass basis. Concentrations of sulfur over 9 mM have an inhibition effect on the degradation of cellulose in the hydrolysis step (Khan and Trottier 1978). Also, sulfur in the form of sulfate is chosen as an electron acceptor for organic carbon oxidation in the anaerobic digestion leading to its

reduction to H_2S, which is detrimental to human health and to the environment (de Jong and Van Ommen 2015).

Some of the micronutrients that are essential for the growth of anaerobes are Ni, Co, Mo, Fe, and Se for methanogens, and Zn, Cu, and Mn for hydrolytic bacteria. However, certain heavy metals have negative effect on anaerobic digestion when their concentrations exceeded 40 mg/L Cu, 20mg/L Cd, 150mg/L Zn, 10mg/L Ni, 340mg/L Pb, and 100 mg/L Cr (Wellinger et al. 2013). Water hyacinth from El Naranjo has higher heavy metal content than that from La Ciénaga (Table 2-2). This might explain the higher doubling time on the anaerobic digestion of El Naranjo. The micronutrients and heavy metals in water hyacinth need to be accounted for in the design of bioconversion processes to minimize the negative effect that some elements might cause to the system performance.

Energy Assessment

The estimated amount of energy required for mechanical harvesting water hyacinth was less than 7% of the produced energy due to methane. However, energy requirements for processing and pre-treating the water hyacinth prior to anaerobic digestion, and to maintain the temperature of the digester have not been considered. Large scale studies using unprocessed instead of ground biomass, cow manure instead of supplemented anaerobic sludge, and the lowest instead of the highest end of mesophilic temperature range are required to accurately access the revenue from this post weed management practice. For the scale-up of the technology, several modifications of the current process will have to be done for cost-effectiveness, including inoculum selection and acclimatization, feed to inoculum ratio, and biogas upgrading. Biological methods

for biogas upgrading offer great potential, high feasibility, and low operational difficulty, which are important to reduce downstream processing costs (Angelidaki et al. 2018). Biogas upgrading for the use of methane as a transportation fuel in the harvesting equipment could be the next step for a sustainable weed management cycle in eutrophic rivers.

2.6 Conclusion

The anaerobic digestion of residual water hyacinth harvested from eutrophic rivers contributes to the sustainability of the weed management practices conducted by environmental agencies in developing countries. The modified Gompertz model estimated a biochemical methane potential of 399.2 ± 32.2 N. L CH_4/Kg VS_{added} for water hyacinth from the Ozama river. The methane production rate when digesting the water hyacinth from brackish water doubled that from freshwater. The doubling time for the anaerobic digestion of freshwater was twice that from brackish waters. The lower performance of freshwater hyacinth during anaerobic digestion is related to its higher content of recalcitrant lignocellulose. The differences in the characteristics of the water hyacinth from both water types were linked to the nutrients in the water source. The brackish water was more eutrophic than that from freshwater. The water hyacinth collected from the Ozama river, to mitigate the effect of the macrophyte debris on the water bodies, could be anaerobically digested to produce more than 10 times the energy consumed in the mechanical harvesting.

CHAPTER III

EFFECT OF HIGH FEED TO INOCULUM RATIO (F/I) AND TEMPERATURE ON THE BIOMETHANATION KINETICS OF WATER HYACINTH

3.1 Abstract

During the anaerobic digestion of the invasive water hyacinth (*Pontederia crassipes* Mart), the optimization of critical process parameters (e.g. feed to inoculum ratio (F/I), temperature, supplementation, and inoculum acclimatization) is important for large scale applications. In the present work, water hyacinth was anaerobically digested at different F/I (1.0, 5.0, 10.0, and 30.0), mesophilic temperatures (30°C, and 40°C), and supplementation settings using non-acclimatized and acclimatized inoculum to determine the process' optimal conditions through kinetics and energy analyses. The F/I ratio had a directly proportional effect on the methane yield [N.mL·CH_4/g·VS], which ranged from 416.8 ± 6.2 (F/I = 1.0) to 263.8 ± 26.9 (F/I = 30.0). The methane production rate [N.mL·CH_4/g·VS·day] was highest at 40°C (9.0 ± 0.8) and lowest at F/I = 30 (5.6 ± 2.8). The biomethanation of water hyacinth followed the modified Gompertz and Chen and Hashimoto models when using the non-acclimatized and acclimatized inoculum, respectively. A 30-day pseudo lag phase was observed at the highest F/I (30) and low temperature (30°C), but was negligible at higher temperature (40°C). For a 5.0 m3 biodigestor, the highest estimated net energy occurred at F/I =30 (370.5 ± 22.6 MJ). The doubling times at 40°C (16.9 ± 0.3 days) were lower than at 30°C (49.6 ± 2.5 days). The anaerobic digestion of water hyacinth in batch mode was optimal at higher F/I ratio and high mesophilic temperature.

3.2 Introduction

Using the invasive water hyacinth (*Pontederia crassipes* Mart) as a feedstock for bioconversion processes like anaerobic digestion can mitigate the costs associated with weed removal from eutrophic water bodies in developing communities. The energy produced during the anaerobic digestion of water hyacinth as a post weed management practice can be more than 10 times the energy consumed in mechanical harvesting (Castro and Agblevor 2020a). The use of this weed as bioenergy feedstock would not only meet the energy needs but also mitigate environmental problems (Chandel et al. 2020) . Parametric studies on the kinetics and energy balance could contribute to the scalability of this bioconversion process. Some of the main factors influencing the anaerobic digestion performance at large scale are related to process control (e.g. organic loading, temperature) and microbiology (Ward et al. 2008; Holm-Nielsen and Oleskowicz-Popiel 2013). However, the studies covering the main effect of these factors on the anaerobic digestion do not consider their economic impact at large scale.

During anaerobic digestion, the increase of organic load compared to the inoculum content has been reported to significantly reduce the methane percentage in biogas (Raposo et al. 2009; Cheng and Zhong 2014). For various substrates, the optimal feed to inoculum ratio (F/I) during anaerobic digestion has been reported to be between 0.3-1.5 on volatile solids (VS) basis (Braguglia et al. 2006; Zeng et al. 2010; Zhou et al. 2010; Cheng and Zhong 2014; Rashed et al. 2017; Go and Ko 2018; Li et al. 2018). For the anaerobic digestion of water hyacinth, the optimal F/I was 2.0 over 4.0, 1.0, and 0.33 when using dung cow as inoculum on VS basis, and 0.05 within the 0.04 to 0.16 range when using poultry litter on total solids (TS) basis (Patil et al. 2012; Bhui et al. 2018).

Studies on anaerobic digestion of water hyacinth addressing an F/I ratio above 5 are scarce. Large-scale batch biodigesters operating at low F/I are not practical because most of the operating volume would be due to inoculum, and the total methane production per batch would be small. Therefore, evaluating the performance and energy implications of the anaerobic digestion of the invasive water hyacinth at high F/I is important for large scale systems.

High F/I ratios of water hyacinth from contaminated water could inhibit the microbial consortium during anaerobic digestion. For easily degradable substrates, such as sugars, the acidogenic reactions are much faster than acetogenic and methanogenic ones, leading to the accumulation of VFA, H_2, and CO_2, and depressed pH (Bagley and Brodkorb 1999). Similarly, the use of feedstock with phytoremediation properties targeting metals could to substrate inhibition. Water hyacinth is not only capable of up taking nutrients but also heavy metals from contaminated waters (Mahmood et al. 2010; Moyo et al. 2013; Gong et al. 2018; Ting et al. 2018). The presence of high heavy metals in a soluble free form within anaerobic reactors leads to the accumulation of intermediate organic compounds and reduction of biogas production (Oleszkiewicz and Sharma 1990; Chen et al. 2007). However, the inhibitory effect of compounds within the anaerobic digesters can be minimized by inoculum acclimatization (Toreci et al. 2011; Wojcieszak et al. 2017; Yangin-gomec et al. 2018). Accounting for inoculum acclimatization when determining the optimal F/I during the anaerobic digestion of water hyacinth is necessary for large-scale applications.

The use of single waste for anaerobic digestion has been associated to unbalanced nutrients (Rabii et al. 2019). Trace minerals such as selenium, molybdenum, manganese,

aluminum and boron stimulate methanogenic activity and are suggested to be added to anaerobic digesters to improve the process performance (Azbar et al. 2001; Rabii et al. 2019). Standard biochemical methane potential includes the addition of not only trace minerals but also vitamins to the assays (Holliger et al. 2016). High performance scalability of the anaerobic digestion of the invasive water hyacinth needs to consider the need for additional nutrients through co-digestion. The effect of supplement addition on the biomethanation of water hyacinth would determine whether this macrophyte can be used as feedstock for large scale systems without additional nutrients or co-substrates.

The energy required for keeping anaerobic digesters under steady temperatures is very important for the process' performance and sustainability. In mesophilic biodigesters, the anaerobic consortia operate at 30-40 °C (Wellinger et al. 2013). When assessing the effect of various temperatures (25°C, 37°C, 45°C) on water hyacinth biomethanation, the best incubation temperature was 37° C (El Amin and Dirar 1986). Similarly, studies on the anaerobic digestion of sludge showed that 38 °C was the optimal mesophilic temperature compared to 34°C and 42°C (Moestedt et al. 2017). However, higher temperatures (i.e. 50°C) are linked to higher organic matter degradation of fibrous materials, higher pH, and higher methane yield (Moset et al. 2015). Agro-waste digestion at 40°C had a higher cumulative gas yield than those at 25°C, 30°C, and 35°C (Uzodinma et al. 2007). Costs related to operating temperature in anaerobic digestion are important for decision-makers during large-scale design. The effect of the lower (30°C) and higher (40°C) mesophilic limit range temperatures on the biomethanation performance and energy consumption in the anaerobic digestion of water hyacinth need to be determined.

Understanding the kinetics of methane production is important for designing and evaluating anaerobic digesters. The suitability of kinetic models on anaerobic digestion has been studied for different types of reactors, inoculums, and feedstocks (Strömberg et al. 2015; Kafle and Chen 2016; Li et al. 2019). The most popular kinetic models used for anaerobic digestion batch systems are First-Order, Chen and Hashimoto, and Modified Gompertz. The First-Order model provides valuable information about hydrolysis kinetics but does not estimate the maximum methane potential and systems failure (Kafle and Chen 2016). Chen and Hashimoto model predicts maximum biological activity and is reliable on predictions about high solid content anaerobic digestion systems (Fongsatitkul et al. 2012). The modified Gompertz model assumes that methane production follows the microbial growth pattern, and predicts maximum methane potential, lag time, and methane production rate. This model has been effectively applied ($R^2 > 0.81$) to batch anaerobic digestion of various feedstocks including water hyacinth (Patil et al. 2012; Sarto et al. 2019; Castro and Agblevor 2020a). The use of these three models on the biomethanation of feedstock gives a holistic picture of the process kinetics. However, studies assessing these kinetic models for the biomethanation of water hyacinth at high F/I under various mesophilic temperatures has not been conducted.

The research goal of this chapter was to determine the optimal conditions for the biomethation of water hyacinth based on kinetics and energy analysis. The main and interaction effect of high F/I ratios, mesophilic temperature, media supplementation on the kinetics of the water hyacinth biomethanation, and their alteration by inoculum acclimatization were studied through factorial experiments. Also, the differences in

kinetics and energy balance between the anaerobic digestion of water hyacinth at 30°C and 40°C were covered.

3.3 Materials and Methods

Biomass

Water hyacinth was collected from the eutrophic freshwaters at El Naranjo (18°34'27.2"N 69°47'09.9"W) within Ozama River (Santo Domingo, Dominican Republic). Biomass sampling, preparation and composition are detailed in Chapter 1.

Inoculum

The microbial consortium was a mixture (1:2) of mesophilic anaerobic sludge collected from North Davis Sewer District (Syracuse, UT, USA) and Central Valley Water Reclamation Facility (CVWRF) in March 2019. The anaerobic sludge from CVWRF (Salt Lake City, UT, USA) was obtained from the Sustainable Waste to Bioproducts Engineering Center (Dr. Ronald Sims, Co-Director) through a joint project and with permission of the Plant Manager, Dr. Phil Heck.

The non-acclimatized sludge had a pH of 8.32, 2.58% TS, and 55% VS. The acclimatized inoculum was defined as the residual sludge of the experimental units after sieving with a 250 μm mesh to get rid of the undigested water hyacinth. The acclimatized inoculum had pH= 7.97, 0.6 ± 0.05% TS, and 49.6 ± 0.7% VS. The non-acclimatized and acclimatized sludge was incubated at 40°C for 72 h prior to use.

Experimental Conditions

The bio-reactions took place in 160 mL clear serum bottles at 100 mL working volume. For the experimental units inoculated with non-acclimatized sludge, the total solids were 3.2±0.6 %. For these units, a 2 x 3 full factorial design was conducted for F/I

at 1.0, 5.0, and 10 on VS basis; and supplemented vs non-supplemented anaerobic media. The supplemented media is a modification of the media used during standardized biochemical methane potential experiments without the addition of resazurin (Angelidaki et al. 2009b). The non-supplemented media is the anaerobic media without vitamins and minerals. Each experimental unit was run in duplicate.

The units inoculated with acclimatized sludge resulted in an un-replicated 3 x 2 x 2 factorial experiment with F/I (5.0, 10.0, and 30.0 on VS basis), non-supplemented anaerobic media (Yes/No); and temperature (30°C and 40°C) were considered as factors (levels). For these units, the average feed and total solids for the experimental units were 2.04 ± 0.12 g, and 2.27 ± 0.05%, respectively.

Biomethane Production

The produced gas was measured via volume displacement using a lubricated glass syringe every 2 to 6 days, and analyzed using an Agilent 7890B Gas Chromatograph (Agilent Technologies, Santa Clara, CA, USA). The method used helium as the carrier gas, the thermo-conductivity detector (TCD) is heated to 250°C, and the column is kept at 25°C. The measured volume (V) was converted to normal volume (V0) using the Ideal Gas Law (Eq. 2-4). The volume of the accumulated methane was reported per mass of VS added (feedstock) to the experimental units.

Kinetic Models

The First-order kinetic parameters for each experimental unit curve were modeled using equation (Eq. 3-1), where W [N.mL CH_4/g VS feed] is the cumulative methane yield at digestion time t, K [day-1] is the first order disintegration rate constant, and WO [N.mL CH_4/g VS feed] represents the total yield of hydrolysable VS at the beginning of

the test. The main kinetic parameters for Chen and Hashimoto model (Eq. 3-2) are A_{CH}, K_{CH}, and μm where K_{CH} is the Chen and Hashimoto kinetic constant [dimensionless], and μm [day^{-1}] is the maximum specific growth rate of microorganisms. The Modified Gompertz model follows the equation used in Chapter 2 (Eq 3-2), where A [N. mL CH4/g VS feed] is the maximum methane produced, Kz [N. L CH_4/Kg feed*day] is the maximum methane production rate, and T_{lag} [days] is the minimum time taken for bacteria to acclimatize to the environment. The doubling time (T_d) was calculated from the model's estimated A.

$$W(t) = W_0\,(1 - e^{-K \cdot t}) \qquad \text{(Eq. 3-1)}$$

$$W(t) = A \cdot EXP\left(-EXP\left((e \cdot k_z/A) \cdot (T_{lag} - t) + 1\right)\right) \qquad \text{(Eq. 3-2)}$$

$$W(t) = A\,(1 - (K_{CH}/(\mu_m \cdot t + K_{CH} - 1)) \qquad \text{(Eq. 3-3)}$$

Energy Analysis

The energy [MJ] produced (Ep) from the biomethanation units and the energy required for heating (Q) were calculated using Eq. 3-4, and Eq. 3-5, respectively. The energy analysis will assume a biodigestor with a working capacity of 5 m^3 (5000 L), which would require different loadings (m) of freshwater hyacinth depending on the F/I ratio (See Appendix B). The bulk density and water content of the fresh biomass were assumed to be 96 Kg/m^3 and 91% (Akendo et al. 2008; Davies and Mohammed 2011). The inoculum was assumed to be anaerobic sludge from a wastewater treatment plant, with 2.5 % w/v solids and a dry density equal to 560 kg/m^3 (O'Kelly 2005). The overall heat capacity (C_p) was calculated using Eq. 3-6. The heat capacity of the fresh feedstock ($C_{p\,F}$) and dry sludge ($C_{p\,S}$) were assumed to be 1.75 KJ/Kg °C and 1.35 KJ/Kg °C, respectively (Vaxelaire and Puiggali 2002; Jayalakshmy and Philip 2010). The heat

capacity of water ($C_{p\ w}$) is 4.19 KJ/Kg °C. The initial temperature for the digestion was set to 20 °C, which is within the range for water hyacinth growth in tropical areas (Duke 1983). BMP [L CH_4/Kg] is the methane yield expressed on a dry biomass basis. The higher heating value (HHV) of methane is 0.0398 MJ/L. This analysis does not take into account the energy consumed in processes like harvesting and milling that are common to all the experimental units and are important at large scale.

$$E_p = m \cdot BMP \cdot HHV_{CH_4} \quad \text{(Eq. 3-4)}$$

$$Q = m \cdot c_p \cdot \Delta T \quad \text{(Eq. 3-5)}$$

$$C_p = (m_F/m)C_{p\,F} + (m_S/m)C_{p\ S} + (m_W/m)C_{p\,W} \quad \text{(Eq. 3-6)}$$

Statistical Analysis

All the measurement units were used for the assessment of the effects of F/I, and media supplementation. The effect of anaerobic media was determined using all non-acclimatized and acclimatized experimental units, resulting in three levels for this independent variable (no media, non-supplemented media, and supplemented media). A subset of the experimental units was analyzed to determine the effect of inoculum acclimatization on the biomethanation of water hyacinth without the influence of confounding factors. The dataset consisted in the data at F/I equal to 5 and 10 for a total of 16 measurement units. Similarly, the effect of temperature was determined using only the measurement units that were digested with acclimatized inoculum.

The data collected from the factorial datasets was analyzed using the function ‘aov’ in R Studio (version 3.6.1). The differences between levels were determined using Tukey's test (Tukey HSD), a post-hoc analysis function in R. For single comparison

between values, t test (www.graphpad.com) was used. The populations were assumed to be independent, normal distributed, and with equal variances.

3.4 Results and Discussion

Media Supplementation

After 105 days of digesting water hyacinth anaerobically, the methane yield [N.mL CH_4/g VS] was not statistically different ($p = 0.697$) when using supplemented media (356.4 ± 44.4), non-supplemented media (334.2 ± 48.3), and no media (301.9 ± 41.5). Also, the methane production rate and lag time between the experimental units digested under the studied media conditions were comparable ($p > 0.317$). These yield values [N.mL CH_4/g VS] are higher ($p = 0.038$) than those produced from sugar-rich wastes such as cranberry (231± 33), and ice-cream (125 ± 48) when co-digested with manure at a F/I below 5 (Lisboa and Lansing 2013). Therefore, water hyacinth from eutrophic freshwater contains the minerals and vitamins required for the anaerobic consortia to efficiently produce biogas. The essential minerals required for the cultivation of methanogens are Fe, Na, Se, Co, Mn, Mo, W, Zn, Ni, B, and Cu, which are present in the water hyacinth under study, with the exception of W and Se (Wolfe 2011; Castro and Agblevor 2020a). Thus, water hyacinth can be used as feedstock for anaerobic digestion without additional supplementation or co-digestion.

Feed to Inoculum Ratio (F/I)

The methane yield and production rate for the biomethanation of water hyacinth were significantly affected by F/I. The yield [N.mL CH_4/g VS] for the anaerobic digestion at F/I =1.0 (416.8 ± 6.2) was the highest ($p < 0.001$, Fig. 3-1) and at F/I =30.0 (263.8 ± 26.9) the lowest ($p < 0.001$, Fig. 3-2) among all the ratios under study.

However, the methane produced [N.mL CH_4/g VS] at F/I =5.0 (336.6 ± 13.2) was not quite different (p = 0.09) than that at F/I =10.0 (318.2 ± 9.3). When using acclimatized inoculum at 30°C, the methane production rate at F/I = 1.0, F/I=5.0, and F/I=10.0 was 8.4 ± 0.8 N.mL CH_4/g VS·day in average, which is higher (p < 0.008) than that at F/I =30.0 (5.6 ± 2.8 N.mL CH_4/g VS·day). The effect of F/I on methane rate has been previously reported to be inversely proportional during the biogas production of sheep paunch manure at F/I between 0.25 and 0.75 (Lawal et al. 2016). The methane yield from the anaerobic digestion of wheat straw at F/I = 4.0 (287.3 N. mL/ g VS) and water hyacinth at F/I = 1.0 (262 N. mL/ g VS) were comparable (p > 0.085) to our results at F/I = 30.0 (Shah et al. 2019). Even though, the performance of the water hyacinth biomethanation seemed to be compromised by an F/I above 10, the methane yield value under these conditions and the F/I effect on the methane rate are comparable to studies from other authors.

The effect of F/I on the lag phase of the water hyacinth biomethanation depended on the acclimatization of the inoculum. The effect of F/I on the length of the lag phase was negligible (p > 0.123) when using acclimatized inoculum. However, when the inoculum was non-acclimatized, the F/I ratio had a directly proportional effect (p < 0.006, Table 3-1) on the lag phase. At F/I = 1.0, the lag phase was more than 4 times that at F/I = 5.0, and almost 8 times higher than at F/I = 10.0. These results are in accordance with previous findings that indicated the lag phase depends on the concentration of bacteria during batch culture (Bertrand 2019).

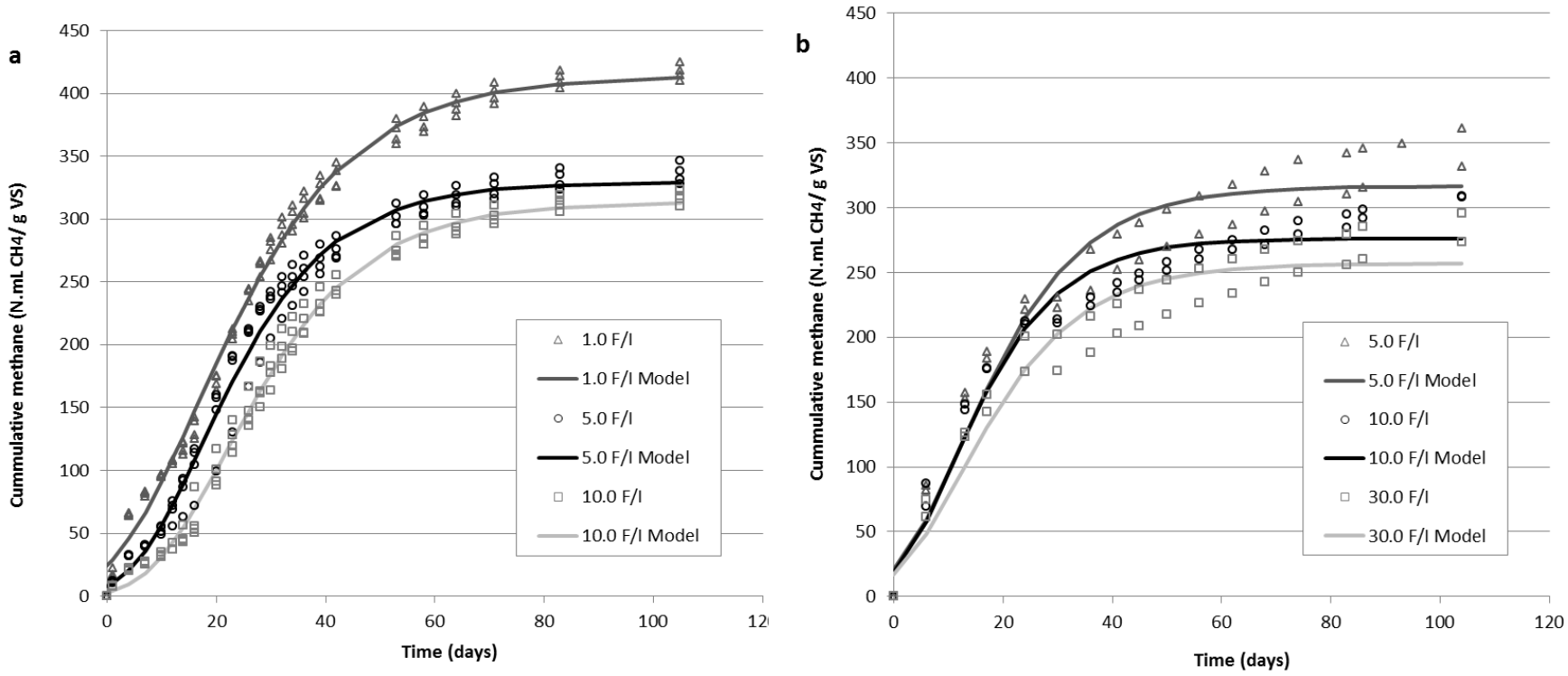

Fig. 3-1 Biochemical methane potential of water hyacinth from Ozama River (Dominican Republic) at different feed to inoculum (F/I) ratios when digested at 40°C using non-acclimatized (a) and acclimatized (b) inoculum.

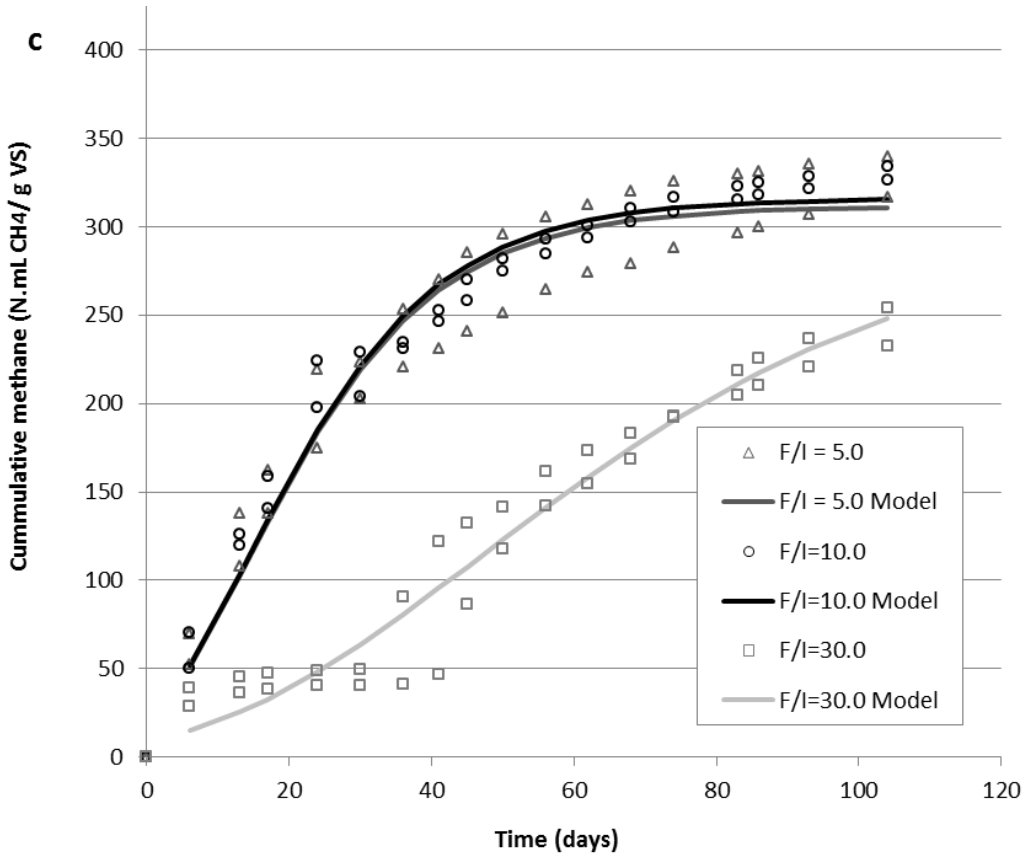

Fig. 3-2 Biochemical methane potential of water hyacinth from Ozama River (Dominican Republic) at different feed to inoculum (F/I) ratios when digested at 30°C.

Inoculum Acclimatization

The differences in methane yield and production rate between acclimatized and non-acclimatized anaerobic sludge were negligible ($p > 0.641$, Table 3-1). However, the biodigestion with non-acclimatized sludge had a longer ($p < 0.0001$) lag phase (6.2 ± 1.9 days) and doubling time (24.0 ± 2.8 days) than that with acclimatized inoculum ($T_{lag} < 1$ day, T_{doub} 16.0 ± 1.4 days). As expected, acclimatizing the anaerobic consortia for the anaerobic digestion of water hyacinth eliminated the lag phase of the sub sequential

batch. This reduction might be due to the high content of calcium and magnesium in the feedstock, since the physiological need of bacteria for these nutrients is highest during lag phase, implying their important role in the transition from lag to exponential phase (Rolfe et al. 2012; Castro and Agblevor 2020a). The biomethanation of water hyacinth when using anaerobic sludge as inoculum would take less than 10 days for exponential production of biogas during the biodigester start up and would continue on that stage when reloading the system.

Temperature

The methane yield for the anaerobic digestion of water hyacinth was not different ($p > 0.176$) at 30°C and 40°C. Similarly, the methane production rate for the biomethanation of water hyacinth at 40°C (9.0 ± 0.8 N.mL CH_4/g VS·day) was higher ($p = 0.0357$, Fig. 3-1) than that at 30°C (6.4 ± 2.5 N.mL CH_4/g VS·day, Fig. 3-2). The effect of temperature on methane production rate depends on the F/I in the system ($p = 0.0138$). When water hyacinth was digested at 30°C using F/I=30, the methane production rate (3.2 ± 0.2 N.mL CH_4/g VS·day) was lower ($p < 0.002$) than the other F/I ratios within the same temperature (7.9 ± 0.8 N.mL CH_4/g VS·day). As a result, in the anaerobic digestion of water hyacinth at 30°C, doubling times increased by at least 3 days ($p < 0.01$, Table 3-1). However, there was no difference ($p > 0.218$) in the methane production rate between the digestions conducted at 40°C. These results are partially in accordance with previous works. For the thermophilic anaerobic digestion of food waste, 10 °C reduction in temperature, from 65°C to 55°C, did not affect ($p = 0.177$) the production rate of methane (Gaby et al. 2017) . When comparing anaerobic digestion of sludge at 34°C, 38°C and 42°C, the methane yield was higher at 38°C but foaming formed at this and

higher temperatures (Moestedt et al. 2017). The biomethanation of water hyacinth at 40°C would lead to higher methane production rates and shorter digestion times without compromising the stability of the process.

Kinetic Models

The methane production per time curve was successfully fitted ($R^2 > 0.993$, Fig. 3-1 a) to the modified Gompertz model when non-acclimatized sludge was used as inoculum at 40°C. However, the explanation of the data by this model decreased after inoculum acclimatization ($R^2 = 0.965 \pm 0.02$, Fig. 3-1 b, 3-2c). The maximum methane potential of water hyacinth when digesting at 40°C with acclimatized sludge is better explained ($p = 0.0003$) by Chen and Hashimoto model ($R^2 = 0.995 \pm 0.01$) than by the modified Gompertz model. After 105 days of digesting water hyacinth with acclimatized sludge at 40°C, the stationary phase had not been reached (Fig. 3-1b), following an exponential pattern proper of Chen and Hashimoto model. The first order kinetic model explained ($R^2 > 0.953$) the hydrolysis stage through the disintegration rate constant (K_H). The disintegration rate was larger ($p < 0.01$, Table 3-1) when the anaerobic digestion was conducted at 40°C with acclimatized sludge, leading to a higher methane production rate (Table 3-1). These results differ from previous studies that evaluated the biomethanation kinetics of food waste and vegetable crop residues that concluded the modified Gompertz model was better fitted than the first order and, Chen and Hashimoto models (Li et al. 2019; Pramanik et al. 2019). The inoculum acclimatization seems to have favored an exponential behavior in the biomethanation of water hyacinth.

Table 3-1 Methane yield (N. mL CH4 /g VS) and kinetic parameters at different feed to inoculum ratios (F/I) and temperature (T) using non-acclimatized (N-ACC) and acclimatized sludge (ACC).

T (°C)	Inoculum	F/I	CH_4 Yield	A	A_{CH}	K_z	K_H	Tl_{ag}	T_{doub}
40	N-ACC	1.0	416.8 ± 6.2	412.9 ± 7.5	639.8 ± 13.8	9.7 ± 0.4	0.028 ± 0.001	1.0 ± 0.3	22.4 ± 0.6
		5.0	336.1 ± 7.9	328.5 ± 7.8	528.1 ± 42.0	9.4 ± 0.6	0.027 ± 0.004	4.7 ± 1.2	22.3 ± 2.4
		10.0	317.0 ± 5.3	313.3 ± 6.3	589.9 ± 34.0	8.2 ± 0.5	0.018 ± 0.002	7.8 ± 0.9	27.2 ± 1.5
40	ACC	5.0	346.3 ± 20.6	314.9 ± 27.2	413.6 ± 39.3	9.6 ± 0.1	0.043 ±0.003	0.0 ± 0.0	16.6 ± 1.6
		10.0	308.4 ± 0.6	276.0 ± 6.9	356.2 ± 13.1	9.5 ± 0.3	0.048 ± 0.007	0.0 ± 0.0	14.7 ± 0.8
		30.0	284.3 ± 15.9	251.3 ± 25.6	340.8 ± 23.8	8.0 ± 0.3	0.042 ± 0.001	0.0 ± 0.0	16.9 ± 0.3
30	ACC	5.0	328.0 ± 16.3	312.0 ± 20.9	420.7 ± 22.6	7.8 ± 1.3	0.035 ± 0.004	0.0 ± 0.0	20.2 ± 1.9
		10.0	330.3 ± 5.2	315.9 ± 11.5	425.4 ± 18.5	8.0 ± 0.7	0.035 ± 0.005	0.0 ± 0.0	20.1 ± 2.5

A [N. mL CH_4/g VS feed] is the methane potential, Kz [N. L CH_4/g VS feed*day] is the methane production rate, T_{lag} [days] is the lag time, and T_{doub} [days] is the doubling time according to the modified Gompertz model; A_{CH} [N. mL CH_4/g VS feed] is the maximum methane potential as Chen and Hashimoto model; and K_H [day^{-1}] is the disintegration rate constant from the First Order model.

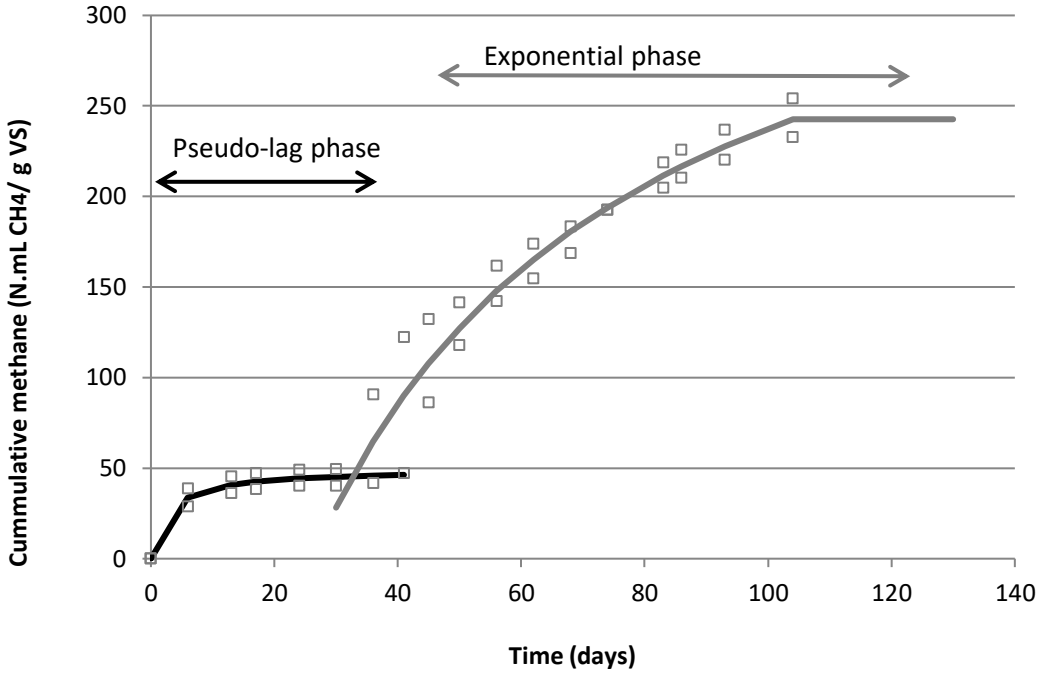

Fig. 3-3 Anaerobic digestion of water hyacinth at 30°C and F/I = 30. Kinetic profile of pseudo-lag and exponential phases that follows the modified Gompertz model.

When water hyacinth at F/I=30 was digested at 30°, the biomethanation profile could not be explained by any of the models under study (Fig. 3-2). The biomethanation kinetics under these conditions is different to previously published works. The kinetic parameters included a period of time that we have named pseudo lag phase, which took place after reaching an initial asymptote and before the exponential phase (Fig. 3-3). The pseudo lag phase lasted 36 days and its asymptote was 43.4 ± 2.5 N.mL CH_4/g VS. During this phase, the methane production followed the modified Gompertz model, which also governed the following exponential phase. The maximum methane potential for the exponential phase was 259.9 ± 16.9 N.mL CH_4/g VS, with a methane production

rate of 3.9 N.mL CH_4/g VS. The anaerobic digestion of water hyacinth high F/I (30) and 30°C could have been assumed to be terminated after 30 days due to low biogas generation and low % CH_4 at that time (Fig. 3-4). However, the consortia seem to have adapted to an F/I = 30, since the biogas produced after 45 days of digestion had a % CH_4 above 65% (Fig. 3-4). Similarly, the production of biogas after more than 120 days of digestion did not seem to have ceased, which implies that the maximum methane potential is higher than the yield at that time (263.6 ± 23.0 N.mL CH_4/g VS, Fig. 3-4).

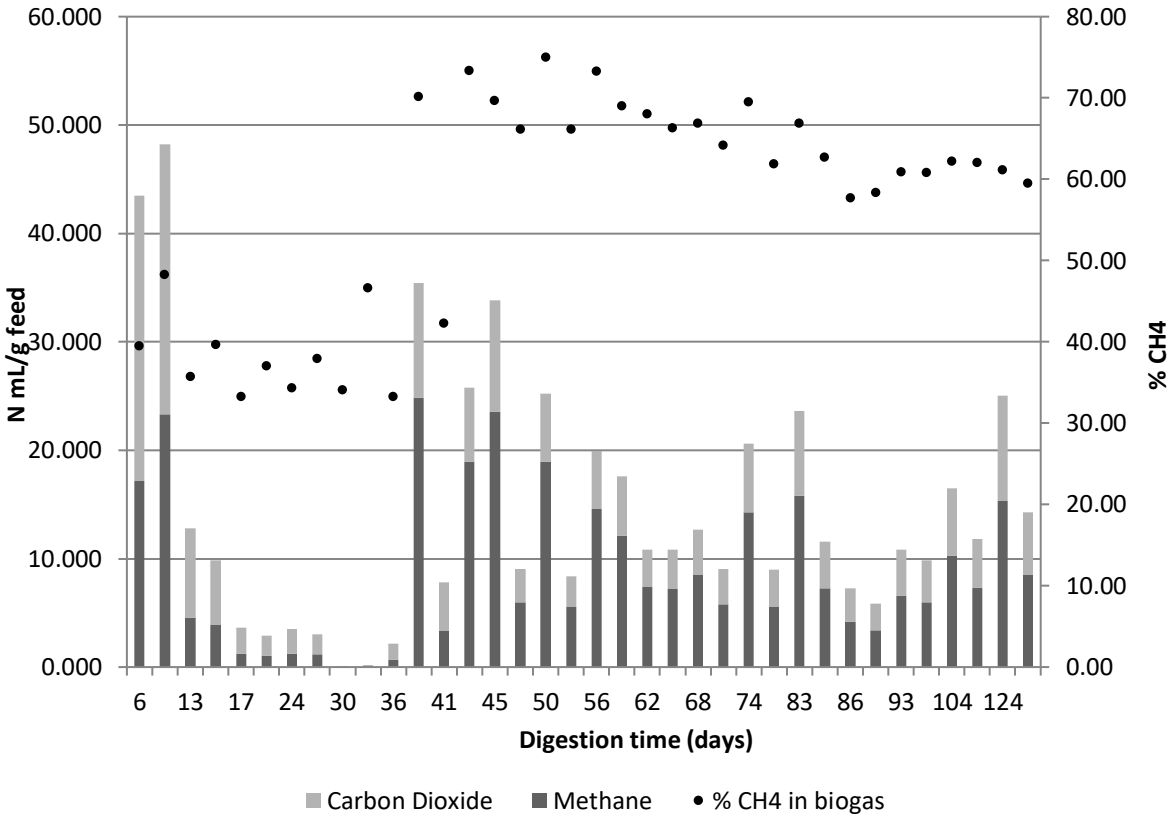

Fig. 3-4 Periodic (~ 4-10 days) biogas production (N.mL/g feed) and methane percentage during the anaerobic digestion of water hyacinth at 30°C and F/I = 30.

Energy Analysis

The conditions for the anaerobic digestion of water hyacinth that required the lowest heating energy were those at higher F/I and lower digestion temperature (Table 3-2). The difference between the produced and the heating energies were highest ($p < 0.01$, Table 2) for F/I=10 at 30°C, and F/I=30 systems at 30 °C and 40°C, and lowest ($p < 0.05$) for F/I=5.0 at 30°C. The anaerobic digestion at F/I = 30.0 resulted in the most energetically efficient system compared to those under study. The insignificant difference ($p > 0.957$) in the net energy Ep-Q between the bio-digestors operating at 30° and 40°C when F/I= 30 is due to the higher yield at 40°C than at 30°C.

The optimal conditions for the batch anaerobic digestion of water hyacinth would generate the highest amount of energy per time while having the minimum energy consumption per batch. The digestion of water hyacinth at F/I=30 and 40°C has the highest difference between the produced and the heating energies per batch (Table 3-2) while keeping low doubling times (16.9 ± 0.3 days). Even though the energy produced from the digestion of water hyacinth at F/I=30 and 30°C is more than 10 times the heating energy (Table 3-2) , the doubling time (49.6 ± 2.5 days) is above 40% ($p < 0.006$) those of the rest of the experimental units. Also, the kinetics under these conditions includes a pseudo lag phase where the production of methane is 20% of the methane yield and lasts more than 30 days. The anaerobic digestion of water hyacinth at high F/I should consider increasing the temperature of the system to overcome the deficiencies of the high substrate loading while keeping the energy efficiency of the large scale systems.

Table 3-2 Energy analysis for the anaerobic digestion of water hyacinth at 30° and 40°C using different F/I for a 5 m3 biodigestor. The assumptions were calculated to keep the study conditions. The mass of the water hyacinth (m $_{Feed}$) and the inoculum (m $_{Sludge}$) were expressed on fresh and dry basis, respectively. The water (m $_{H2O}$) considered in the study is from the sludge.

Conditions		Assumptions [kg]			Parameters for Analysis				Energy analysis [MJ]		
T [°C]	F/I	m_{Feed}	m_{Sludge}	m_{H2O}	m_{total} [Kg]	c_p Slurry [KJ/ Kg °C]	ΔT [°C]	Yield $_{CH4}$ [L CH_4/Kg VS]	Q	E_p	$\boldsymbol{E_p - Q}$[1]
	5.0	269	53.8	2098	2421	3.85	10	328.0 ± 16.3	93.2	316.0 ± 15.7	**222.8± 15.7 A**
30	10.0	347	34.7	1354	1736	3.65	10	330.3 ± 5.2	63.4	410.5±6.5	**347.1 ± 6.5 B**
	30.0	425	14.2	552	991	3.10	10	263.6 ± 23.0	30.7	400.4±34.8	**369.7 ± 30.7 B**
	5.0	269	53.8	2098	2421	3.85	20	346.3 ± 20.6	186.4	333.7±19.8	**147.3 ± 19.3 C**
40	10.0	347	34.7	1354	1736	3.65	20	308.4 ± 0.6	126.8	383.3± 0.7	**256.5 ± 0.7 A**
	30.0	425	14.2	552	991	3.10	20	284.3 ± 15.9	61.4	432.8±24.2	**371.4 ± 24.2 B**

[1] Different letters indicate a significant difference between sites for unpaired t-test (alpha =0.05).

3.5 Conclusion

The anaerobic digestion of water hyacinth at different F/I ratios, mesophilic temperatures, supplementation conditions, and inoculum acclimatization were conducted through factorial experiments. The study showed that using anaerobic media with and without vitamin and minerals did not improve the methane yield or rate in the batch systems. However, the F/I ratio affected the biomethanation performance. At F/I = 30, the methane yield (263.8 ± 26.9 N.mL CH_4/g VS) and rate (5.6 ± 2.8 N.mL CH_4/g VS·day) were lower than at F/I = 1.0, F/I = 5.0, and F/I = 10.0. Digesting the biomass at higher temperatures did not affect the methane yield but increased the production rate [N.mL CH_4/g VS·day] from 6.4 ± 2.5 at 30°C to 9.0 ± 0.8 at 40°C, which lead to shorter digestion times. The highest difference between the energy produced and the heating energy consumed during the anaerobic digestion of water hyacinth occurred at F/I =30 at 30° and 40°C. However, the doubling times at 30°C were almost 3 times that at 40°C since 30 days pseudo lag phase was observed during the biomethanation of water hyacinth at the lower temperature. The digestion of water hyacinth at high F/I (30) using high mesophilic temperature (40°C) seem to be feasible.

CHAPTER IV

EFFECT OF WET AIR OXIDATION ON THE COMPOSITION AND BIOMETHANATION OF WATER HYACINTH

4.1 Abstract

Water hyacinth (*Pontederia crassipes*) is an invasive weed considered a potential feedstock for biorefinery due to its rapid growth and phytoremediation properties when cultivated in wastewaters. For the first time, the effects of wet air oxidation (WAO) and alkaline wet air oxidation (AWAO) on the structure and biomethanation kinetics of water hyacinth were studied. Water hyacinth (50 g/L) was pretreated using WAO and AWAO (0.15 g Na_2CO_3/ g feed), at 170°C under 0.4 MPa air for 30 min. After WAO and AWAO, the fixed carbon [% w/w] of water hyacinth (25.9 ± 0.8) was reduced to an average of 21.4 ± 1.6. The volatiles [% w/w] in the WAO solid residue were higher (69.0 ± 0.7) than in the AWAO (60.5 ± 1.2) and unpretreated biomass (62.9 ± 0.2), but the soluble COD [mg / g feed] of WAO (153.5 ± 4.1) was half that of AWAO (310.3 ± 4.1). The AWAO biomass showed higher cellulose deconstruction and lignin and extractives removal compared to WAO and unpretreated biomass. The methane production rate [N. mL CH_4/g feed day] during the biomethanation of water hyacinth (4.1 ± 0.2) increased 63% after WAO (6.7 ± 1.5), and 117% after AWAO (8.9 ± 0.7). AWAO increased the methane potential [N. mL CH_4/g feed] of water hyacinth by 24%, from 153.7 ± 1.9 to 191 ± 4.1. The biomethanation of water hyacinth after AWAO was better than WAO and unpretreated biomass.

4.2 Introduction

One of the most important factors influencing the performance of biorefinery systems is the feedstock. A promising feedstock for bioconversion processes must have high productivity, low acquisition and conversion costs, and minimum environmental impact and land use (Wyman 2013). Water hyacinth (*Pontederia crassipes*) is an invasive aquatic plant considered an ecologically and economically sustainable feedstock for bioenergy production. This macrophyte grows very rapidly and does not require arable land or freshwater for cultivation. Water hyacinth doubling times are 6-7 days under optimal conditions (Reddy 1984; Gutiérrez et al. 2001). This plant can grow in wastewaters contaminated with heavy metals, and organic and inorganic compounds such as sulfates, phosphates, nitrates, nitrites, ammonia, and formaldehyde while keeping yields of 50-60 ton (dry wt)/ ha per year (Mahmood et al. 2010; Moyo et al. 2013; Koutika and Rainey 2015; Gong et al. 2018; Ting et al. 2018; Dölle et al. 2020; Gaurav et al. 2020). Production costs of water hyacinth from the harvesting to the drying of the biomass have been estimated to be around $40 per ton of dry biomass (Hronich et al. 2008). One of the most promising bioconversion routes for aquatic plants such as water hyacinth is anaerobic digestion (Wellinger et al. 2013). Reported biochemical methane potential (BMP) of water hyacinth under various conditions ranges from 114 to 552 L biogas/ kg VS (Mathew et al. 2013; Patil et al. 2014b; Hernández-Shek et al. 2016; Priya et al. 2018; Castro and Agblevor 2020a). The estimated energy produced from the biomethanation of a ton of fresh water hyacinth from eutrophic water bodies has been estimated to be 10 times higher than the energy required for harvesting (Castro and Agblevor 2020a). However, the productivity of bioconversion processes could be

increased by reducing the recalcitrance of lignocellulosic feedstock like water hyacinth (Tian et al. 2005; Xu et al. 2019; Zoghlami and Paës 2019; Rezania et al. 2020; Sankaran et al. 2020). Pretreating water hyacinth before anaerobic digestion could increase the digestibility and improve the biomethanation of this feedstock.

Effective pretreatments of lignocellulosic feedstock for biorefinery systems should recover lignin, protein, oils, and other materials found in the biomass for posterior use in different bioconversion processes. Aqueous pretreatment converts the biomass into reactive intermediates, which are compounds that are dissolved in water and that can be biologically, thermochemically, or catalytically converted to biofuels and chemicals (Wyman 2013). Alkaline pretreatment removes lignin and increases the surface area and porosity of the biomass, and improves the effective transport of cellulolytic enzymes into the biomass cell walls (Wyman 2013; Kim et al. 2016; Šoštarić et al. 2020). Unlike sodium hydroxide pretreatments, aqueous alkaline pretreatments using sodium carbonate, aqueous ammonia, and calcium carbonate have higher cellulose and hemicellulose recovery rates for feedstocks such as corn stover, sugarcane bagasse, and rice straw and wheat straw (Chang et al. 1998; Klinke et al. 2002; Kim et al. 2009; Morone et al. 2018). Even though aqueous pretreatments generally require subsequent downstream processes to concentrate the released macromolecules for bioethanol production, this is unnecessary in wet anaerobic digestion, whose solid contents are below 15% (Wellinger et al. 2013). Even though alkaline aqueous pretreatments are promising for the anaerobic digestion of lignocellulosic materials, studies on their effect on the structure and biomethanation of water hyacinth are scarce.

Wet air oxidation (WAO) is an aqueous pretreatment process that relies on the action of pressurized air under aqueous conditions to solubilize hemicellulose. The resulting biomass is mainly cellulose, with some residual hemicellulose and acid-insoluble lignin whereas, the liquid fraction consists of the degradation products from lignin and hemicellulose, such as monomeric phenols, furans, and carboxylic acids (Wyman 2013; Den et al. 2018). The acids have been previously shown to be effective for lignin degradation in lignocellulosic materials with low lignin content such as water hyacinth (Demesa et al. 2020). WAO differs from other hydrothermal pretreatments such as hot liquid water and steam explosion in the use of an oxidizing agent (e.g. air, oxygen), and the operating pressure(Pérez et al. 2008; Zhuang et al. 2016; Hamraoui et al. 2020). Even though steam explosion is widely used for the deconstruction of lignocellulosic biomass, the formation of by-products that are inhibitory for cellulose hydrolysis and the fermentation of hydrolysates is one of its drawbacks (Martin et al. 2008). The main degradation product of WAO is a carboxylic acid, which is an intermediate metabolite of methane in the anaerobic digestion pathway (Klinke et al. 2002; Wellinger et al. 2013; Demesa et al. 2020). Wet air oxidation is not commonly considered as a pretreatment of lignocellulosic materials for bioconversion processes (Abraham et al. 2020; Rezania et al. 2020). Wet oxidation at temperatures ranging from 125 °C to 320 °C and pressures from 0.5 to 30 MPa is generally used for the treatment of aqueous waste and the production of acetic acid from lignocellulosic material (Kolaczkowski et al. 1999; Kang et al. 2016). However, studies on the use of WAO as a pretreatment method for the bioconversion of lignocellulosic material are scarce.

For bioconversion processes, the addition of alkali during wet oxidation of lignocellulosic biomass is linked to an increase in sugar yield and reduction in the formation of acetic acids due to degradation of hemicellulose. Alkaline wet air oxidation (AWAO) is an efficient pretreatment method for delignification and deacetylation that reduces the crystallinity and improves the digestibility of cellulose while minimizing the production of phenols and furans (Klinke et al. 2002; Morone et al. 2018). Even though studies on the WAO of lignocellulosic materials for biofuels and bioenergy are scarce, AWAO has been successfully used on various feedstocks for these applications. In the alkaline oxidation of sugarcane bagasse, corn stover, rice husk, and wheat straw for bioconversion processes, using 0.002 g to 0.067 g Na_2CO_3 /g of biomass at 185-195 °C and 0.3 to 1.2 MPa O_2have yielded 57 to 99% sugar recovery (Klinke et al. 2002; Varga et al. 2003; Martín and Thomsen 2007; Wyman 2013; Sharma et al. 2015). Alkaline wet oxidation pretreatment of yard waste at 12 bar O_2 and 185 °C double the yield of methane during anaerobic digestion (Lissens et al. 2004). However, the feasibility of biomass pretreatment to minimize the lignocellulose recalcitrance depends on the feedstock due to the variability in the cell wall structure and composition (Wyman 2013). Several pretreatment methods have been applied to water hyacinth before bioconversion such as enzymatic hydrolysis, dilute acid hydrolysis, ionic liquid, crude glycerol, alkaline, and thermal pretreatments including hot air oven, microwave, autoclave, and hot water bath (Guragain et al. 2011; Lin et al. 2015; Barua and Kalamdhad 2017; Zhang et al. 2018; Sarto et al. 2019). However, the effect of WAO and AWAO to pretreat water hyacinth before bioconversion has not been studied.

The goal of this chapter is to study the effects of WAO and AWAO under lower pressure conditions on the structure and biomethanation kinetics of water hyacinth feedstock. In this section we report the effect of various pretreatment regimes on the maximum methane potential (A), methane production rate (K_d), lag phase (T_{lag}), and doubling time ($T_{doubling}$).

4.3 Material and Methods

Biomass

Samples of water hyacinth were collected from freshwaters at El Naranjo (18°34'27.2"N 69°47'09.9"W) within Ozama River. The biomass was prepared as described in section 2.3 Biomass Harvesting and Preparation. The characteristics of the water hyacinth under study are described in section 2.4.

Pretreatment

The pressurized reactor used for all the pretreatments was a 300 mL Parr 4560 (Parr Instrument Company, Moline, IL, USA). Biomass (5% w/w), alkali (when applicable), and deionized water were heated to 170 °C for 30 min under constant agitation. The reactions took place under pressure, with an initial air pressure of 60 psi (0.4 MPa). For the AWAO, 0.15 ± 0.05 g Na_2CO3/g biomass was added to the vessels. The resulting pH before the WAO and AWAO pretreatments were 6.40 ± 0.04, and 10.45 ±0.04, respectively. The pH after WAO was 4.99 ± 0.05 and after AWAO was 7.34 ± 0.16. The pH of the WAO slurry was adjusted to 7.14± 0.07 using KOH solution before the anaerobic digestion.

For the analysis of the aqueous and solid residues, the slurry was centrifuged at 3000 g for 15 min and vacuum filtered. The solid residue was washed with deionized water and dried at 45 °C before analysis.

Proximate and Ultimate Analyses

The thermogravimetric analysis (TG) and ultimate analysis of unpretreated biomass and solid residues from pretreatment was carried out according to their corresponding subsections within section 2.3. The protein content was estimated using the nitrogen conversion factor (NF = 6.25).

FT-IR Spectra

Mid-infrared spectra were collected over a wavenumber range of 4000 cm^{-1} to 600 cm^{-1} using a NICOLET IS20 PRO MID-IR (Thermo Fischer Scientific, Waltham, MA, USA) spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory (i.e., Smart iTXTM). The samples were scanned sixteen times at a resolution of 4 cm^{-1}, and the spectra were corrected for background absorbance by subtracting the spectrum of the empty ATR crystal. The spectra analysis was made according to previous works on the characterization of lignocellulosic biomass using FT-IR (Acquah et al. 2016).

Chemical Oxygen Demand (COD)

The maximum chemical energy present in the aqueous residue from pretreated water hyacinth that can be converted to biogas by microbes was assessed through the soluble COD (Wellinger et al. 2013). The liquid portion of the pretreated biomass was obtained by centrifugation and filtration (0.45 um) of the supernatant. For the control, the unpretreated water hyacinth was added to deionized water at 5% w/v and soaked for 30

min. The mixture was centrifuged at 3000 g for 20 min, and vacuum filtered with GF/A glass microfiber filter. The diluted samples were digested with the HACH COD High Range (COD HR) kit. COD (mg/L) was measured using a DR 500 Benchtop UV-VIS spectrophotometer (Hach Company, Loveland, CO, USA). The results were reported in mg COD / g feed.

Anaerobic Digestion

The biomethanation of water hyacinth was conducted in 160 mL serum bottles with a 110 mL working volume. Each serum bottle was loaded with 70 mL of biomass slurry, containing 3.55 ± 0.1 g of feed (pretreated or unpretreated biomass) and 2.13 g volatiles, 30 mL of inoculum, and 10 mL of deionized water. The inoculum was a mixture of anaerobic sludge from two mesophilic wastewater plants, North Davis Sewer District (Syracuse, UT, USA) and Central Valley Water Reclamation Facility (Salt Lake City, UT, USA) after adaptation to the feedstock. The sludge had 2.58 ± 0.10 % of total solids, 54.0 ± 0.4 VS%, and pH 7.8 ± 0.1. The serum bottles (digesters) contained 4.0 ± 0.3% total solids, feed to inoculum ratio (F/I) of 5.0, and pH 7.2 ± 0.2. The digesters were incubated at 38.0 ± 1.0 °C.

Gas Measurement

The produced gas was measured via volume displacement using a lubricated syringe every 2 to 5 days and analyzed using an Agilent 7890B Gas Chromatograph (Agilent Technologies, Santa Clara, CA, USA). The measured volume (V) was converted to normal volume (V0) using the Ideal Gas Law (Eq. 2-4), where T0 =273.15 K and P0 =101,325 Pa. The barometric pressure (P) and temperature (T) were recorded during the

gas measurements. The volume of the accumulated methane was reported per mass of feedstock added to the experimental units.

Modified Gompertz Model

The modified Gompertz model was fitted as described in section 2.3.

Statistical Analysis

The Solver tool in Excel was used to fit each replicate to the modified Gompertz model. The estimated kinetic parameters (A, K_d, T_{lag}, and $T_{doubling}$) of the digestors were compared using analysis of variance (aov) and Tukey's test (Tukey HSD), in R Studio (version 3.6.1). For the comparison of operational profiles, proximate and ultimate analyses, and methane yields in each digestor, the unpaired t-test (www.graphpad.com) was used. The populations were assumed to be independent, normal distributed, and with equal variances.

4.4 Results and Discussion

Operational Profiles

The operation parameters such as pH, maximum temperature and pressure define the suitability of a pretreatment process for a specific conversion route. During the oxidation, the batch Parr reactor temperatures rose above 170 ° C due to exothermic reactions taking place (Alvira et al. 2011). There was no statistically significant difference between the maximum temperatures (176.5 ± 4.2 °C) and pressure (1.1 ± 0.2 MPa) attained during WAO and AWAO (p = 0.158). The pH of the feedstock for bioconversion processes such as anaerobic digestion should be between 6.5 and 7.8 for microbial viability (Wellinger et al. 2013). The pretreatment that generated pH conditions suitable for further biological conversion was AWAO (7.3 ± 0.2). The WAO slurry had a

lower pH (5.0 ± 0.1, p = 0.001) than that from AWAO, and required pH adjustment before biomethanation.

Thermal Degradation

The volatile content (Table 4-1) of unpretreated and pretreated water hyacinth was released between 200 – 350 °C (Fig. 4-1) during TGA analysis of the materials. Each sample was run in triplicates and the average weight loss temperatures calculated. . The unpretreated biomass had two weight loss regimes and the DTGA showed a clear peak at T_{max} = 314.9 ± 2.4 °C and a shoulder at 250 ±1.4 °C. The shoulder at 250 ±1.4 C for the unpretreated biomass was attributed to hemicellulose degradation while the peak at Tmax = 314.9 ± 2.4 °C was assigned to cellulose degradation (Yang et al. 2007; Nguyen Thi et al. 2017). The shoulder corresponding to hemicellulose maximum thermal degradation (T_{max}) in the unpretreated water hyacinth (Fig. 4-1) was not present after pretreating the biomass, indicating complete degradation of hemicellulose during WAO and AWAO. Complete degradation of hemicellulose in water hyacinth after hydrothermal treatment followed by acid/water wash has been reported (Yao et al. 2020). However, only partial degradation of hemicellulose was achieved when water hyacinth was pretreated using boiling, steaming, and ultra-sonicating methods (Harun et al. 2011). Similarly pretreatment of rice straw using microwave-alkali-acid did not degrade all the hemicellulose present in this feedstock (Akhtar et al. 2017). Thus, both the WAO and AWAO were as effective as the hydrothermal acid/water washing method for the pretreatment of water hyacinth, but better than the boiling water, steaming and ultra-sonication methods.

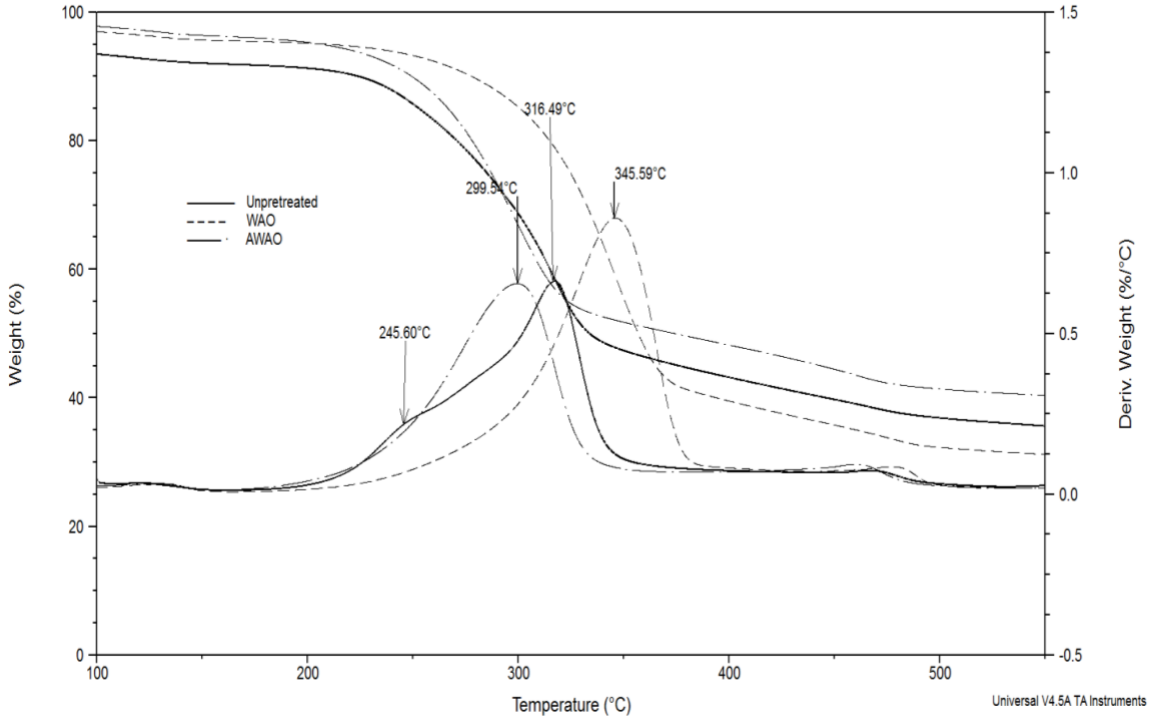

Fig. 4-1 Curves of the differential thermogravimetric analysis of unpretreated and pretreated water hyacinth. The pretreatments under study are Wet Air Oxidation (WAO) and Alkaline Wet Air Oxidation (AWAO).

WAO and AWAO affected the cellulose maximum decomposition temperature of water hyacinth differently. The AWAO lowered (p = 0.009) the maximum cellulose decomposition temperature from Tmax = 314.9 ± 2.4 °C to Tmax = 299.5 ± 5.2 °C (Fig.4-1), which suggests a reduction in the degree of cellulose crystallinity. Hideno showed that as the degree of cellulose crystallinity decreased, the maximum degradation temperature of microcrystalline cellulose decreased (Hideno 2016). Thus, AWAO water hyacinth biomass feedstock should be relatively easier to digest compared to the

unpretreated material. In contrast, the WAO sample had the highest ($p < 0.002$) DGTA cellulose decomposition temperature (T_{max} = 341.7 ± 5.6 °C), which suggested that the WAO pretreatment increased the degree of crystallinity of the cellulose in this material compared to both the unpretreated and AWAO solids. It appears the WAO attacked the hemicellulose and the amorphous cellulose and thus increasing the crystallinity of the cellulose (Pardo et al. 2019). The WAO results are in accord with acidic systems such as the hydrothermal treated and water/acid washed water hyacinth, which had higher maximum degradation temperature (~ 400°C) than the raw biomass (~350 °C) (Yao et al. 2020). The addition of alkali in the WAO of water hyacinth seems to prevent the increase in the degree of cellulose crystallinity in the biomass solid residue.

Table 4-1 Proximate analysis of unpretreated water hyacinth and solid residues from pretreated biomass (mean ± SD), on a dry weight basis

	Proximate Analysis (% w/w)		
	Volatiles	Fixed carbon	Ash
Unpretreated	62.9 ± 0.2 A	25.9 ± 0.8 A	11.1 ± 0.9 A
WAO	69.0 ± 0.7 B	20.1 ± 0.7 B	10.9 ± 0.2 A
AWAO	60.5 ± 1.2 A	22.7 ± 0.8 C	16.8 ± 0.9 B

The same letters within each column mean no statistical difference for t-test (α= 0.05).

Proximate Analysis

The proximate analysis of the unpretreated and pretreated water hyacinth showed that the solid residues from WAO had a relatively higher ($p = 0.001$, Table 4-1) volatile content than the unpretreated biomass and the solid residue from AWAO. The volatiles in the biomass before and after AWAO were not different ($p > 0.22$). The solid residues from the pretreated biomass had lower ($p < 0.003$) fixed carbon (21.4 ± 1.6 % w/w) than the unpretreated biomass (25.9 ± 0.8 % w/w). The lowest fixed carbon ($p < 0.0013$, Table 4-1) in the solid residues is achieved after WAO. The ash content in the water hyacinth after AWAO was higher ($p = 0.0015$, Table 4-1) and after WAO no different ($p = 0.726$) than before pretreatment. These results could be explained by the solubilization of organic compounds, such as acid soluble lignin and hemicellulose, resulting in lower volatiles and higher fixed carbon and ash per unit mass of the AWAO solid residue. A reduction in volatiles and an increase in fixed carbon were reported in previous work after pretreating water hyacinth with torrefaction, and hydrothermal treatment followed by acid/water wash (Yao et al. 2020). The higher volatiles, and the lower fixed carbon and ash content suggest that the solid residue from WAO water hyacinth may be more suitable for biomethanation than that from AWAO if the cellulose crystallinity does not influence the bioavailability of this biomass component.

Ultimate Analysis

The ultimate analysis showed that the nitrogen content in the AWAO solid residue is lower ($p < 0.006$, Table 4-2) than in the unpretreated biomass. Consequently, the lowest protein content was estimated for the solid residues from AWAO (8.6 ± 1.2 %w/w) compared to that from WAO (13.8 ± 0.2 % w/w) and unpretreated water hyacinth

(14.4 ± 1.2 % w/w). This is explained by the protein solubility from the biomass by NaOH when the pH is above 7 (Abu-Salem and L. HusseinY. Foda 1975; Bals et al. 2007). The C/N of the unpretreated water hyacinth (16.7 ± 0.8) is below the optimal range (20-30) that ensures a proper anaerobic digestion process (Wellinger et al. 2013; Gil et al. 2019). The WAO and AWAO increased ($p < 0.020$) the C/N ratio of the water hyacinth solid residues to 20.0 ±1.3 and 26.6 ± 1.3, respectively. The effect of WAO and AWAO pretreatments on the organic elemental composition of the water hyacinth did not compromise biomethanation performance indicators like C/N.

Table 4-2 Ultimate analysis of unpretreated water hyacinth biomass and solid residues of pretreated water hyacinth (mean ± SD), on a dry weight basis

	Ultimate Analysis (% w/w)			
	C	H	N	O
Unpretreated	38.4 ± 0.6 A	4.4 ± 0.1 A	2.3 ± 0.2 A	43.7 ± 0.9 A
WAO	44.0 ± 1.3 B	4.9 ± 0.2 A	2.2 ± 0.03 A	38.1 ± 1.5 B
AWAO	37.3 ± 1.1 A	4.5 ± 0.2 A	1.4 ± 0.2 B	40.8 ± 1.5 A B

The same letters within each column mean no statistical difference for t-test (α= 0.05).

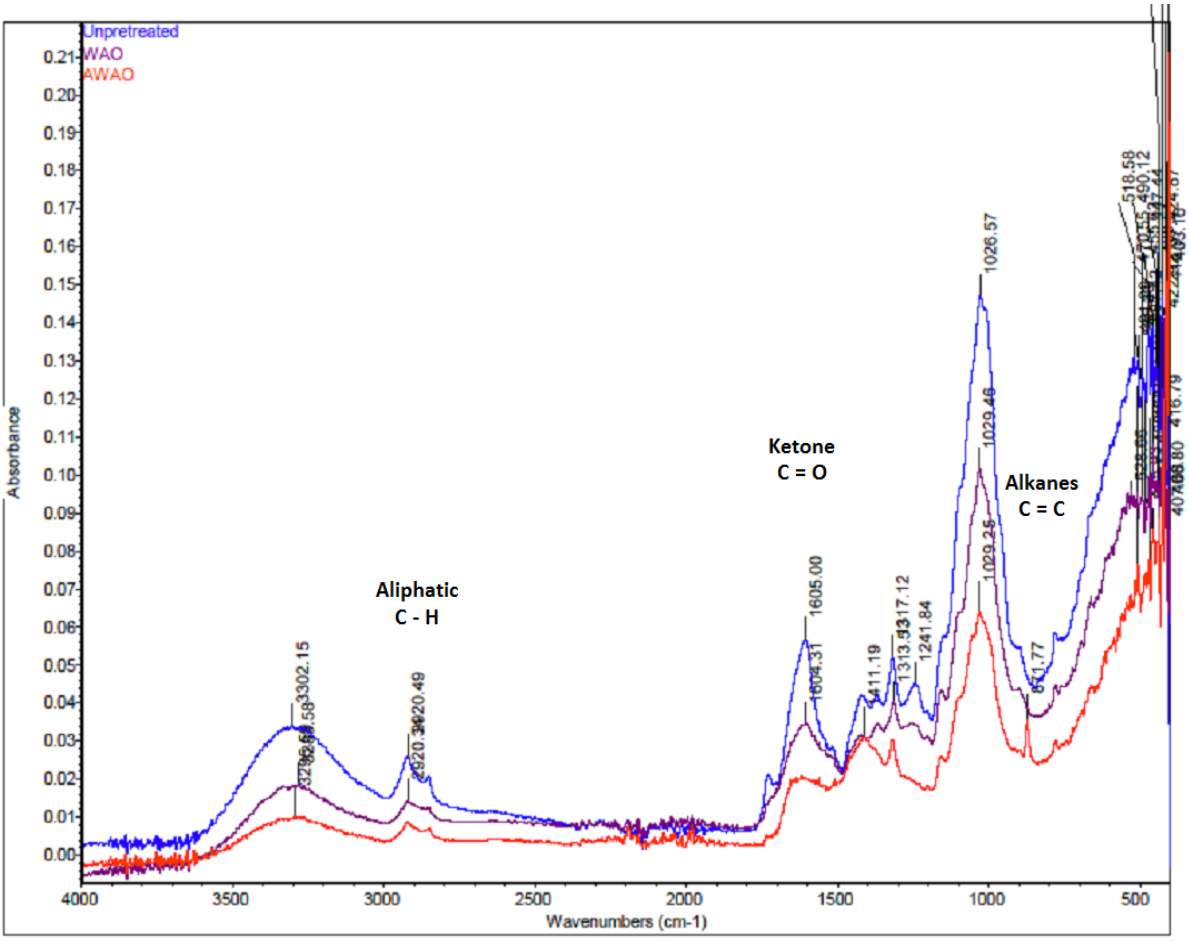

Figure 4-2 FT-IR spectra from unpretreated water hyacinth, and from Wet Air Oxidation (WAO) and Alkaline Wet Air Oxidation (AWAO) solid residues.

FT-IR Spectra

The region containing the most spectral information on the molecular and chemical composition of a material is 1800 to 650 cm^{-1} (Acquah et al. 2016). The peaks intensity at 2920 cm^{-1} and 1605 cm^{-1} is high in the unpretreated water hyacinth, reduced after WAO, and negligible in AWAO solid residues (Fig. 4-2). The peak at 2920 cm^{-1} corresponds to the bending and stretching of C – H and its aromatic ring vibration in lignin, and that at 1605 cm^{-1} to C – O stretching or C = O stretching vibration in ketones

or flavones (Yang et al. 2007; Thyrel 2014; Acquah et al. 2016). The lignin and extractives in water hyacinth are removed effectively during AWAO, but only partially during WAO. Similarly, the presence of peaks at 1411 cm^{-1} and 871 cm^{-1} in the AWAO solid residues suggests C – H deformation of cellulose during the pretreatment (Raspolli Galletti et al. 2015; Acquah et al. 2016). These peaks are not present in the spectra from the WAO solids because the cellulose crystallinity increased (Fig. 4-1). These results are in accordance with previous studies where the addition of an alkali (Na_2CO_3) during the wet air oxidation of rice straw reduced the recalcitrance and increased the cellulose accessibility of the biomass (Morone et al. 2018). The FTIR spectra of the AWAO water hyacinth show that the pretreatment can significantly reduce the recalcitrance of the biomass by solubilizing lignin and extractives and reducing the crystallinity of the cellulose which facilitated its anaerobic digestion.

Chemical Oxygen Demand

The COD of the aqueous phase from the unpretreated water hyacinth (26.6 ± 0.97 mg/ g biomass negative control) was comparable ($p = 0.080$) to that other studies (20.7 ± 4.08 mg COD/ g water hyacinth)(Sarto et al. 2019). The liquid residue of the aqueous pretreated biomass is expected to contain the degradation products from the hemicellulose such as monosaccharides and furans (Wyman 2013). The COD (mg/ g biomass) of the filtrate from AWAO (310.3 ± 4.1) was twice ($p < 0.0001$) that from WAO (153.5 ± 4.1). The highest COD (mg / g biomass) from acid pretreated water hyacinth at 1-5% w/w sulfuric acid (136.8) was lower ($p < 0.020$) than our results from the WAO and AWAO biomass (Sarto et al. 2019). Thus, the aqueous residue from AWAO pretreated water hyacinth is better for anaerobic digestion than that from WAO.

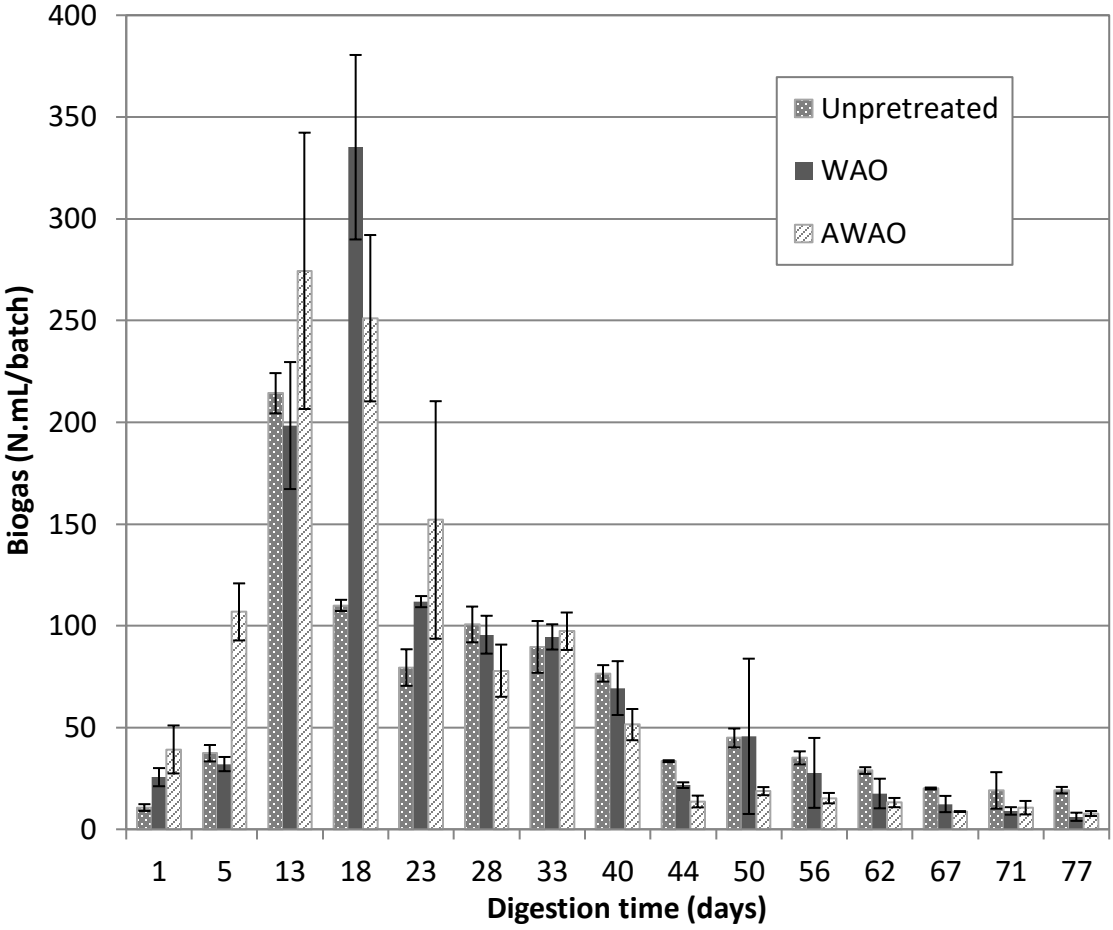

Fig. 4-3 Biogas yield during the anaerobic digestion of unpretreated, wet air oxidized (WAO), and alkaline wet air oxidized (AWAO) water hyacinth. Error bars are the standard deviation of the mean value

Anaerobic Digestion

During anaerobic digestion of water hyacinth, the maximum biogas yield (N. mL/batch) of unpretreated (214.6 ± 9.9, $p < 0.001$) water hyacinth was produced between the 6th and 13th days, and that from WAO (335.2 ± 99.2, $p < 0.0126$) biomass between the 14th and 18th days of digestion (Fig. 4-3). The maximum biogas yield from AWAO biomass occurred from the 6th to the 13th (274.4 ± 67.9) but was not different ($p >$

0.077) to those from the 14th to the 18th (251.1 ± 40.9), and from the 19th to the 23rd (152.0 ± 58.4). The earlier maximum biogas yields in the unpretreated and AWAO water hyacinth compared to the WAO biomass is expected due to the higher degree of cellulose crystallinity observed in the latter (Fig. 4-1). These results could also be due to the presence of the inhibitory compounds for the anaerobic digestion (e.g. phenols, vanillin), which are minimum under alkaline conditions (AWAO) (Barakat et al. 2012; Sierra-Ramirez, Rocio; Holtzapple, Mark; Piamonte 2013; Wirth et al. 2015). Similarly, the maximum cumulative methane yield from the AWAO biomass was reached earlier (40 days) than that from WAO and unpretreated biomass (Fig. 4-4) because the AWAO has twice as much COD and the cellulose was less crystalline.

After 30 days of digestion, the cumulative methane produced [N.mL CH4/ g feed] from the AWAO biomass (161.7 ± 7.7) was 35 % higher (p = 0.018) than those from WAO (119.9 ± 17.1) and 55% greater (p = 0.0005) than unpretrated biomass (104.3 ± 5.5). The AWAO results are lower (p = 0.032) than serial pretreatments such as microwave-heated alkali followed by enzymatic hydrolysis that yielded 185.8 N.mL CH4/ g feed from the one-stage methane fermentation of water hyacinth (Lin et al. 2015). The methane yield from water hyacinth after traditional alkaline pretreatment (1% NaOH for 48-h soaking) and co-digestion (65:35) with sheep waste (95.6 N.mL CH4/ g feed) were lower (p = 0.004) than that from AWAO biomass but comparable (p > 0.111) to those from unpretreated and WAO water hyacinth (Patil et al. 2014a).

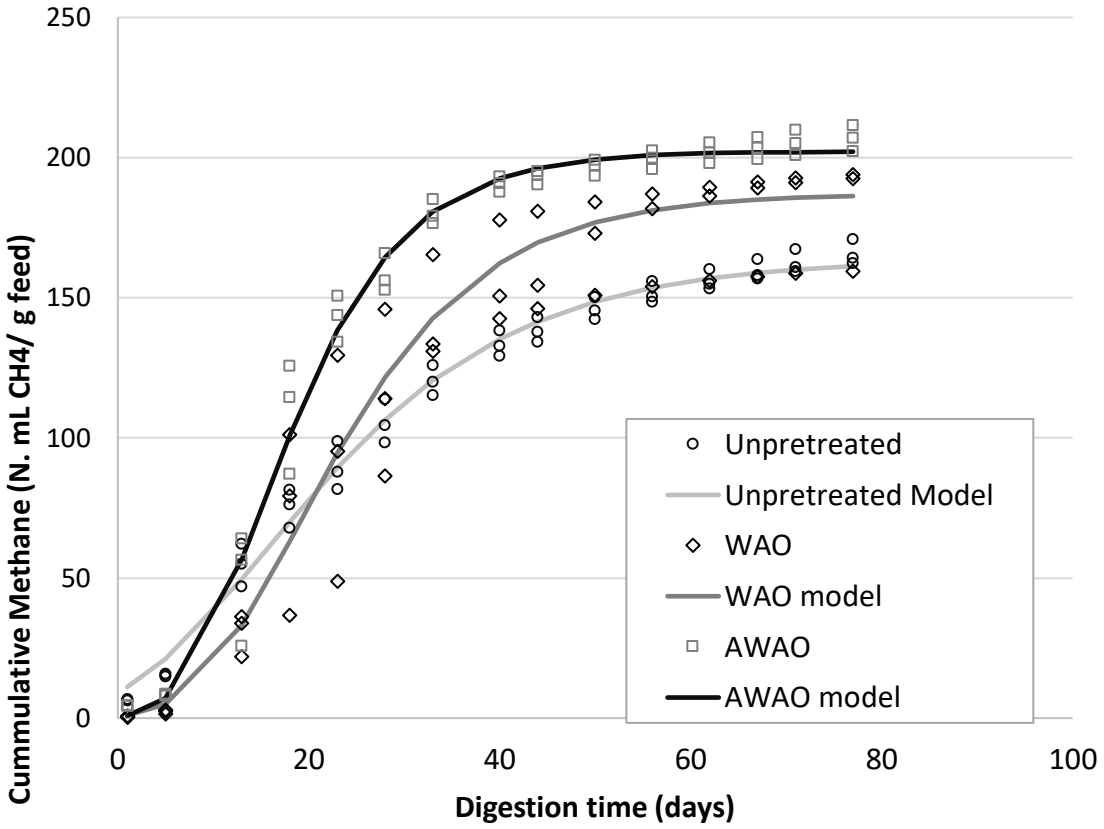

Fig. 4-4 Methane production and modified Gompetz models for the unpretreated, Wet Air Oxidized (WAO), and Alkaline Wet Air Oxidized (AWAO) water hyacinth

The unpretreated water hyacinth reached steady state methane production in the biogas (%CH_4) after 5 days, whereas those from the WAO and AWAO biomass reached the steady state after more than 23 and 13 days of digestion, respectively (Fig. 4-5). This response could be due to the presence of WAO and AWAO pretreatment byproducts (e.g. phenols, furans), which are expected to be utilize by the anaerobic consortia after adaptation (Barakat et al. 2012; Sierra-Ramirez, Rocio; Holtzapple, Mark; Piamonte 2013; Wirth et al. 2015). Similarly, during the first 15 days of digestion, %CH_4 was

higher ($p < 0.0001$) in the biogas from the unpretreated (58.0 ± 10.5 %) than that from the pretreated biomass. However, the cumulative methane yield [N. mL CH4/ g feed] at that time was lower ($p = 0.0348$) for the unpretreated (49.8 ± 5.5) than for the AWAO (66.8 ±7.7) biomass. After 15 days, the $\%CH_4$ from AWAO (68.5 ± 6.5 %) was the highest ($p < 0.0001$) followed by that from WAO (61.1 ± 7.0 %), while $\%CH_4$ from the unpretreated biomass (57.8 ± 3.7%) was steady ($p = 0.924$). During the anaerobic digestion of water hyacinth, the higher biogas yield and $\%CH_4$ in a shorter time was achieved after AWAO.

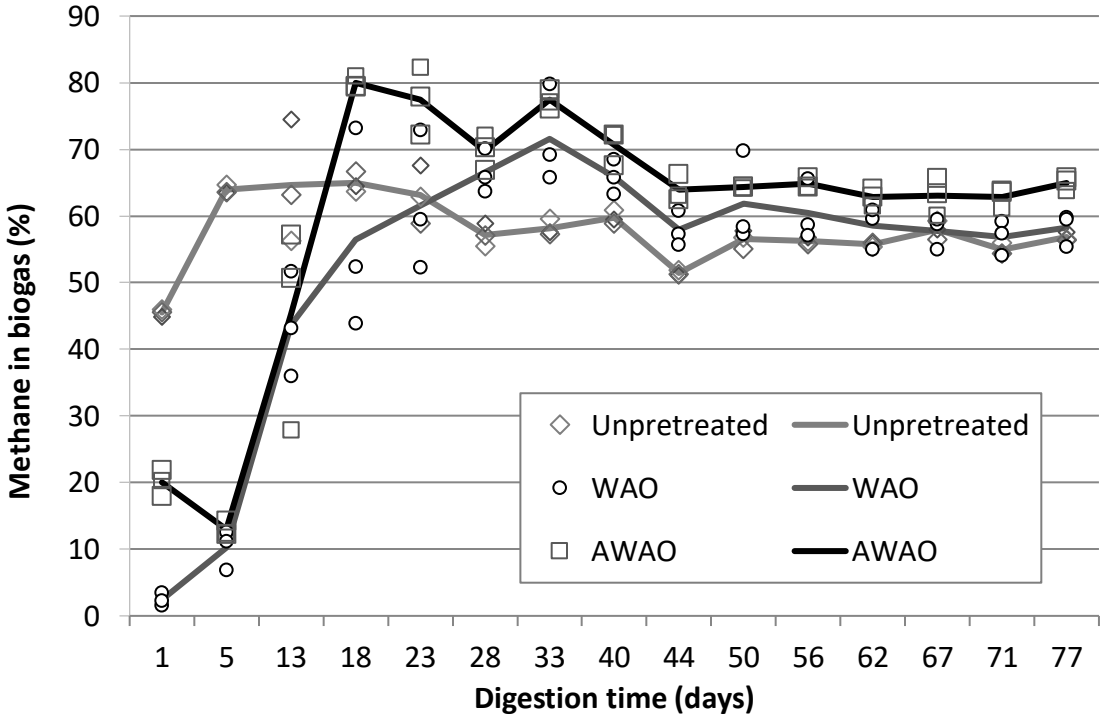

Fig. 4-5 Percentage of methane in the biogas during the anaerobic digestion of water hyacinth before pretreatment and after Wet Air Oxidation (WAO), and Alkaline Wet Air Oxidation (AWAO).

Table 4-3 Kinetic parameters (mean ± SD) from the modified Gompertz model for the biomethanation of water hyacinth before and after wet air oxidation (WAO) and alkaline wet air oxidation (AWAO).

Parameter [1]	Unpretreated	WAO	AWAO
A [N. mL CH4/g feed]	153.7 ± 1.9 A	171.2 ± 19.0 AB	191.0 ± 4.1 B
Kz [N. mL CH4/g feed · day]	4.1 ± 0.2 A	6.7 ± 1.5 B	8.9 ± 0.7 B
Tlag [day]	2.7 ± 0.6 A	9.7 ± 3.7 B	7.5 ± 2.5 B
Tdoubling [day]	22.2 ± 1.6 A	23.0 ± 5.5 AB	18.6 ± 1.4 B
RMSE	3.8 ± 0.8	4.7 ± 0.9	4.4 ± 1.4
R^2	0.994	0.994	0.996

The same letters within each row mean no statistical difference for *t*-test (α = 0.05).
[1]A is the maximum methane produced, Kz is the absolute growth rate, Tlag is the lag time, and $T_{doubling}$ is the doubling time. RMSE is the root mean square error, and R^2 is the variation of the measurements explained by the models.

Biomethanation Kinetics

After 77 days of anaerobic digestion, the maximum methane potential (A) from AWAO water hyacinth was more than 24% higher (p = 0.004, Table 4-3) than before pretreatment. However, the A for the biomass after WAO was similar (p = 0.236) to the unpretreated biomass. The total methane yield after pretreating water hyacinth with AWAO (195.81 ± 4.8 N. mL CH_4/ g feed) was 10 times higher (p = 0.001) than after 5% v/v sulfuric acid pretreatment (10.9 mL CH_4/ g feed), and 77 % higher (p = 0.001) than after ionic liquid pretreatment (Gao et al. 2013; Sarto et al. 2019). The methane production rate during the anaerobic digestion of the WAO and AWAO water hyacinth

was more than 20% higher ($p < 0.03$, Table 4-3) and the doubling time after AWAO shorter ($p = 0.04$, Table 4-3) than before pretreatment. The kinetics showed that AWAO of water hyacinth had the best performance for biomethanation when compared to WAO and other previously studied pretreatment methods.

Even though AWAO increased the biomethanation performance of water hyacinth, the costs associated to alkali and the energy consumed during biomass size reduction, heating and stirring were not considered in this analysis. The next chapter presents studies on the parametrization of AWAO to minimize the energy expenditure and chemical costs, and to increase the process performance for the biomethanation of water hyacinth, as a third-generation bioconversion process.

4.5 Conclusion

Water hyacinth was subjected to wet air oxidation (WAO) and alkaline wet air oxidation (AWAO) for the first time to determine the effect of these aqueous pretreatments on the structure and biomethanation of this lignocellulosic biomass. During both pretreatments, hemicellulose was completely solubilized and fixed carbon was in the solid portion was reduced. The FTIR analysis showed that cellulose deconstruction, and lignin and extractives removal better attained after AWAO than after WAO. After AWAO, the thermal degradability of the solid residues was higher than for the unpretreated and WAO biomass. The biomethanation potential of the aqueous residue from AWAO (310.3± 4.1 mg COD/g feed) doubled that from WAO (153.5 ± 4.1 mg COD/g feed). As a result, pretreating water hyacinth with AWAO caused an increase in the maximum methane potential from 153.7 ± 1.9 to 191.0 ± 4.1 N. mL CH_4/g feed. Similarly, the biomethanation of AWAO had more than 60% higher production rate, and

shorter doubling time (18.6 ± 1.4 days) than before pretreatment (22.2 ± 1.6 days). The methane in the biogas from AWAO water hyacinth was the highest (68.5 ± 6.5 % CH_4) within the stationary phase compared to WAO and unpretreated biomass.

CHAPTER V

PARAMETRIC STUDIES AND BIOCHAR EFFECT ON THE BIOMETHANATION OF WET AIR OXIDIZED WATER HYACINTH

5.1 Abstract

Biochar concentration [g/ g feed] at 0 g/g, 0.25 g/g, and 0.5 g/g, alkali concentration [g Na_2CO_3/ g Feed] at 0.07, and 0.14, and pretreatment temperature [°C] at 80, 100, 170, were used to determine the optimal conditions for the alkali wet air oxidation (AWAO) of water hyacinth and the effect of biochar on this system through kinetic studies. The net energy from the pretreated and unpretreated biomass was estimated to assess the feasibility of AWAO for the biomethanation of water hyacinth. The operational profiles showed better pressure stability for the pretreatment conducted at lower temperatures (80 - 100 °C) than at 170 °C. After 21 days of digestion, the methane rate yield [N. mL CH4/ g feed *day] for the biomass pretreated at lower temperatures and alkali dosage (80 °C , 0.07 g Na_2CO_3/ g) was higher (10.0 ± 0.7) than the biomass pretreated at high temperature and alkali concentration (3.6 ± 2.0) and the unpretreated biomass (5.4 ± 0.1). Also, the methane yield for the biomass pretreated at 80°C was twice that for that pretreated at 170 °C. The biomethanation of the water hyacinth pretreated at higher temperatures and low alkaline concentration were improved by adding poultry litter biochar. After 31 days of digestion, the energy produced from the pretreated water hyacinth was estimated to be 464.6 ± 19.0 MJ/ ton while that from the raw biomass was 339.6 ± 42.3 MJ/ton.

5.2 Introduction

The integration of thermochemical byproducts into biochemical processes opens the possibility of minimizing the impact of thermochemical residues on the environment while enhancing the productivity of biological systems. Anaerobic digestion is a biological process where biomass is degraded by a consortium of anaerobic bacteria and archaea in four steps: hydrolysis of macromolecules, acidification, production of acetic acid, and production of methane (Wellinger et al. 2013; de Jong and Van Ommen 2015). The combination of anaerobic digestion and pyrolysis has been considered a promising approach to overcome some challenges of the former such as the use of recalcitrant materials as feedstocks, process efficiency, product quality, and management of effluents and emissions (Masebinu et al. 2019). Pyrolysis is able to degrade lignocellulosic derivatives into liquids, solids, and non-condensable gases by heating the biomass beyond their thermal stability under anoxic conditions (Moldoveanu 2009; Wang and Luo 2017; Zaman et al. 2017). The yield of the pyrolytic products (i.e. bio-oil, syngas, and biochar) depends on the processing conditions like temperature and residence time (Masebinu et al. 2019). Currently, fast pyrolysis is of high interest due to its main resulting product ((bio-oil, an energy-rich liquid that serves as intermediate for the production of drop-in fuels, biobased chemicals, and hydrogen fuel (Wang and Brown 2017)). At least 10% of the product obtained from fast pyrolysis is a carbonaceous solid residue, i.e. biochar (Lehmann and Joseph 2009; Masebinu et al. 2019). Recycling this solid residue to be used on other applications would reduce the waste generated from thermochemical processes.

Contrary to the gaseous and liquid products resulting from pyrolysis, biochar has been traditionally linked to environmental solutions rather than exclusively energy production (Lehmann and Joseph 2009). In agriculture, the application of biochar to arable land has increased soil quality, minimized the effect of extreme soil conditions, enhanced the crop productivity, and increased minerals and vitamins content in the crops (Revell et al. 2012a, b; Jatav et al. 2017; Akachukwu et al. 2018; Romdhane et al. 2019; Sikder and Joardar 2019). Also, biochar has been used as a filter to remove microbial, organic and inorganic materials, including heavy metals, nitrogen and phosphorus from contaminated waters (Gwenzi et al. 2017; Sana and Khatoon 2017; Perez-mercado et al. 2018). In fermentation, biochar has been reported to enhance the production of bioethanol and increase the microbial growth of Saccharomyces cerevisiae (Diallo 2014). The use of biochar in the anaerobic digestion of various feedstocks has shown increase in the $\%CH_4$ in biogas, reduction in substrate-induced inhibition, increase in macro- and micronutrients digestate quality, and biogas upgrade by CO_2 sequestration (Shen et al. 2015; Linville et al. 2017; Capson-tojo et al. 2018; Masebinu et al. 2019; Pan et al. 2019). Using biochar as an aid for anaerobic digestion enhances the productivity of the bioconversion process while recycling a pyrolytic waste.

Studies have been conducted to reveal the properties of biochar that contribute to the improvement of the anaerobic digestion performance. Yet, the effect of this material on the anaerobic digestion of lignocellulosic feedstock after pretreatment has not been explored. Pretreatment of lignocellulosic materials such as water hyacinth improves the availability of biodegradable compounds and leads to higher methane yields (Chapter IV). The formation of degradation compounds from the AWAO pretreatment reactions

such as monomeric phenols, furans, and carboxylic acids have shown no inhibition to the anaerobic consortium (Rivard and Grohmann 1991; Barakat et al. 2012). However, the neutralization of the pretreated biomass might lead to sulfate formation and the inhibition of the methanogens (Khanal and Huang 2005). Sulfate adsorption onto biochar has been reported to follow the pseudo-second-order model and to be due to electrostatic interaction (Zhao et al. 2019). On the other hand, biochar has been reported to be inhibitory to the microbial consortium at high concentrations (Diallo 2014; Shen et al. 2016). Therefore, the effect of biochar at different loadings on the anaerobic digestion of pretreated lignocellulosic material needs to be assessed to improve this bioconversion process.

The parameterization of the alkaline wet air oxidation (AWAO) of water hyacinth, and the assessment of the effect of poultry litter biochar as an aid for the anaerobic digestion of the pretreated biomass contribute to the scaling up of the integrated system. The costs associated to the AWAO of water hyacinth could be reduced by utilizing lower temperatures and less alkali during processing. The temperatures commonly used for AWAO are above 170°C, however, the materials that are pretreated (e.g. rice straw, corn stover, ..) have higher cellulose and lignin content than water hyacinth (Shawky et al. 2011; Wyman 2013; Castro and Agblevor 2020a). In this chapter, biochar concentration [g/ g feed] at 0 g/g, 0.25 g/g, and 0.5 g/g, alkali concentration [g Na_2CO_3/ g Feed] at 0.07, and 0.14, and pretreatment temperature [°C] at 80, 100, 170, were studied as an unreplicated full factorial design to determine the optimal conditions for AWAO of water hyacinth and the effect of biochar on this system. The methane yield, methane production rate, and lag time were determined from the

modified Gompertz model and set as the experiment dependable variables. The feasibility of AWAO for the biomethanation of water hyacinth was determined by comparing the net energy from the pretreated and unpretreated biomass.

5.3 Materials and methods

Biomass

Water hyacinth from El Naranjo (18°34'27.2"N 69°47'09.9"W), Ozama River (Dominican Republic) was collected and prepared as described in (Castro and Agblevor 2020a). The final particle size of the biomass was 0.850-2.00 mm.

Biochar

The biochar used for the study was from 500°C fast pyrolysis of chicken litter processed in an industrial rotary kiln reactor by Amaron Energy (Salt Lake City, UT, USA). The material was sieved using a Ro-Tap model E test shaker (WS Tyler, Mentor, OH, USA) equipped with No. 100, No. 20, and No. 10 US standard meshes and had a particle size of 0.85-2.00 mm.

Surface Area

Biochar's specific surface area was determined using the Monosorb (Quantachrome Instruments, Boynton Beach, FL) based on BET (Brunauer, Emmett and Teller) theory. About 0.1-0.2 g of biochar was degassed at 300°C for three hours and nitrogen/helium was used as carrier gas.

Proximate and Ultimate Analyses

The proximate and ultimate analyses of biochar were carried out according to their corresponding subsections within section 2.3.

Inorganic Elemental Analysis

For the total inorganic elemental composition, 1.0 g of sample was analyzed according to the corresponding subsection of section 2.3 by Utah State University Analytical lab (USUAL), Logan, UT, USA.

Alkaline Wet Air Oxidation (AWAO)

The reactions took place under pressure in a 300 mL Parr 4560 (Parr Instrument Company, Moline, IL, USA). The vessel containing 3.5 g of biomass (5% w/w), at 0.07 or 0.14 g Na_2CO_3 / g biomass, and 80 mL of deionized water. The reactor was then initially pressurized with air to 0.4 MPa (60 psi) before heating to different temperatures (80 °C, 100 °C, and 170 °C) for 25 min under constant agitation.

Anaerobic Digestion (AD)

The biomethanation of the samples was conducted in 160 mL serum bottles with a 110 mL working volume. Each bottle was loaded with 70 mL of biomass slurry, containing 3.50 ± 0.03 g of feed (pretreated or unpretreated biomass), and 40 mL of inoculum. The inoculum was a mixture of anaerobic sludge from two mesophilic wastewater plants, North Davis Sewer District (Syracuse, UT, USA) and Central Valley Water Reclamation Facility (Salt Lake City, UT, USA) recycled from previous anaerobic digestions. The sludge had 0.67 ± 0.08 % total solids, 50.3 ± 0.4 VS%, and pH 7.8 ± 0.1. The serum bottles (digesters) contained 4.3 ± 0.2% total solids and feed to inoculum ratio (F/I) of 15.6 ± 0.12 on VS basis. The digesters were incubated at 37 °C. The produced gas was measured as described in the corresponding subsection within section 4.3.

The percent of volatile solids destroyed (% $VS_{Destroyed}$) was calculated according to Eq. 5-1, where VS_{in} and VS_{out} are the percent volatiles in solid state before and after digestion, whereas W_{in} and W_{out} are the corresponding mass values.

$$\%VS_{Reduction} = \left((VS_{in} * M_{in} - VS_{out} * M_{out})\ x\ 100\%\right) / VS_{in} * M_{in} \quad \text{(Eq. 5-1)}$$

Kinetic Models

The kinetic parameters under the various AWAO conditions were determined for the Modified Gompertz, and Chen and Hashimoto models using the Solver tool in Excel. The equations (Eq. 3-2, and Eq. 3-3) and parameters for the models are described in the corresponding subsection of section 3.3.

Characterization of Residues

For the analysis of the aqueous and solid AWAO residues before and after the anaerobic digestion, the slurries were centrifuged at 3000 g for 20 min. The pellets were dried at 45 °C before analysis.

Thermogravimetric Analysis

The proximate analysis and thermal degradability assessment were carried out according to their corresponding subsections within section 2.3 using a TGA-Q500 (TA Instruments, New Castle, DE, USA).

Lignocellulose Composition

The carbohydrates and acid insoluble lignin were determined following ASTM E 1758-01 and ASTM E 1721. The main monosaccharides found in water hyacinth (i.e. glucose, xylose, and arabinose) were measured using a LC-20AD UFLC equipped with a RID-20A (Shimadzu Corp., Kyoto, Japan). The samples were injected at 0.60 mL/min using deionized water as mobile phase and were passed through a BP-800Pb column

(Benson Polymeric, Reno, NV, USA) at 80°C for separation. More details are shown in the subsection 'Summative Analysis' within section 2.3.

Energy Analysis

The feasibility of the pretreated biomass was assessed through the estimation of the net energy produced for the different experimental conditions. The energy [MJ] produced (Ep) from the biomethanation of water hyacinth and the energy required for heating (Q) during the pretreatment were calculated using Eq. 2-7, and Eq. 5-2, respectively. The overall heat capacity (Cp) of the slurry was calculated using Eq. 5-3. The energy analysis assumed the processing of 1 ton of fresh water hyacinth. The water content and heat capacity of the fresh feedstock (plant leaves) were assumed to be 91% and 1.75 kJ/kg °C (Akendo et al. 2008; Jayalakshmy and Philip 2010). The ambient temperature was assumed to be 20°C and the heat lost to be negligible during the pretreatment. Since the optimal retention time for mesophilic anaerobic digesters is 15-30 days (Mir et al. 2016), BMP [L_{CH4}/kg] was assumed to be the methane yield at 31 days of digestion. The higher heating value (HHV) of methane is 0.0398 MJ/L.

$$Q = m \cdot c_p \cdot \Delta T \qquad \text{(Eq. 5-2)}$$

$$C_p = (m_{Feed}/m)C_{p\,Feed} + (m_{Water}/m)\,C_{p\,Water} \qquad \text{(Eq. 5-3)}$$

Statistical Analysis

The data collected from the factorial datasets was analyzed using the function 'aov' in R Studio (version 3.6.1). The differences between levels were determined using Tukey's test (Tukey HSD), a post-hoc analysis function in R. For single comparison between values, *t* test (www.graphpad.com) was used. The populations were assumed to be independent, normal distributed, and with equal variances.

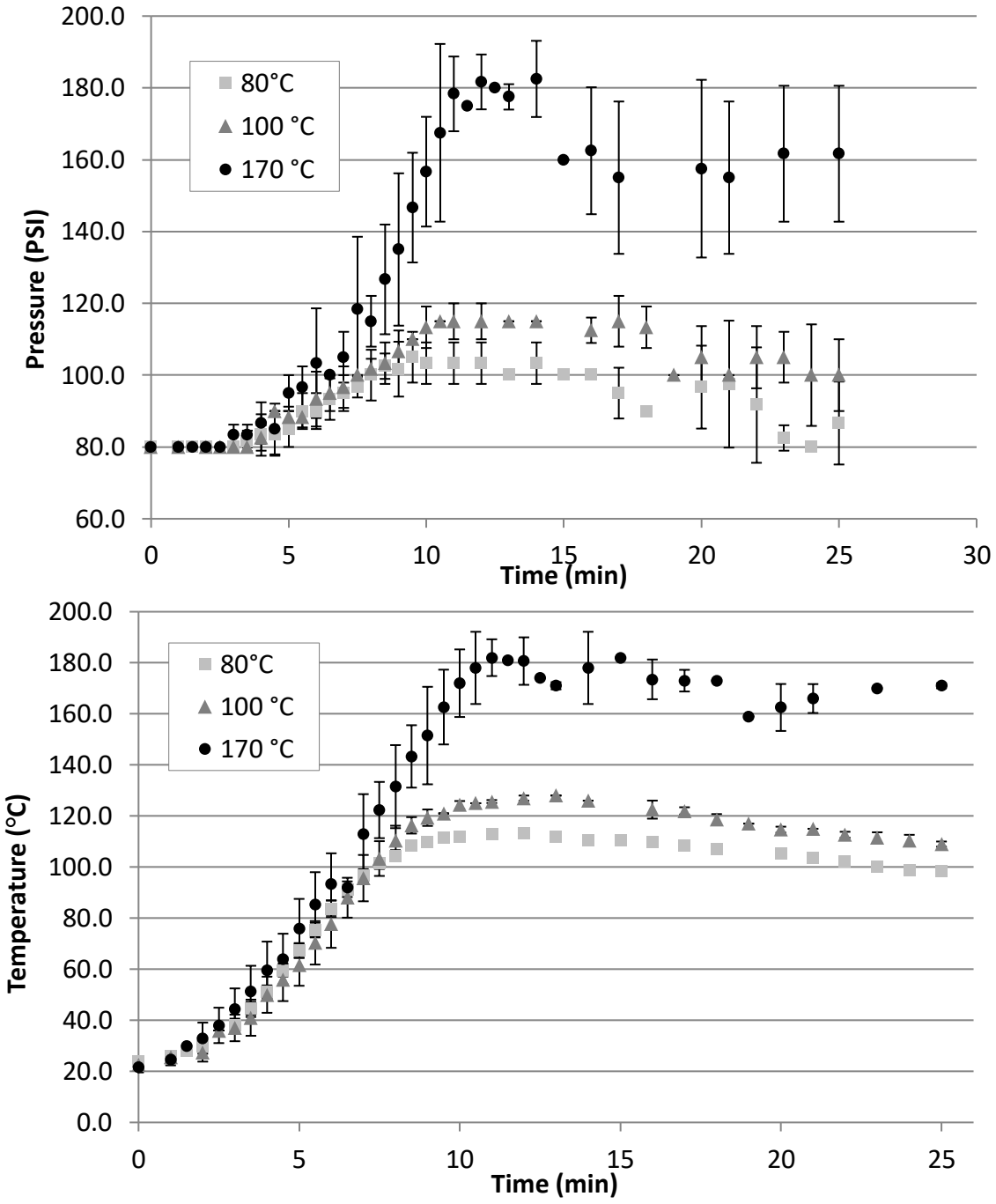

Figure 5-1 Operative curves of temperature and pressure during the Alkaline Wet Air Oxidation (AWAO) of water hyacinth.

5.4 Results and Discussion

Biochar Composition

Poultry litter biochar had a BET specific surface area of 6.0 ± 0.8 m^2/g. The volatile, fixed carbon, and ash contents of the biochar were 21.6 ± 0.2 % w/w, 40.1 ± 0.5 % w/w, and 38.4 ± 0.7 % w/w, respectively. The organic elemental composition [% w/w] of biochar was 38.9 ± 0.08 C, 2.07 ± 0.02 H, 4.8 ± 0.08 N, 15.9 ± 0.7 O, and <0.01 S. Nitrogen in biochar was almost twice ($p = 0.0001$) that in water hyacinth (1.8 ± 0.2 % w/w), based on previous results (Castro and Agblevor 2020a). The macronutrients [% w/w] in the biochar's ash were 6.4 ± 4.5 Ca, 1.4 ± 0.3 K, 1.3 ± 0.1 P, 0.6 ± 0.04 Mg, and 0.3 ± 0.04 S; the main minerals [mg/ kg] were 2839 ± 469.5 Na, 850.5 ± 183 Fe, 598 ± 12.0 Si, 303 ± 0.7 Al, 134 ± 48.1 Sr, 8.6 ± 0.4 Ba, and, 23.0 ± 3.8 B; and the heavy metals present were [mg/ kg] 246.5 ± 17.7 Mn, 35.2 ± 1.8 Cu, 26 ± 2.1 Zn, 16.4 ± 0.1 Cr, 4.60 ± 0.12 Ni, and 2.2 ± 0.3 Mo. The elements below the detection limit (<0.05 mg/kg) in the biochar's ash were As, Cd, Co, Pb, and Se.

AWAO Operational Conditions

The AWAO reactions appeared to be exothermic because temperature always rose above the set point for all experiments; thus, maximum temperature reached during the AWAO of water hyacinth at 80 °C was112.7 ± 1.2 °C which was lower (p <0.0001) than at 100 °C (126.8 ± 2.1 °C) and 170 °C (185.3 ± 5.4 °C). However, the maximum pressure at 170 °C (185.3 ± 5.4 °C) was much higher than at 80 °C (0.7 ± 0.04 MPa) and 100 °C (0.8 ± 0.05 MPa, which were no different ($p = 0.09$). The temperature and pressure profiles during the AWAO of water hyacinth showed less variation at 80°C and 100°C compared to 170°C (Fig. 5-1). The operating conditions of AWAO at 80°C and 100°C, and 0.07 g Na_2CO_3/g feed were more suitable for large-scale than at 170°C due to

the pressure stability, safety, lower chemical consumption and minimum energy requirements.

Biomethanation Kinetics

The Analysis of Variance (ANOVA) showed that the AWAO temperature significantly affects the methane yield ($p < 0.0156$) and methane production rate ($p < 0.004$) during the anaerobic digestion of water hyacinth (Appendix C). After 21 days, the water hyacinth pretreated with 0.07 g Na_2CO_3/ g at 80°C had produced 30% higher methane yield ($p = 0.003$, Table 5-1) than the unpretreated biomass which was almost twice ($p = 0.0004$) the rate of the later. After 55 days of digestion, the methane yield [N. mL CH_4 /g feed] for the biomass pretreated using AWAO at 80°C with 0.07 g Na_2CO_3/ g feed was(150.9 ± 6.1 which was higher ($p <0.005$, Table 5-1) than at 100°C and 170°C using 0.14 g Na_2CO_3/ g feed but not statistically different from the untreated biomass. This could be due to the generation of inhibitory byproducts at higher temperatures. Therefore, pretreating the feed at lower temperature and alkali would increase the digestion rate because of the higher availability of sugars from the biomass.

Effect of Biochar on the Biomethanation of AWAO Water Hyacinth

Even though the effect of the AWAO alkali concentration and the biochar addition on the biomethanation of water hyacinth was negligible ($p > 0.350$) on the ANOVA (Appendix C), the impact of biochar on the methane yield seemed to be constrained by the AWAO alkali concentration during the first 21 days of digestion (Fig. 5-2). At lower concentrations of alkali (0.07 g Na_2CO_3/ g feed), there was a positive correlation between the concentration of biochar and the methane yield, which suggests that biochar could act as an alkali agent in our system.

Table 5-1 Methane yield [N. mL CH_4 /g $_{feed}$] and kinetics after digesting unpretreated and Alkaline Wet Air Oxidized (AWAO) water hyacinth under different pretreatment temperature and alkali concentration.

		21 days of digestion		55 days of digestion	
T [°C]	Alkali [g Na_2CO_3/ g feed]	CH_4 Yield [N. mL CH_4/g feed]	K_z [N. mL CH_4/ g feed *day]	CH_4 Yield [N. mL CH_4/g feed]	K_z [N. mL CH_4/ g feed *day]
Un-pretreated		75.9 ± 8.8 A	5.4 ± 0.1 A C	124.9 ± 15.4 A B	3.8 ± 0.5 A
80	0.07	109.4 ± 1.8 B	10.0 ± 0.7 B	150.9 ± 6.1 A	6.4 ± 0.03 B
	0.14	105.8 ± 9.8 B	7.7 ± 1.7 A B D	147.0 ± 12.5 A B	6.1 ± 0.8 B
100	0.07	113.8 ± 0.9 B	8.6 ± 2.3 A B	141.2 ± 19.8 A B	5.5 ± 2.3 A B C
	0.14	39.5 ± 10.1 C	4.6 ± 0.6 C	128.3 ± 3.7 B	2.7 ± 0.3 C
170	0.14	47.4 ± 16.1 A C	3.6 ± 2.0 C D	124.4 ± 8.9 B	3.2 ± 0.9 A C

A is the methane potential, K_z is the methane production rate, and T_{lag} is the lag time, according to the modified Gompertz model. The same letters within each column mean no statistical difference for the *t*-test (α= 0.05).

The impact of biochar on the biomethanation kinetics of the AWAO water hyacinth depends not only on the alkali concentration but also on the pretreatment temperature. After 21 days of digestion, the effect of biochar on the methane yield at 80°C was negligible ($p > 0.65$, Table 5-2) at low and high alkali concentration. After 31 days of digestion the addition of biochar (0.05-0.10 g/ g feed) to the system increased ($p = 0.0057$) the yield [N. mL CH_4 /g feed] from 55.1 ± 8.3 to 133.9 ± 1.5 at 100°C and low alkali concentration but had not impact ($p = 0.827$) on the yield (57.2 ± 8.6) of the biomass pretreated at 100°C and high alkali concentrations. On the other hand, the biomethanation of water hyacinth pretreated at 170°C failed at low alkali concentration. The addition of biochar at concentrations above 0.05 g/ g feed improved the yield to an amount comparable to those obtained at higher alkali concentration under the same temperature (Table 5-2). The highest methane yield after 31 days of digestion was obtained when water hyacinth was subjected to AWAO at 80°C, at a 100°C and 0.07 g Na_2CO_3/g feed when at least 5% of biochar was used, at 170°C and 0.07 g Na_2CO_3/g feed when 10% of biochar was added, and at 170°C and 0.14 g Na_2CO_3/g without biochar. These results suggest that biochar could have neutralized bioproducts (e.g. carboxylic acids) produced at temperatures above 80°C that would require alkali concentration above 0.07 g Na_2CO_3/ g feed. Further studies focused solely on the effect and mechanisms of actions of biochar on the anaerobic digestion of AWAO water hyacinth should be conducted.

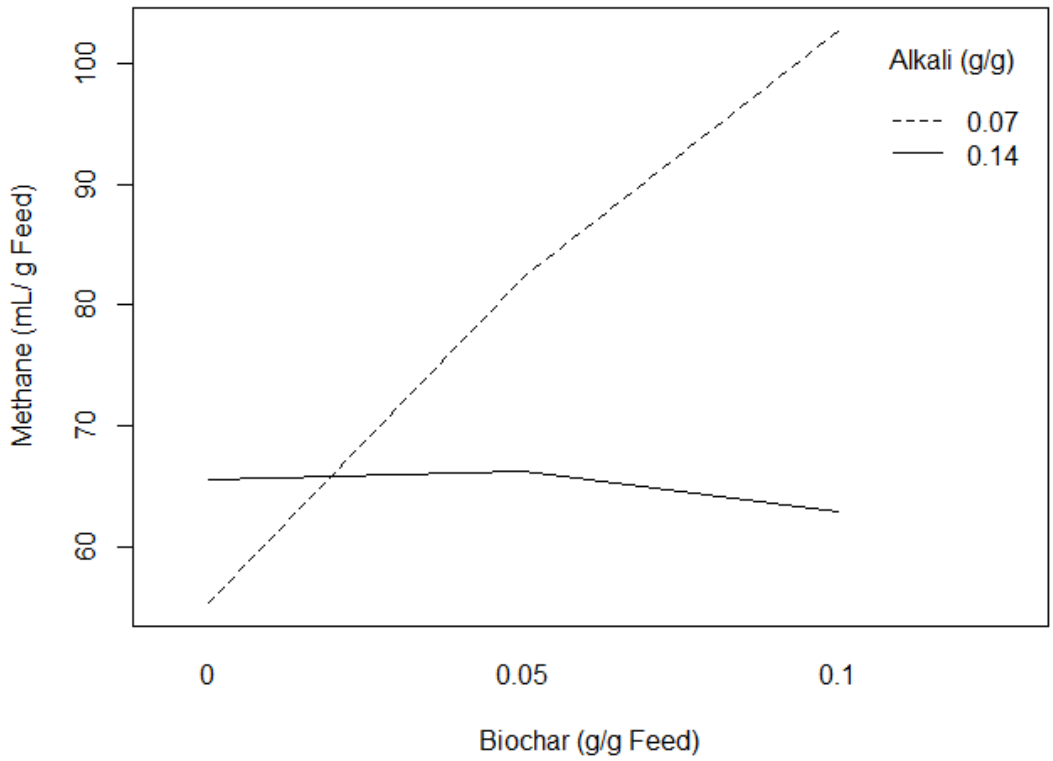

Figure 5-2 Interaction plot between alkali concentration [g Na2CO3/ g feed] and biochar [g / g feed] on the biomethanation of water hyacinth. Plot generated using R Studio.

Table 5-2 Methane yield [N. mL CH_4 /g feed] and kinetics after digesting unpretreated and Alkaline Wet Air Oxidized (AWAO) water hyacinth under different temperature, biochar and alkali concentrations.

T [°C]	Biochar [g / g feed]	Alkali [g Na_2CO_3/ g feed]	Yield [N. mL CH_4 /g feed]	
			21-day	31-day
80	0.00	0.07-0.14	104.9 ± 9.3 AB	129.6 ± 8.7 AB
	0.05 - 0.10	0.07	108.3 ± 0.3 A	126.6 ± 0.5 A
		0.14	109.5 ± 10.4 AB	136.0 ± 13.2 AB
100	0.00	0.07-0.14	28.5 ± 5.5 C	55.1 ± 8.3 CD
	0.05 - 0.10	0.07	113.8 ± 0.9 B	133.9 ± 1.5 B
		0.14	45.9 ± 1.1 DE	57.2 ± 8.6 CD
170	0.00 - 0.05	0.07	27.2 ± 4.0 C	30.0 ± 3.2 D
	0.10		76.2 ± 14.5 D	104.2 ± 13.2 ABC
	0.00	0.14		
	0.05-0.10		38.2 ± 2.3 CE	64.8 ± 7.9 C

The same letters within each column mean no statistical difference for the *t*-test (α= 0.05).

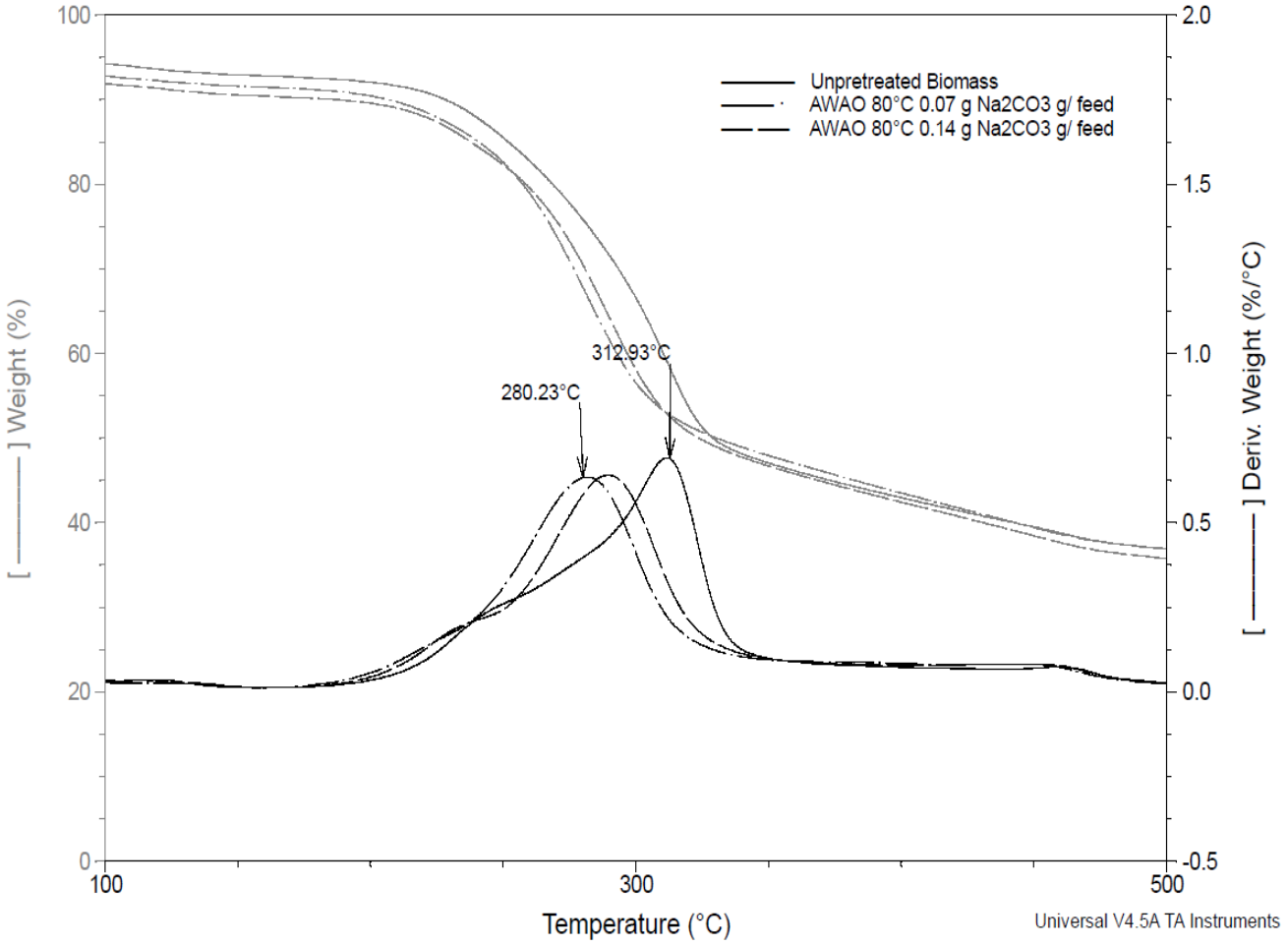

Fig. 5-3 Curves of the differential thermogravimetric analysis of unpretreated and pretreated water hyacinth (AWAO at 80°C with 0.07 g and 0.14 g of Na_2CO_3 per g of biomass).

Effect of AWAO on Water Hyacinth

The characteristics of the AWAO solid residues before and after anaerobic digestion validate the effectiveness of the process conditions on the biomass structure. The maximum degradation temperature of the water hyacinth (316.9 ± 3.2 °C) was higher ($p < 0.04$, Fig. 5-3) than that of the biomass after AWAO at 80°C when using 0.07 g (284.0 ± 9.3 °C) and 0.14 g (286.5 ± 8.1° C) of Na_2CO_3 per g feed. Adding larger amounts of alkali did not decrease the maximum degradation temperature significantly ($p = 0.801$). The structural change due to AWAO at 80°C is comparable with that observed in Chapter 4, when the biomass was pretreated at 170 °C and 0.14 g Na_2CO_3/ g feed (Castro and Agblevor 2020c). Thus, the improvement in the biomass thermal degradation attained after AWAO was not compromised by reducing the temperature and alkali concentration from 170° C to 80° C and from 0.14 to 0.07 g Na_2CO_3/ g feed.

The water hyacinth after been subjected to AWAO at lower alkali and temperature had higher ($p = 0.03$, Table 5-3) volatiles and lower ($p = 0.005$) ash than the unpretreated biomass'. The reduction in ash content was expected since almost 50% of the ash in this biomass was reported to be extractable (Castro and Agblevor 2020a). The ash can be easily removed by the carboxylic acids produced during the pretreatment. Similarly, the lignin content in the pretreated biomass was lower ($p = 0.015$) than in the unpretreated water hyacinth. In contrast, the holocellulose (% w/w) in raw water hyacinth (43.5 ± 4.4) was not different ($p = 0.727$) than after AWAO (44.8 ± 1.6). For both, raw and pretreated water hyacinth, the cellulose was 26.4 ± 3.5 % w/w, and the hemicellulose was 17.7 ± 3.8 % w/w in average. The structure of the water hyacinth was affected by the

AWAO under lower alkali concentration and temperature, making the material more easily digestible by increasing the volatiles and reducing the lignin content.

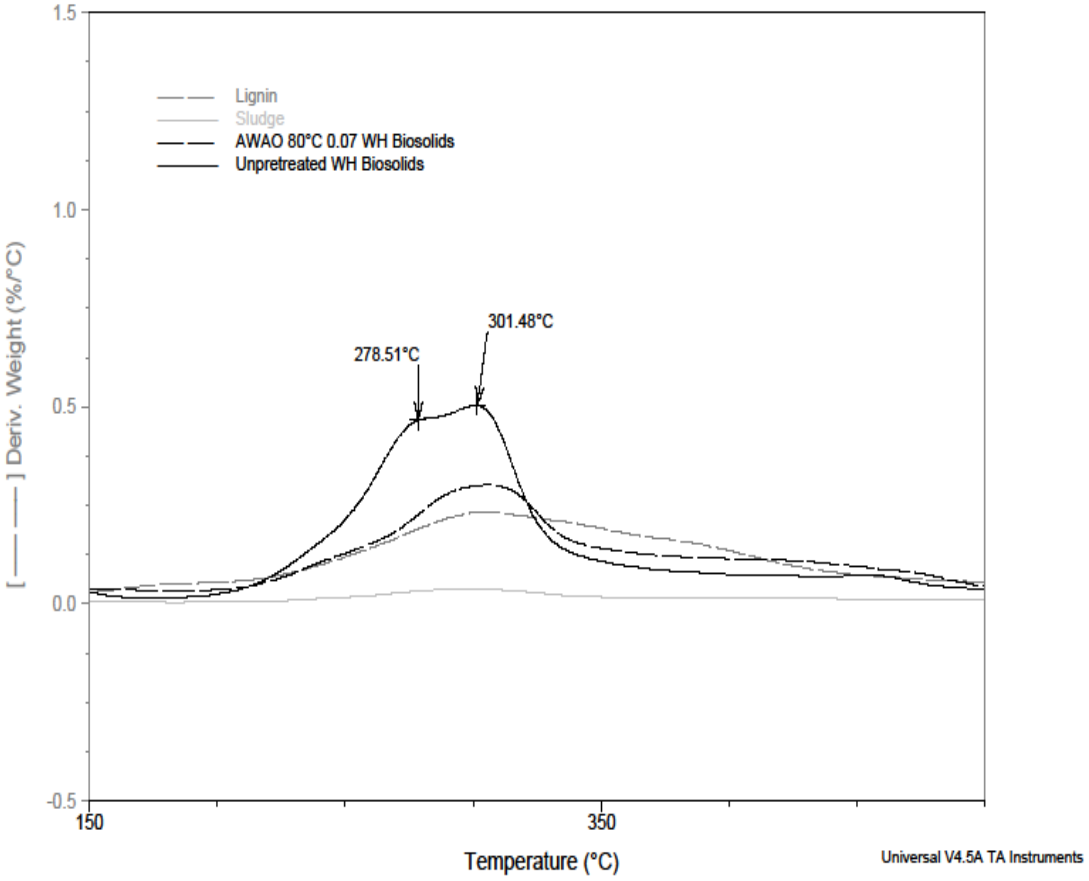

Fig 5-4 Curves of the differential thermogravimetric analysis of the biosolids from the unpretreated and pretreated biomass (AWAO at 80°C with 0.07 g Na_2CO_3 /g).

Table 5-3. Proximate analysis and structural composition of water hyacinth before (biomass) and after (biosolids) anaerobic digestion under raw and pretreated (AWAO 0.07 g Na_2CO_3 / g feed) conditions.

		Proximate Analysis (% w/w)				Structural Composition (% w/w)		
		Biomass (g)	Volatiles	Fixed Carbon	Ash	Cellulose	Hemi-cellulose	Lignin
Before Anaerobic Digestion (Biomass)	Raw	3.6 ± 0.03^{A}	59.9 ± 0.7^{A}	19.9 ± 0.2^{A}	20.3 ± 0.6^{A}	26.2 ± 2.0^{A}	17.3 ± 2.4^{A}	17.7 ± 0.2^{A}
	Pretreated	2.8 ± 0.6^{AB}	64.2 ± 1.9^{B}	21.7 ± 0.7^{B}	14.2 ± 1.3^{B}	26.7 ± 1.0^{A}	18.1 ± 0.6^{A}	14.7 ± 1.1^{B}
After Anaerobic Digestion (Biosolids)	Raw	2.0 ± 0.04^{BC}	55.4 ± 5.4^{AC}	23.9 ± 0.1^{C}	20.7 ± 5.3^{A}	11.0 ± 3.2^{B}	10.8 ± 2.4^{B}	38.3 ± 5.6^{C}
	Pretreated	1.2 ± 0.4^{C}	48.1 ± 1.8^{C}	23.6 ± 1.2^{C}	28.3 ± 1.1^{C}	4.2 ± 1.1^{B}	6.4 ± 2.6^{B}	44.0 ± 0.7^{C}

The same letters within each column mean no statistical difference for the unpaired *t*-test ($\alpha = 0.05$).

Matter Reduction in the Biomethanation of Water Hyacinth

After 55 days of digestion, the percentage of digested solids from the pretreated water hyacinth (66.7 %) was higher than that from the raw biomass (44.4 %). Also, the VS in the pretreated water hyacinth was reduced ($p = 0.13$) from almost 65% to less than 50%, but there was no reduction ($p = 0.363$) in the VS of raw water hyacinth. Similarly, 42.8 ± 10.4 % VS and 71.3 ± 9.8 % VS were destroyed during the anaerobic digestion of raw and pretreated water hyacinth, respectively. These results suggest an enhancement in digestibility of water hyacinth when pretreated at lower temperature and alkali concentration compared to raw biomass.

The structural composition of the biosolids that were recovered from the anaerobic digestion of water hyacinth differed from that of the undigested biomass. As expected, the cellulose content in the biosolids was less than half ($p < 0.03$) that from the raw and pretreated water hyacinth. The hemicellulose content was reduced ($p = 0.025$) in the biosolids from pretreated water hyacinth but not significantly ($p = 0.114$) in the raw biomass. This could be explained by the effect of AWAO on hemicellulose, which is solubilized due to the oxidative stress that takes place in the pressurized vessel. The thermal degradation profile for the AD residues shows that the structure of the biosolids from the unpretreated water hyacinth is more complex than that from the pretreated biomass since the former seems to have two merged peaks with a small shoulder, and the later only one broad peak (Fig. 5-4). Based on these results, the biosolids from the unpretreated hyacinth seems to contain lignin and residual holocellulose. The biosolids from the pretreated biomass have a TGA profile similar to that of amorphous lignin (Fig. 5-4). Pretreating water hyacinth before biomethanation would reduce the biosolids

generation in the system. Only 60%, 43% and 34% of biosolids is recycled in United States, Canada, and Europe, respectively (Apedaile 2001). Unless the characteristics of the biosolids are adequate for soil applications, this material is either incinerated or taken to the landfill.

Biosolids Elemental Composition

After digesting water hyacinth anaerobically, the inorganic composition of the biomass changed. The concentration of some macronutrients (i.e. Ca, P, and S, Table 5-4) was higher in the biosolids than in the unpretreated water hyacinth. This suggests that the concentration of these minerals in water hyacinth was higher than the amount needed for the metabolic function of the consortia during anaerobic digestion. However, inorganic ions including carbonate, ammonium, phosphate, and sulfide are produced via mineralization of the organic compounds in the majority of the anaerobic digestion processes (Fermoso et al. 2019). The content of other macronutrients was either reduced (K) or unchanged (Mg) after the bioconversion process. Mg is important during the AD to stimulate methane production, but if present in concentrations above 40 mg Mg+/ L, the effect is negligible, or inhibition occurs (Romero-Güiza et al. 2016). The recommended concentrations of Mg and K in the feedstock for anaerobic digestion are Mg 47.3mg/g COD, and 720.2 mg K /g COD (Chen and Cheng 2007). The steady concentration of Mg and K in the water hyacinth biosolids compared to the raw biomass indicates that the elements participated in the metabolic pathways at the right concentration.

Table 5-4 Inorganic elements in the biosolids from raw and AWAO (0.07 g Na_2CO_3 / g feed at 80°C) water hyacinth from Ozama river. The values are on a dry ash basis.

		Water Hyacinth	Biosolids	
			Raw	Pretreated
Macronutrients (% w/w)	Ca	11.3 ± 0.6[a]	19.8 ± 2.8[b]	18.1 ± 1.1[b]
	K	17.9 ± 2.0[a]	10.1 ± 1.2 [b]	6.0 ± 1.5 [b]
	Mg	1.3 ± 0.1[a]	1.5 ± 0.04 [a]	1.4 ± 0.01 [a]
	P	0.9 ± 0.06[a]	4.3 ± 1.0 [b]	3.4 ± 0.2 [b]
	S	0.3 ± 0.09[a]	1.4 ± 0.1[b]	1.1 ± 0.1[b]
Micronutrients (% w/w)	Fe	1.2 ± 0.04[a]	3.0 ± 0.03 [b]	2.6 ± 0.3 [b]
	Mn	0.3 ± 0.01[a]	0.5 ± 0.03 [b]	0.5 ± 0.03 [b]
	Al	1.7 ± 0.06[a]	3.7 ± 0.4 [b]	3.5 ± 0.4 [b]
	Na	0.6 ± 0.2[a]	1.1 ± 0.2 [a]	2.9 ± 0.5 [b]
	Si	1.3 ± 0.3[a]	4.6 ± 0.08 [b]	4.1 ± 0.2 [b]
Trace Minerals (mg/Kg)	Cu	54.3 ± 5.2[a]	487.7 ± 33.4 [b]	428.8 ± 16.8 [b]
	Ni	37.8 ± 19.1[a]	320.7 ± 21.5 [b]	657.1 ± 14.4 [c]
	Mo	5.5 ± 3.0[a]	22.6 ± 1.2 [b]	28.1 ± 1.8 [b]
	Co	7.6 ± 0.1[a]	19.1 ± 0.2 [b]	23.4 ± 0.0 [c]
	Zn	114.3 ± 7.5[a]	911.4 ± 198 [b]	848.2 ± 117 [b]
	As	1.9 ± 0.03[a]	7.2 ± 5.1 [a b]	7.9 ± 1.6 [b]
	Cd	0.4 ± 0.1[a]	1.9 ± 0.2 [b]	1.3 ± 0.2 [b]
	Cr	26.1 ± 0.1[a]	89.9 ± 14.6 [b]	143.0 ± 14.9 [b]
	Pb	1.9 ± 1.0 [a]	37.2 ± 2.0 [b]	26.5 ± 6.4 [b]

[a, b, c] Different letters within each row indicate a significant difference between sites for *t* test (alpha =0.05), using the observed values of biosolids as hypothetical values.

The micronutrients (i.e. Fe, Mn, Al, Si) in water hyacinth were higher than the biosolids derived from the raw and pretreated biomass (Table 5-4). There was no significant difference in the macro and micronutrients present in the raw and pretreated water hyacinth biosolids. However, the Na content in the biosolids from pretreated water hyacinth was higher than in the unpretreated biomass and in the raw biosolids. This is explained by the addition of sodium carbonate (alkali) during the AWAO pretreatment. Similarly, the concentration of trace minerals in the biosolids was much higher than in the undigested water hyacinth (Table 5-4), which indicates that these metals were not used significantly during the conversion process or mineralization took placed. The amount of Cu, Mo, Zn, As, Cd, Cr, and Pb in the biosolids derived from raw water hyacinth was comparable to that derived from pretreated biomass. Biosolids have been used to fertilize different types of micronutrient-deficient soils, including alkaline soils, dryland, and sandy soil (Moral et al. 2002; Barbarick and Ippolito 2007; Ozores-Hampton et al. 2011) The biosolids of the water hyacinth from the Ozama river are rich in micronutrients and have higher K than P, which differs from the composition of common biosolids where P is higher than K (Badzmierowski and Evanylo). Further studies need to be conducted exploring the effect of the biosolids derived from the unpretreated and pretreated water hyacinth from Ozama river.

Energy Analysis

The energy expenditure during the pretreatment of cellulosic feedstock has been considered for the feasibility of various thermal and chemical pretreatments for bioconversion processes (Castro et al. 2015; Cheng et al. 2019a, b). After 31 days of digestion, the energy produced from the pretreated water hyacinth (464.6 ± 19.0 MJ/ ton)

was higher (p = 0.0095) than that from raw biomass (339.6 ± 42.3 MJ/ton). However, the energy consumed during the AWAO at 80°C was 105.0 MJ per ton of fresh biomass (Appendix D). The net energy from the pretreated biomass was 359.6 ± 19.0 MJ/ ton, which is not different (p = 0.499) than that from raw biomass. In order to take advantage of the higher biomethanation generated after the AWAO, renewable energy generation methods for the pretreatment process should be considered (e.g. solar panels).

5.5 Conclusion

In this chapter, the optimal conditions on the AWAO of water hyacinth regarding reaction temperature and alkali concentration, and the effect of biochar were determined through kinetic studies. The pressure and temperature profiles for the AWAO showed that the operational conditions for the pretreatment conducted at lower temperatures (80 - 100 °C) would be more stable and safer to operate at large scale than that at 170 °C. Similarly, the digestion speed [N. mL CH4/ g feed *day] for the biomass pretreated at lower temperatures and alkali dosage (80 °C , 0.07 g Na_2CO_3/ g) was higher (10.0 ± 0.7) than the biomass pretreated at high temperature and alkali concentration (3.6 ± 2.0) and the unpretreated biomass (5.4 ± 0.1) after 21 days of digestion. The addition of biochar helped to improve the biomethanation of the water hyacinth pretreated at higher temperatures and low alkaline concentration, suggesting an alkalinity effect in the system. The energy produced from the pretreated water hyacinth was higher than that from the raw biomass. However, the energy required for pretreatment makes the net energy negligible. Renewable energy generation such as solar panels need to be integrated in the system for the AWAO to improve the feasibility of the process.

CHAPTER VI

SUMMARY AND CONCLUSION

The purpose of this dissertation was to study the biomethanation of water hyacinth (*Pontederia crassipes* Mart.) from the eutrophic Ozama River (Santo Domingo, Dominican Republic), as a post weed management practice to mitigate the environmental management costs related to weed control and to contribute to the transition from fossil fuel based to biobased economy in developing countries located in tropical and subtropical areas that are affected by this invasive weed.

6.1 Variation in Biomass Composition and Biomethane Potential in Ozama River

The composition and biomethanation of water hyacinth from two sites (brackish vs freshwater) within Ozama River were compared. The brackish water (La Cienaga, Santo Domingo) had the highest nutrient content (P and N) and the freshwater (El Naranjo, Santo Domingo) had the higher concentration of metals. The productivity of the brackish water, indicated by the biomass chlorophyll *b* content and the bulk density, was 30% higher than that from freshwater. The water hyacinth from brackish water had higher non-structural components (26.4 ± 0.1% extractives, and 18.8 ± 1.9% proteins) than the freshwater. In contrast, higher structural components (41.2 ± 2.8 % holocellulose) were found in the water hyacinth from freshwater. The biochemical methane potential of water hyacinth from both sites was not statistically different (399.2 ± 32.2 N. mL CH_4 /g VS_{added}). However, the biomethanation of water hyacinth from brackish waters occurred faster (22.5 N. mL CH_4 /g VS_{added}· day) than that from freshwater (10.0 N. mL CH_4 /g VS_{added}· day) because high content of lignocellulose is tied to longer hydrolysis times.

5.6 Energy Produced from Mechanically Harvested Water Hyacinth

After 60 days of digestion, the biochemical methane potential of water hyacinth from Ozama river using modified Gompertz model was estimated to generate 846.5 MJ of energy per ton of fresh biomass. Based on previous studies on the mechanical harvesting of water hyacinth, only 57.9 MJ was estimated to be needed to harvest a ton of water hyacinth from Ozama river. These results suggest that the biomethanation of water hyacinth could help to mitigate weed management costs by using the generated methane for transportation. Other costs for this suggestion need to be considered to maintain the process feasibility such as size reduction and labor. In addition, cleaning the biogas before usage is an important factor to consider if the goal is to use in harvesting machines or as an incentive for those living in the surroundings and willing to collaborate with manual harvesting. This approach would reduce the costs associated to mechanical harvesting, including the initial investment in acquiring the harvesting equipment.

5.7 Optimization of Water Hyacinth's Anaerobic Digestion

Some of the critical process parameters of the anaerobic digestion are the feed to inoculum ratio (F/I), digestion temperature, media supplementation, and inoculum acclimatization. These parameters were evaluated using kinetics and energy analysis as indicators of the biomethanation performance when using the water hyacinth from Ozama river (El Naranjo) as a feedstock. The biomethanation of water hyacinth was not improved by the addition of vitamins and minerals. The water hyacinth from El Naranjo proved to have the nutrients required for the anaerobic consortia to thrive . The non-acclimatized consortia followed the modified Gompertz model, but the acclimatized followed the Chen and Hashimoto model, which does not consider lag or adaptation

phase during the bioconversion process. A pseudo lag phase was observed during the biomethanation of water hyacinth at low mesophilic temperature (30°C) and high F/I (30). This phenomenon was not present at higher temperature (40°C). As expected, the higher the temperature, the faster the methane production. The average methane production rate [N.mL·CH_4/g·VS·day] during the biomethanation of water hyacinth at 40°C was 9.0 ± 0.8, and at 30°C was 7.9 ± 0.8 for F/I below 30 but only 3.2 ± 0.2 for F/I equal to 30. Similarly, the methane yield [N.mL·CH_4/g·VS] was the highest (416.8 ± 6.2) at F/I = 1.0 and decreased at higher F/I down to 263.8 ± 26.9 (F/I= 30). However, the biomethanation conducted at 30°C and F/I = 30 was estimated to require the lowest heating energy and resulted in the most efficient setting for batch systems.

5.8 Alkaline Wet Air Oxidation of Water Hyacinth

Since water hyacinth is a lignocellulosic material, the improvement of the methane production by alkaline and non-alkaline oxidative aqueous pretreatments was evaluated. The effects of Wet Air Oxidation (WAO) and Alkaline WAO (AWAO) under low pressure conditions on the structure and biomethanation kinetics of water hyacinth feedstock were determined. The biomass was pretreated using WAO and AWAO (0.15 g Na_2CO_3/ g feed), at 170°C under 0.4 MPa air for 30 min. The AWAO biomass showed higher lignin and extractives removal and cellulose deconstruction compared to WAO and unpretreated biomass. The methane production rate during the anaerobic digestion of water hyacinth was increased in 63% after WAO and in 117% after AWAO. Similarly, AWAO increased the methane potential [N. mL CH_4/g feed] of water hyacinth from 153.7 ± 1.9 to 191 ± 4.1. The biomethanation of water hyacinth after AWAO was better than after WAO and under unpretreated conditions.

5.9 Optimization of Alkaline Wet Air Oxidation for the Biomethanation of Water Hyacinth

The preferred pretreatment of water hyacinth for the biomethanation would be at lower temperature and alkali concentration. After 21 days of digestion, the water hyacinth pretreated with 0.07 g Na_2CO_3/ g at 80°C had produced 30% higher methane yield than the unpretreated biomass at almost twice the rate of the later. Furthermore, the thermogravimetric analysis showed that the hemicellulose was dissolved, and the cellulose crystallinity was reduced under these conditions.

5.10 Effect of Biochar on the Biomethanation of Wet Air Oxidized

The addition of poultry litter biochar on the alkaline wet air oxidized water hyacinth did not improve significantly the methane yield or rate after 30 days. During the first 21 days of digestion, a positive correlation between the methane yield and the concentration of biochar was observed after pretreating the biomass with AWAO at 0.07 g Na_2CO_3/ g feed. This result suggests that the poultry litter biochar could act as an alkali during the biomethanation of AWAO water hyacinth. Similarly, the effect of biochar on the biomethanation of water hyacinth depends on the pretreatment temperature. After 31 days of digestion we observed that the higher the temperature, the higher the concentration of biochar needed to improve the process. This behavior seems to be due to the higher acid production at higher temperatures and the need for higher amounts of alkali or biochar to improve the system and avoid fouling.

5.11 Characteristics of the Bio solids from Water Hyacinth

The pretreated water hyacinth produced less biosolids (33.3 %w/w) than the raw biomass (55.6%). The biosolids from the raw and pretreated biomass had higher mineral

content than the undigested water hyacinth. The potassium in the system was found to be higher than the phosphorus, offering a competitive difference when compared to most biosolids. Deeper studies need to be conducted exploring the effect of the biosolids derived from the unpretreated and pretreated water hyacinth from Ozama river.

5.12 Future Prospects

The use of the harvested water hyacinth from Ozama river promises to be a feasible post weed management practice in the Dominican Republic or in any area with tropical conditions. The AWAO technology increases the methane yield of the system which translates to higher energy production that could be used as fuel for harvesting or as incentive for manual collection of water hyacinth by local residents. Also, pretreating AWAO would generate less solid residue which means longer periods between solid removal. However, the pretreatment of this weed would require extra energy that would eliminate the extra energy generated compared to the unpretreated biomass. Therefore, the integration of this technology and other renewable energy alternatives for heating and stirring could help to increase the profitability of the system. For instance, solar panels can be installed in countries located near the equator, like the Dominican Republic. Also, the co-digestion of water hyacinth with other wastes readily available near Ozama river affected areas could be considered in the near future to reduce the littering and produce energy from waste. The biomethanation of water hyacinth as a post weed management practice is an important step in the sustainability of environmental management practices.

REFERENCES

Abraham A, Mathew AK, Park H, et al (2020) Pretreatment strategies for enhanced biogas production from lignocellulosic biomass. Bioresour Technol 301:122725. https://doi.org/https://doi.org/10.1016/j.biortech.2019.122725

Abu-Salem F, L. HusseinY. Foda (1975) Effect of some variables on the extractability of proteins, urease activity, free alpha-amino groups and soluble carbohydrates from soybean meals. Qual Plant 24:247–256

Acquah GE, Via BK, Fasina OO, Eckhardt LG (2016) Rapid Quantitative Analysis of Forest Biomass Using Fourier Transform Infrared Spectroscopy and Partial Least Squares Regression. J Anal Methods Chem 1–10. https://doi.org/http://dx.doi.org/10.1155/2016/1839598

Agblevor F, Pereira J (2013) Progress in the summative analysis of biomass feedstocks for biofuel production. In: Wyman C (ed) Aqueous pretreatment of plant biomass for biological and chemical conversion to fuels and chemicals. pp 335–354

Ahn DJ, Se KK, Yun HS (2012) Optimization of pretreatment and saccharification for the production of bioethanol from water hyacinth by Saccharomyces cerevisiae. Bioprocess Biosyst Eng 35:35–41. https://doi.org/10.1007/s00449-011-0600-5

Ahn J-H, Do TH, Kim SD, Hwang S (2006) The effect of calcium on the anaerobic digestion treating swine wastewater. Biochem Eng J 30:33–38

Akachukwu D, Gbadegesin MA, Ojimelukwe PC, Atkinson CJ (2018) Biochar Remediation Improves the Leaf Mineral Composition of Telfairia occidentalis

Grown on Gas Flared Soil. Plants 7:1–10. https://doi.org/10.3390/plants7030057

Akendo ICO, Gumbe LO, Gitau AN (2008) Dewatering and Drying Characteristics of Water Hyacinth (Eichhornia Crassipes) Petiole . Part II . Drying Characteristics. Agric Eng Int CIGR Ejournal X:1–11

Akhtar N, Goyal D, Goyal A (2017) Characterization of microwave-alkali-acid pre-treated rice straw for optimization of ethanol production via simultaneous saccharification and fermentation (SSF). Energy Convers Manag 141:133–144. https://doi.org/https://doi.org/10.1016/j.enconman.2016.06.081

Alimi T, Akinyemiju A (1990) An Economic Analysis of Water Hyacinth Control Methods in Nigeria. J Aquat Plant Manag 28:105–107

Allen E, Wall DM, Herrmann C, Murphy JD (2016) A detailed assessment of resource of biomethane from first, second and third generation substrates. Renew Energy 87:656–665. https://doi.org/10.1016/j.renene.2015.10.060

Alvira P, Ballesteros M, Negro MJ, Toma E (2011) Pretreatment Technologies for Lignocellulose-to-Bioethanol Conversion. In: Biofuels: Alternative Feedstocks and Conversion Processes. pp 149–176

Angelidaki I, Alves M, Bolzonella D, et al (2009a) Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays. Water Sci Technol 59:927–934. https://doi.org/10.2166/wst.2009.040

Angelidaki I, Alves M, Bolzonella D, et al (2009b) Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays. Water Sci Technol. https://doi.org/10.2166/wst.2009.040

Angelidaki I, Sanders W (2004) Assessment of the anaerobic biodegradability of

macropollutants. 117–129

Angelidaki I, Treu L, Tsapekos P, et al (2018) Biogas upgrading and utilization: Current status and perspectives. Biotechnol Adv 36:452–466

Apedaile E (2001) A perspective on biosolids management. Can J Infect Dis 12:202–204. https://doi.org/10.1155/2001/801432

Azbar N, Ursillo P, Richard E. Speece (2001) EFFECT OF PROCESS CONFIGURATION AND SUBSTRATECOMPLEXITY ON THE PERFORMANCE OF ANAEROBIC PROCESSES. Water Res 35:817–829

Badzmierowski M, Evanylo G Nutrient Content, Value, and Management of Biosolids. Sch PLANT Environ Sci VIRGINIA TECH

Bagley DM, Brodkorb TS (1999) Modeling Microbial Kinetics in an Anaerobic Sequencing Batch Reactor: Model Development and Experimental Validation. Water Environ Res 71:1320–1332

Bals B, Teachworth L, Dale B (2007) Extraction of Proteins from Switchgrass Using Aqueous Ammonia within an Integrated Biorefinery. Appl Biochem Biotechnol 143:187–198. https://doi.org/10.1007/s12010-007-0045-0

Barakat A, Monlau F, Steyer J-P, Carrere H (2012) Effect of lignin-derived and furan compounds found in lignocellulosic hydrolysates on biomethane production. Bioresour Technol 104:90–99

Barbarick KA, Ippolito JA (2007) Nutrient Assessment of a Dryland Wheat Agroecosystem after 12 Years of Biosolids Applications. Agron J 99:715–722. https://doi.org/10.2134/agronj2006.0221

Barua VB, Kalamdhad AS (2017) Effect of various types of thermal pretreatment

techniques on the hydrolysis, compositional analysis and characterization of water hyacinth. Bioresour Technol 227:147–154. https://doi.org/10.1016/j.biortech.2016.12.036

Bennich T, Belyazid S (2018) Understanding the Transition to a Bio-Based Economy : Exploring Dynamics Linked to the Agricultural Sector in Sweden. Sustainability 10:1–22. https://doi.org/10.3390/su10051504

Bertrand RL (2019) Lag Phase Is a Dynamic , Organized , Adaptive , and Evolvable Period That Prepares Bacteria for Cell Division. J Bacteriol 201:1–21

Bhui I, Matthew AK, Chaudhury S, Balachandran S (2018) Influence of volatile fatty acids in different inoculum to substrate ratio and enhancement of biogas production using water hyacinth and salvinia. Bioresour Technol 270:409–415

Bhuvaneshwari M, Sangeetha K (2016) Investigation of Physical , Chemical and Structural Characterization of Eichhornia crassipes Fiber. 01:92–96

Biswas B, Singh R, Krishna BB, et al (2017) Pyrolysis of azolla, sargassum tenerrimum and water hyacinth for production of bio-oil. Bioresour Technol. https://doi.org/10.1016/j.biortech.2017.03.044

Braguglia CM, Mininni G, Tomei MC, Rolle E (2006) Effect of feed / inoculum ratio on anaerobic digestion of sonicated sludge. Water Sci Technol 54:77–84. https://doi.org/10.2166/wst.2006.549

Bryant CB (1969) Aquatic weed harvesting – effects and costs. Weeds Trees Turf October:14–17

Buller LS, Ortega E, Bergier I, et al (2015) Sustainability assessment of water hyacinth fast pyrolysis in the Upper Paraguay River basin, Brazil. Sci Total Environ 532:281–

291. https://doi.org/10.1016/j.scitotenv.2015.05.129

Capson-tojo G, Girard C, Rouez M, et al (2018) Addition of biochar and trace elements in the form of industrial FeCl 3 to stabilize anaerobic digestion of food waste : dosage optimization and long-term study. J Chem Technol Biotechnol 94:505–515. https://doi.org/10.1002/jctb.5797

Castro YA, Agblevor FA (2020a) Biomethanation of invasive water hyacinth from eutrophic waters as a post weed management practice in the Dominican Republic, a developing country. Environ Sci Pollut Res 27:14138–14149. https://doi.org/10.1007/s11356-020-07927-w

Castro YA, Agblevor FA (2020b) Interaction effect of high feed to inoculum ratio (F/I) and temperature on the biomethanation kinetics of water hyacinth. SN Appl Sci 2:1–9. https://doi.org/10.1007/s42452-020-03626-w

Castro YA, Agblevor FA (2020c) Effect of wet air oxidation on the composition and biomethanation of water hyacinth. Biomass Convers Biorefinery. https://doi.org/10.1007/s13399-020-00825-8

Chamier J, Schachtschneider K, le Maitre DC, et al (2012) Impacts of invasive alien plants on water quality, with particular emphasis on South Africa. Water SA 38:345–356. https://doi.org/10.4314/wsa.v38i2.19

Chandel AK, Garlapati VK, Jeevan Kumar SP, et al (2020) The role of renewable chemicals and biofuels in building a bioeconomy. Biofuels, Bioprod Biorefining n/a: https://doi.org/10.1002/bbb.2104

Chang VS, Nagwani M, Holtzapple MT (1998) Lime Pretreatment of Crop Residues Bagasse and Wheat Straw. Appl Biochem Biotechnol 74:135–159

Chantada A (1991) [Environment, crisis, and development: thoughts on the Ozama and Isabela rivers]. Estud Soc 24:5–36

Chen Y, Cheng JJ (2007) Effect of Potassium Inhibition on the Thermophilic Anaerobic Digestion of Swine Waste. Water Environ Res. https://doi.org/10.2175/106143007X156853

Chen Y, Cheng JJ, Creamer KS (2007) Inhibition of anaerobic digestion process: A review. Bioresour Tehnol 99:4044–4064

Cheng X, Zhong C (2014) Effects of Feed to Inoculum Ratio , Co-digestion , and Pretreatment on Biogas Production from Anaerobic Digestion of Cotton Stalk. Energy & Fuels 28:3157–3166

Cybulska I, Chaturvedi T, Alassali A, et al (2014) Characterization of the chemical composition of the halophyte salicornia bigelovii under cultivation. Energy and Fuels. https://doi.org/10.1021/ef500478b

Daddy F, Abubakar S, Owotunse S (2002) EFFECTS OF DIFFERENT SOURCES OF WATER ON WATER HYACINTH GROWTH PERFORMANCE. In: International Conference on Water Hyacinth. National Institute for Freshwater Fisheries Research, Nigeria, New Bussa, Nigeria, Nigeria, pp 130–140

Davies RM, Mohammed US (2011) Moisture-dependent Engineering Properties of Water Hyacinth Parts. Singapore J Sci Res 1:253–263

de Jong W, Van Ommen JR (2015) “Biomass, a sustainable energy source for the future – Fundamentals of conversion processes”

Deka D, Das SP, Ravindran R, et al (2018) Water Hyacinth as a Potential Source of Biofuel for Sustainable Development. In: Sarma A., Singh V., Bhattacharjya R. KS

(ed) Urban Ecology, Water Quality and Climate Change. Springer, pp 351–363

Demesa AG, Laari A, Sillanpaa M (2020) Value-added chemicals and materiales from lignocelulosic biomass: carboxylic acids and cellulose nanocrystals. In: Sillanpaa M (ed) Advanced Water Treatment: Advanced Oxidation Processes. Elsevier Science, pp 387–393

Den W, Sharma VK, Lee M, et al (2018) Lignocellulosic Biomass Transformations via Greener Oxidative Pretreatment Processes: Access to Energy and Value-Added Chemicals. Front Chem 6:141. https://doi.org/10.3389/fchem.2018.00141

Diallo O (2014) Effect of Poultry Litter Biochar on Saccharomyces cerevisiae Growth and Ethanol Production from Steam-exploded Poplar and Corn Stover. Utah State University

Dölle K, Tong J, Q. Wang (2020) Water Hyacinths–biomass Production Potential at a Waste Water Treatment Plant. Water Hyacinths–biomass Prod Potential a Waste Water Treat Plant 23:1–10. https://doi.org/https://doi.org/10.9734/jabb/2020/v23i230138

Duke JA (1983) Handbook of Energy Crops. Purdue University. Center for New Crops and Plant Products

Edelman DJ (2019) Managing the Urban Environment of Santo Domingo, the Dominican Republic. Curr Urban Stud 7:76–142. https://doi.org/10.4236/cus.2019.71005

Edwige S, Mahunon R, Aina MP, et al (2018) Optimization process of organic matter removal from wastewater by using Eichhornia crassipes. Environ Sci Pollut Res 25:29219–29226

El Amin HB, Dirar HA (1986) Biogas Production from Water Hyacinth [Eichhornia

Crassipes]: Influence of Temperature. In: El-Halwagi MM (ed) Biogas Technology, Transfer and Diffusion. Springer Netherlands, Dordrecht, pp 437–445

Etter H (1972) Effect of nitrogen nutrition upon sugar content and dry weight of juvenile lodgepole pine and white spruce. Can J For Res 2:434–440

Feijoo G, Soto M (1995) Sodium inhibition in the anaerobic digestion process : Antagonism and adaptation phenomena. Enzyme Microb Technol 17:180–188. https://doi.org/10.1016/0141-0229(94)00011-F

Fermoso FG, Van Hullebusch E, Collins G, et al (2019) Trace Elements in Anaerobic Biotechnologies. IWA Publishing

Fongsatitkul P, Elefsiniotis P, Wareham DG (2012) Two-phase anaerobic digestion of the organic fraction of municipal solid waste : estimation of methane production. Waste Manag Res 30:720–726. https://doi.org/10.1177/0734242X11429987

Gaby JC, Zamanzadeh M, Horn SJ (2017) The effect of temperature and retention time on methane production and microbial community composition in staged anaerobic digesters fed with food waste. Biotechnol Biofuels 10:302. https://doi.org/10.1186/s13068-017-0989-4

Gallert C, Winter J (2005) Bacterial Metabolism in Wastewater Treatment Systems. In: Jördening H, Winter J (eds) Environmental Biotechnology. Wiley VCH, pp 1–48

Gao J, Chen L, Yan Z, Wang L (2013) Effect of ionic liquid pretreatment on the composition, structure and biogas production of water hyacinth (Eichhornia crassipes). Bioresour Technol 132:361–364. https://doi.org/https://doi.org/10.1016/j.biortech.2012.10.136

García R, Pizarro C, Lavín AG, Bueno JL (2013) Biomass proximate analysis using

thermogravimetry. Bioresour Technol 139:1–4. https://doi.org/10.1016/j.biortech.2013.03.197

Gaurav GK, Mehmood T, Cheng L, et al (2020) Water hyacinth as a biomass: A review. J Clean Prod 122214. https://doi.org/https://doi.org/10.1016/j.jclepro.2020.122214

Gavilán H (2018) Inician recogida de basura en el Ozama con barcos especiales. List. D.

Gerbens-Leenes PW (2017) Bioenergy water footprints, comparing first, second and third generation feedstocks for bioenergy supply in 2040. Eur Water 373–380

Gettys LA, Haller WT, Bellaud M (2009) BIOLOGY AND CONTROL OF AQUATIC PLANTS - A Best Management Practices Handbook. October 210

Gil A, Siles JA, Serrano A, et al (2019) Effect of Variation in the C /[N 1 P] Ratio on Anaerobic Digestion. Environ Prog Sustain Energy 58:1–9. https://doi.org/10.1002/ep.12922

Givnish TJ (1988) Adaptation to Sun and Shade : Aust J Plant Physiol 15:63–92

Go B, Ko AA (2018) Effects of inoculum to feedstock ratio on anaerobic digestion for biogas production. Int J Hydrol 2:567–571. https://doi.org/10.15406/ijh.2018.02.00027

Gong Y, Zhou X, Ma X, Chen J (2018) Sustainable removal of formaldehyde using controllable water hyacinth. J Clean Prod 181:1–7. https://doi.org/10.1016/j.jclepro.2018.01.220

Gupta GC (1980) Use of Water Hyacinths in Wastewater Treatment (A Brief Literature Review). J Environ Health 43:80–82

Guragain YN, De Coninck J, Husson F, et al (2011) Comparison of some new pretreatment methods for second generation bioethanol production from wheat straw

and water hyacinth. Bioresour Technol 102:4416–4424. https://doi.org/10.1016/j.biortech.2010.11.125

Gutiérrez EL, Ruiz EF, Uribe EG, Martínez JM (2001) Biomass and Productivity of Water Hyacinth and Their Application in Control Programs. In: Julien MH, Hill MP, Center TD, Jianqing D (eds) ACIAR Proceedings. pp 109–119

Gwenzi W, Chaukura N, Noubactep C, Mukome FND (2017) Biochar-based water treatment systems as a potential low-cost and sustainable technology for clean water provision. J Environ Manage 197:732–749. https://doi.org/10.1016/j.jenvman.2017.03.087

Hamraoui K, Gil A, El Bari H, et al (2020) Evaluation of hydrothermal pretreatment for biological treatment of lignocellulosic feedstock (pepper plant and eggplant). Waste Manag 102:76–84. https://doi.org/https://doi.org/10.1016/j.wasman.2019.10.020

Harun MY, Dayang Radiah AB, Zainal Abidin Z, Yunus R (2011) Effect of physical pretreatment on dilute acid hydrolysis of water hyacinth (Eichhornia crassipes). Bioresour Technol 102:5193–5199. https://doi.org/https://doi.org/10.1016/j.biortech.2011.02.001

Hernández-Shek MA, Cadavid-Rodríguez LS, Bolaños I V., Agudelo-Henao AC (2016) Recovering biomethane and nutrients from anaerobic digestion of water hyacinth (Eichhornia crassipes) and its co-digestion with fruit and vegetable waste. Water Sci Technol 73:355–361

Hidayat S, Susanty S, Riveli N, et al (2018) Synthesis and characterization of CMC from water hyacinth for lithium-ion battery applications. AIP Conf Proc 1927:. https://doi.org/10.1063/1.5021216

Hideno A (2016) Comparison of the thermal degradation properties of crystalline and amorphous cellulose, as well as treated lignocellulosic biomass. BioResources 11:6309–6319. https://doi.org/10.15376/biores.11.3.6309-6319

Holliger C, Alves M, Andrade D, et al (2016) Towards a standardization of biomethane potential tests. Water Sci Technol 74:2515–2522. https://doi.org/10.2166/wst.2016.336

Holm-Nielsen JB, Oleskowicz-Popiel P (2013) 10 - Process control in biogas plants. In: Wellinger A, Murphy J, Baxter DBT-TBH (eds) Woodhead Publishing Series in Energy. Woodhead Publishing, pp 228–247

Hossain E, Sikder H, Kabir H, Sarma SM (2015) Nutritive value of water hyacinth (Eichhornia crassipes). Online J Anim Feed Res

Hronich JE, Martin L, Plawsky J, Bungay HR (2008) Potential of Eichhornia crassipes for biomass refining. J Ind Microbiol Biotechnol 35:393–402. https://doi.org/10.1007/s10295-008-0333-x

Hussain Z, Bashir N, Khan MI, et al (2017) Production of highly upgraded bio-oils through two-step catalytic pyrolysis of water hyacinth. Energy & Fuels. https://doi.org/10.1021/acs.energyfuels.7b01252

ICCP (2014) Climate Change Synthesis Report

Jatav HS, Jayant H, Kumar S, et al (2017) Role of Biochar : In agriculture sector its implication and perspective. Int J Chem Stud 5:14–18

Jayalakshmy MS, Philip J (2010) Thermophysical Properties of Plant Leaves and Their Influence on the Environment Temperature. Int J Thermophys 31:2295–2304. https://doi.org/10.1007/s10765-010-0877-7

Jetter KM, Nes K (2018) The Cost to Manage Invasive Aquatic Weeds in the California Bay-Delta. UC Giannini Found Agric Econ 21:9–11

Jones RW (2001) Integrated Control of Water Hyacinth on the Nseleni / Mposa Rivers and Lake Nsezi , Kwa Zulu-Natal , South Africa. Forestry 102:123–129

Julong Q (2018) Aquatic Weed Harvester / Aquatic Plant Harvester. In: Environ. Technol. Co., Ltd

Kafle GK, Chen L (2016) Comparison on batch anaerobic digestion of five different livestock manures and prediction of biochemical methane potential (BMP) using different statistical models. Waste Manag 48:492–502. https://doi.org/https://doi.org/10.1016/j.wasman.2015.10.021

Kang S, Zhang G, Yang Q, et al (2016) A New Technology for Utilization of Biomass Hydrolysis Residual Humins for Acetic Acid Production. BioResources 11:9496–9505

Khan AW, Trottier TM (1978) Effect of sulfur-containing compounds on anaerobic degradation of cellulose to methane by mixed cultures obtained from sewage sludge. Appl Environ Microbiol

Khanal SK, Huang J (2005) Effect of High Influent Sulfate on Anaerobic Wastewater Treatment. Water Environ Res 77:3037–3046. https://doi.org/10.2175/106143005X73929

Kim JS, Lee YY, Hyun T (2016) Bioresource Technology A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. Bioresour Technol 199:42–48. https://doi.org/10.1016/j.biortech.2015.08.085

Kim TH, Gupta R, Lee YY (2009) Pretreatment of Biomass by Aqueous Ammonia for

Bioethanol Production. In: J. M (ed) Biofuels. Methods in Molecular Biology. Humana Press, Totowa, NJ, pp 79–91

Klinke HB, Ahring BK, Schmidt AS, Thomsen AB (2002) Characterization of degradation products from alkaline wet oxidation of wheat straw. Bioresour Technol 82:15–26

Kolaczkowski ST, Plucinski P, Beltran FJ, et al (1999) Wet air oxidation: A review of process technologies and aspects in reactor design. Chem Eng J. https://doi.org/10.1016/S1385-8947(99)00022-4

Koutika LS, Rainey HJ (2015) A review of the invasive, biological, and beneficial characteristics of aquatic species Eichhornia crassipes and Salvinia molesta. Appl Ecol Environ Res 13:263–275

Lage-pinto F, Oliveira JG, Da M, et al (2008) Chlorophyll a fluorescence and ultrastructural changes in chloroplast of water hyacinth as indicators of environmental stress. Environ Exp Bot 64:307–313. https://doi.org/10.1016/j.envexpbot.2008.07.007

Lawal AA, Dzivama AU, Wasinda MK (2016) Effect of inoculum to substrate ratio on biogas production of sheep paunch manure. Res Agric en 62:8–14. https://doi.org/10.17221/30/2014-RAE

Lehmann J, Joseph S (2009) Biochar for Enviromental Management: Science and Technology. Earthscan, London

Lewandowski I (2017) Bioeconomy. Springer

Li P, Li W, Sun M, et al (2019) Evaluation of Biochemical Methane Potential and Kinetics on the Anaerobic Digestion of Vegetable Crop Residues. Energies 12:1–14.

https://doi.org/10.3390/en12010026

Li Y, Jin Y, Borrion A, Li J (2018) Influence of feed/inoculum ratios and waste cooking oil content on the mesophilic anaerobic digestion of food waste. Waste Manag 73:156–164

Lichtenthaler HK (1987) Chlorophylls Carotenoids: Pigments of Photosynthetic Biomembranes. Methods Enzymol 148:350–382

Lin R, Cheng J, Song W, et al (2015) Characterisation of water hyacinth with microwave-heated alkali pretreatment for enhanced enzymatic digestibility and hydrogen/methane fermentation. Bioresour Technol 182:1–7. https://doi.org/10.1016/j.biortech.2015.01.105

Lin S, Yang H, Na Z, Lin K (2018) A novel biodegradable arsenic adsorbent by immobilization of iron oxyhydroxide (FeOOH) on the root powder of long-root Eichhornia crassipes. Chemosphere 192:258–266. https://doi.org/10.1016/j.chemosphere.2017.10.163

Linville JL, Shen Y, Leon PAI, et al (2017) In-situ biogas upgrading during anaerobic digestion of food waste amended with walnut shell biochar at bench scale. Waste Manag Res 35:669–679. https://doi.org/10.1177/0734242X17704716

Lisboa MSo, Lansing S (2013) Characterizing food waste substrates for co-digestion through biochemical methane potential (BMP) experiments. Waste Manag 33:2664–2669

Lissens G, Thomsen AB, De Baere L, et al (2004) Thermal Wet Oxidation Improves Anaerobic Biodegradability of Raw and Digested Biowaste. Environ Sci Technol 38:3418–3424. https://doi.org/10.1021/es035092h

Liu H, Xu M, Zhang Q, et al (2013) Effective utilization of water hyacinth resource by Co-gasification with coal: Rheological properties and ash fusion temperatures of hyacinth-coal slurry. Ind Eng Chem Res. https://doi.org/10.1021/ie402163c

Livermore DF, Bruhn HD, Pollock BW (1971) Processing characteristics of subsurface macrophytes of Madison, Wisconsin, lakes in relation to mechanical harvesting systems. Hidrobiologia 12:341–350

Lokesh K, Ladu L, Summerton L (2018) Bridging the Gaps for a ' Circular ' Bioeconomy : Selection Criteria , Bio-Based Value Chain and Stakeholder Mapping. Sustainability 10:1–24. https://doi.org/10.3390/su10061695

Luo G, James Strong P, Wang H, et al (2011) Kinetics of the pyrolytic and hydrothermal decomposition of water hyacinth. Bioresour Technol. https://doi.org/10.1016/j.biortech.2011.04.048

Mahmood T, Malik S, Hussain S (2010) Biosorption and recovery of heavy metals from aqueous solutions by eichhornia crassipes (water hyacinth) ash. BioResources 5:1244–1256

Mani S, Womac AR, Ye XP, Narayan S (2008) Bulk Density of Wet and Dry Wheat Straw and Switchgrass Particles. Appl Eng Agric 24:351–358

Martin C, Marcet M, Thomsen AB (2008) Comparison between wet oxidation and steam explosion as pretreatment methods for enzymatic hydrolysis of sugarcane bagasse. BioResources 3:670–683

Martín C, Thomsen AB (2007) Wet oxidation pretreatment of lignocellulosic residues of sugarcane, rice, cassava and peanuts for ethanol production. J Chem Technol Biotechnol 82:174–181. https://doi.org/10.1002/jctb.1648

Masebinu SO, Akinlabi ET, Muzenda E, Aboyade AO (2019) A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. Renew Sustain Energy Rev 103:291–307

Mathew AK, Bhui I, Banerjee SN, et al (2013) Biogas production from locally available aquatic weeds of Santiniketan through anaerobic digestion. Clean Technol Environ Policy. https://doi.org/10.1007/s10098-014-0877-6

Mccarty PL, Mckinney RE (1961) Salt Toxicity in Anaerobic Digestion. Water Pollut Control Fed 33:399–415

Melignani E (2019) Growth , accumulation and uptake of Eichhornia crassipes exposed to high cadmium concentrations. Environ Sci Pollut Res 26:22826–22834

Miño E., Sakuno Y, Okuda T, et al (2011) Field Survey and Satellite Validation of Water Quality Parameters of Rivers in the Surroundings of Santo Domingo Metropolitan Area , Dominican Republic. pp 27–31

Mir MA, Hussain A, Verma C (2016) Design considerations and operational performance of anaerobic digester : A review. Cogent Eng 3:1181696. https://doi.org/10.1080/23311916.2016.1181696

Moestedt J, Rönnberg J, Nordell E (2017) The effect of different mesophilic temperatures during anaerobic digestion of sludge on the overall performance of a WWTP in Sweden. Water Sci Technol 76:3213–3219. https://doi.org/10.2166/wst.2017.367

Moldoveanu S (2009) Pyrolysis of Organic Molecules: Applications to Health and Environmental Issues. Elsevier

Moral R, Moreno Caselles J, Pérez-Murcia MD, Pérez-Espinosa A (2002) IMPROVING THE MICRONUTRIENT AVAILABILITY IN CALCAREOUS SOILS BY

SEWAGE SLUDGE AMENDMENT. Commun Soil Sci Plant Anal 33:3015–3022

Morone A, Chakrabarti T, Pandey RA (2018) Effect of chemical input during wet air oxidation pretreatment of rice straw in reducing biomass recalcitrance and enhancing cellulose accessibility. Korean J Chem Eng 35:2403–2412. https://doi.org/10.1007/s11814-018-0129-2

Moset V, Poulsen M, Wahid R, et al (2015) Mesophilic versus thermophilic anaerobic digestion of cattle manure: methane productivity and microbial ecology. Microb Biotechnol 8:787–800. https://doi.org/10.1111/1751-7915.12271

Moyo P, Chapungu L, Mudzengi B (2013) Effectiveness of water Hyacinth (Eichhornia crassipes) in remediating polluted water : The case of Shagashe river in Masvingo , Zimbabwe. Adv Appl Sci Res 4:55–62

Nguyen Thi BT, Ong LK, Nguyen Thi DT, Ju YH (2017) Effect of subcritical water pretreatment on cellulose recovery of water hyacinth (Eichhornia crassipe). J Taiwan Inst Chem Eng 71:55–61. https://doi.org/10.1016/j.jtice.2016.12.028

Nigam JN (2002) Bioconversion of water-hyacinth (Eichhornia crassipes) hemicellulose acid hydrolysate to motor fuel ethanol by xylose – fermenting yeast. J Biotechnol 97:107–116

O'Kelly BC (2005) Mechanical properties of dewatered sewage sludge. Waste Manag 25:47–52. https://doi.org/https://doi.org/10.1016/j.wasman.2004.08.003

Oleszkiewicz JA, Sharma VK (1990) Inhibition of anaerobic processes by heavy metals-A Review. Biol Waters 31:45–67

Ozores-Hampton M, Stansly PA, Salame TP (2011) Soil Chemical, Physical, and Biological Properties of a Sandy Soil Subjected to Long-Term Organic

Amendments. J Sustain Agric 35:243–259. https://doi.org/10.1080/10440046.2011.554289

P.l.c. B (2019) BP Energy Outlook 2019

Pan J, Ma J, Xiaxia L, et al (2019) Effects of different types of biochar on the anaerobic digestion of chicken manure. Bioresour Technol 275:258–265

Parayil U, Velukutty B, Gopinath A, Muraleedharan S (2006) The impact of a salinity barrier on the partitioning of heavy metals in sediments of a tropical backwater system The impact of a salinity barrier on the partitioning of heavy metals in sediments of a tropical backwater system. Chem Speciat Bioavailab ISSN 18:153–167. https://doi.org/10.1080/09542299.2006.11073750

Pardo LMF, Mendoza JGS, Galán JEL (2019) Influence of pretreatments on crystallinity and enzymatic hydrolysis in sugar cane residues. Brazilian J Chem Eng 36:131–141. https://doi.org/10.1590/0104-6632.20190361s20180093

Patil JH, AntonyRaj MAL, Shankar BB, et al (2014a) Anaerobic Co-digestion of Water Hyacinth and Sheep Waste. Energy Procedia 52:572–578. https://doi.org/https://doi.org/10.1016/j.egypro.2014.07.112

Patil JH, Raj MA, Muralidhara PL, et al (2012) Kinetics of Anaerobic Digestion of Water Hyacinth Using Poultry Litter as Inoculum. Int J Environ Sci Dev 3:94–98. https://doi.org/10.7763/IJESD.2012.V3.195

Patil JH, Sanil PH, Chaitra D (2014b) Study on biomethanation of water hyacinth using primary sludge as inoculum Study on biomethanation of water hyacinth using primary sludge as inoculum

Pavlostathis SG, Giraldo-Gomez E (1991) Kinetics of anaerobic treatment. Water Sci

Technol 24:35–59. https://doi.org/10.2166/wst.1991.0217

Pavlović D, Nikolić B, Đurović S, et al (2014) Chlorophyll as a measure of plant health : Agroecological aspects. Pestic Phytomed (Belgrade), 29:21–34. https://doi.org/10.2298/PIF1401021P

Pellegrini MOO, Horn CN, Almeida RF (2018) Total evidence phylogeny of Pontederiaceae (Commelinales) sheds light on the necessity of its recircumscription and synopsis of Pontederia L . PhytoKeys 83:25–83. https://doi.org/10.3897/phytokeys.108.27652

Perez-mercado LF, Lalander C, Berger C, Dalahmeh SS (2018) Potential of Biochar Filters for Onsite Wastewater Treatment : Effects of Biochar Type , Physical Properties and Operating Conditions. Water 10:1–18. https://doi.org/10.3390/w10121835

Pérez JA, Ballesteros I, Ballesteros M, et al (2008) Optimizing Liquid Hot Water pretreatment conditions to enhance sugar recovery from wheat straw for fuel-ethanol production. Fuel 87:3640–3647. https://doi.org/https://doi.org/10.1016/j.fuel.2008.06.009

Pozo S, Sánchez-Fung JR, Santos-Paulino AU (2013) Economic Development Strategies in the Dominican Republic. In: Fosu AK (ed) Achieving Development Success: Strategies and Lessons from the Developing World. OUP Oxford, pp 384–404

Pramanik SK, Suja FB, Porhemmat M, Pramanik BK (2019) Performance and Kinetic Model of a Single-Stage Anaerobic Digestion System Operated at Different Successive Operating Stages for the Treatment of Food Waste. Processes 7:

Priya P, Nikhitha SO, Anand C, et al (2018) Biomethanation of water hyacinth biomass.

Bioresour Technol 255:288–292. https://doi.org/10.1016/j.biortech.2018.01.119

QiuLing C, XiuYun L, JiangDong Y, et al (2017) Recycling water hyacinth by gasification in supercritical water. Recycl water hyacinth by Gasif Supercrit water 2163–2170

Rabii A, Aldin S, Dahman Y, Elbeshbishy E (2019) A Review on Anaerobic Co-Digestion with a Focus on the Microbial Populations and the Effect of Multi-Stage Digester Configuration. Energies 12:1–25. https://doi.org/10.3390/en12061106

Radu T, Blanchard RE, Andrew D. Wheatley (2017) Biogas for sustainable rural communities. In: Kalyuzhnova Y, Pomfret R (eds) Sustainable Energy in Kazakhstan, 1st edn. London, p 20

Raposo F, Borja R, Martin MA, et al (2009) Influence of inoculum-substrate ratio on the anaerobic digestion of sunflower oil cake in batch mode: Process stability and kinetic evaluation. Chem Eng J 149:70–77. https://doi.org/10.1016/j.cej.2008.10.001

Rashed M, Mamun A, Torii S (2017) Comparison effect of feedstock to inoculum ratios on biogas yields of cafeteria , vegetable , fruit wastes with cattle manure using co-digestion process vegetable , fruit wastes with cattle manure using co-digestion process. Int J Green Energy 14:665–673. https://doi.org/10.1080/15435075.2017.1318071

Raspolli Galletti AM, D'Alessio A, Licursi D, et al (2015) Midinfrared FT-IR as a tool for monitoring herbaceous biomass composition and its conversion to furfural. J Spectrosc 2015:. https://doi.org/10.1155/2015/719042

Reddy KR (1984) Water Hyacinth (Eichhornia crassipes) Biomass production in Florida. Biomass 6:167–181

Revell KT, Maguire RO, Agblevor FA (2012a) Influence of Poultry Litter Biochar on Soil Properties and Plant Growth. Soil Sci 177:402–408. https://doi.org/10.1097/SS.0b013e3182564202

Revell KT, Maguire RO, Agblevor FA, Sites F (2012b) Field Trials With Poultry Litter Biochar and Its Effect on Forages , Green Peppers , and Soil Properties. Soil Sci 177:573–579. https://doi.org/10.1097/SS.0b013e3182741050

Rezania S, Oryani B, Cho J, et al (2020) Different pretreatment technologies of lignocellulosic biomass for bioethanol production: An overview. Energy 199:117457. https://doi.org/https://doi.org/10.1016/j.energy.2020.117457

Rezania S, Ponraj M, Din MFM, et al (2015a) The diverse applications of water hyacinth with main focus on sustainable energy and production for new era: An overview. Renew Sustain Energy Rev 41:943–954. https://doi.org/10.1016/j.rser.2014.09.006

Rezania S, Ponraj M, Talaiekhozani A, et al (2015b) Perspectives of phytoremediation using water hyacinth for removal of heavy metals, organic and inorganic pollutants in wastewater. J Environ Manage 163:125–133. https://doi.org/10.1016/j.jenvman.2015.08.018

Rivard C, Grohmann K (1991) Degradation of furfural (2-furaldehyde) to methane and carbon dioxide by an anaerobic consortium. Appl Biochem Biotechnol 28–29:285–295

Rolfe MD, Rice CJ, Lucchini S, et al (2012) Lag phase is a distinct growth phase that prepares bacteria for exponential growth and involves transient metal accumulation. J Bacteriol 194:686–701. https://doi.org/10.1128/JB.06112-11

Romdhane L, Awad YM, Radhouane L, et al (2019) Wood biochar produces different

rates of root growth and transpiration in two maize hybrids (Zea mays L .) under drought stress. Arch Agron Soil Sci 65:846–866. https://doi.org/10.1080/03650340.2018.1532567

Romero-Güiza MS, Mata-Alvarez J, Chimenos JM, Astals S (2016) The effect of magnesium as activator and inhibitor of anaerobic digestion. Waste Manag 56:137–142. https://doi.org/https://doi.org/10.1016/j.wasman.2016.06.037

Roshanak S, Rahimmalek M, Amir S, Goli H (2016) Evaluation of seven different drying treatments in respect to total flavonoid , phenolic , vitamin C content , chlorophyll , antioxidant activity and color of green tea (Camellia sinensis or C . assamica) leaves. J Food Sci Technol 53:721–729. https://doi.org/10.1007/s13197-015-2030-x

Saha P, Shinde O, Sarkar S (2017) Phytoremediation of industrial mines wastewater using water hyacinth. Int J Phytoremediation ISSN 19:87–96. https://doi.org/10.1080/15226514.2016.1216078

Salas H, Martino P (1988) Evaluación y control de la contaminación de las aguas superficiales en la vecindad de Santo Domingo

Sana S, Khatoon M (2017) To Evaluate the Efficiency of Char and Biochar for Waste Water Treatment. J waste Recycl 2:1–6

Sankaran R, Parra Cruz RA, Pakalapati H, et al (2020) Recent advances in the pretreatment of microalgal and lignocellulosic biomass: A comprehensive review. Bioresour Technol 298:122476. https://doi.org/https://doi.org/10.1016/j.biortech.2019.122476

Santos L, Silva F, Santos L, et al (2017) Potential Bio-Oil Production from Invasive Aquatic Plants by Microscale Pyrolysis Studies. J Braz Chem Soc 29:151–158.

https://doi.org/10.21577/0103-5053.20170124

Sarto S, Hildayati R, Syaichurrozi I (2019) Effect of chemical pretreatment using sulfuric acid on biogas production from water hyacinth and kinetics. Renew Energy 132:335–350. https://doi.org/10.1016/j.renene.2018.07.121

Sekar A, Ansari M (2018) Phyto-remediation of total dissolved solids (TDS) by Eichhornia Crassipes, Pistia Stratiotes and Chrysopogon Zizanioides from second stage RO-Brine solution. Res J Chem Environ 22:

Shah FA, Rashid N, Mahmood Q, Ali A (2019) Effect of Pretreatment and Substrate Ratios in Biorefinery Employing Co-digestion of Plant Biomass and Poultry Waste. Front Energy Res 6:1–14. https://doi.org/10.3389/fenrg.2018.00143

Sharma A, Ghosh A, Pandey RA (2015) Wet Air Oxidation Pretreatment of Mixed Lignocellulosic Biomass to Enhance Enzymatic Convertibility. Korean Chem Eng Res 53:216–223. https://doi.org/10.9713/kcer.2015.53.2.216

Shawky BT, Mahmoud MG, Ghazy EA, et al (2011) Enzymatic hydrolysis of rice straw and corn stalks for monosugars production. J Genet Eng Biotechnol 9:59–63. https://doi.org/https://doi.org/10.1016/j.jgeb.2011.05.001

Shen Y, Linville J, Urgun-Dermitas M, et al (2015) Producing pipeline-quality biomethane via anaerobic digestion of sludge amended with corn stover biochar with in-situ CO2 removal. Appl Energy 158:300–309

Shen Y, Linville JL, Leon PAI, et al (2016) Towards a sustainable paradigm of waste-to-energy process_ Enhanced anaerobic digestion of sludge with woody biochar. J Clean Prod 135:1054–1064

Shen Y, Zhu W, Li H, et al (2018) Enhancing cadmium bioremediation by a complex of

water-hyacinth derived pellets immobilized with Chlorella sp. Bioresour Technol 257:157–163. https://doi.org/10.1016/j.biortech.2018.02.060

Shirinpur-valadi A, Hatamzadeh A, Sedaghathoor S (2019) Study of the accumulation of contaminants by Cyperus alternifolius , Lemna minor , Eichhornia crassipes , and Canna × generalis in some contaminated aquatic environments. Environ Sci Pollut Res 26:21340–21350

Sierra-Ramirez, Rocio; Holtzapple, Mark; Piamonte N (2013) Fundamentals of Biomass Pretreatment at High pH. In: Wyman CE (ed) Aqueous pretreatment of plant biomass for biological and chemical conversion to fuels and chemicals.

Sikarwar VS, Zhao M, Fennell PS, et al (2017) Progress in biofuel production from gasification. Prog. Energy Combust. Sci.

Sikder S, Joardar JC (2019) Biochar production from poultry litter as management approach and effects on plant growth. Int J Recycl Org Waste Agric 8:47–58

Sindhu R, Binod P, Pandey A, et al (2017) Water hyacinth a potential source for value addition: An overview. Bioresour Technol 230:152–162. https://doi.org/10.1016/j.biortech.2017.01.035

Smith J ame. L (1984) Mechanical harvesting of aquatic plants. Report 3 Evaluation of the Limnos system.

Šoštarić T, Petrović M, Stojanović J, et al (2020) Structural changes of waste biomass induced by alkaline treatment: the effect on crystallinity and thermal properties. Biomass Convers Biorefinery. https://doi.org/10.1007/s13399-020-00766-2

Strömberg S, Nistor M, Liu J (2015) Early prediction of Biochemical Methane Potential through statistical and kinetic modelling of initial gas production. Bioresour Technol

176:233–241. https://doi.org/https://doi.org/10.1016/j.biortech.2014.11.033

Suttibak S, Loengbudnark W (2018) Production of charcoal briquettes from biomass for community use. IOP Conf Ser Mater Sci Eng 297:. https://doi.org/10.1088/1757-899X/297/1/012001

Swenson HA, Baldwin HL (1965) A primer on water quality

Thyrel M (2014) Spectroscopic Characterization of Lignocellulosic Biomass

Tian S, Nakamura K, Cui T, Kayahara H (2005) High-performance liquid chromatographic determination of phenolic compounds in rice. 1063:121–128. https://doi.org/10.1016/j.chroma.2004.11.075

Ting WHT, Tan IAW, Salleh SF, Wahab NA (2018) Application of water hyacinth (Eichhornia crassipes) for phytoremediation of ammoniacal nitrogen: A review. J Water Process Eng 22:239–249. https://doi.org/10.1016/j.jwpe.2018.02.011

Toreci I, Droste RL, Kennedy KJ (2011) Mesophilic Anaerobic Digestion with High-Temperature Microwave Pretreatment and Importance of Inoculum Acclimation. Water Environ Res 83:549–559. https://doi.org/10.2175/106143010X12780288628651

Uzodinma EOU, Ofoefule, AU, Eze JI, Onwuka ND (2007) Optimum Mesophilic Temperature of Biogas Production from Blends of Agro-Based Wastes. Trends Appl Sci Res 2:39–44. https://doi.org/10.3923/tasr.2007.39.44

Vandermeulen V, Van der Steen M, Stevens C V, Van Huylenbroeck G (2012) Industry expectations regarding the transition toward a biobased economy. Biofuels, Bioprod Biorefining 6:453–464. https://doi.org/10.1002/bbb.1333

Varga E, Schmidt AS, Reczey K, Thomsen AB (2003) Pretreatment of corn stover using

wet oxidation to enhance enzymatic digestibility. Appl Biochem Biotechnol 104:37–50. https://doi.org/10.1385/abab:104:1:37

Vaxelaire J, Puiggali JR (2002) ANALYSIS OF THE DRYING OF RESIDUAL SLUDGE: FROM THE EXPERIMENT TO THE SIMULATION OF A BELT DRYER. Dry Technol 20:989–1008. https://doi.org/10.1081/DRT-120003773

Vaz SJ (2016) Analytical Techniques and Methods for Biomass. Springer, Brasilia

Venter N, Cowie BW, Witkowski ETF, et al (2017) The amphibious invader: Rooted water hyacinth's morphological and physiological strategy to survive stranding and drought events. Aquat Bot 143:41–48

Wang D, Huang H, Shen F, et al (2016) Effects of biomass densification on anaerobic digestion for biogas production. RSC Adv 6:91748–91755

Wang J, Fu Z, Qiao H, Liu F (2019) Assessment of eutrophication and water quality in the estuarine area of Lake Wuli, Lake Taihu, China. Sci Total Environ 650:1392–1402

Wang K, Brown R (2017) Prospects for fast pyrolysis of biomass. In: Fast Pyrolysis of Biomass: Advances in Science and Technology. Royal Society of Chemistry, p 276

Wang S, Luo Z (2017) Pyrolysis of Biomass. Berlin

Ward AJ, Hobbs PJ, Holliman PJ, Jones DL (2008) Optimisation of the anaerobic digestion of agricultural resources. Bioresour Technol 99:7928–7940. https://doi.org/10.1016/j.biortech.2008.02.044

Wellinger A, Murphy J, Baxter D (2013) The Biogas Handbook: Science, Production and Applications, 1st edn. Woodhead Publishing

Wilson JR, Rees M, Holst N, et al (2001) Water Hyacinth Population Dynamics. Proc

ACIAR Biol Integr Control Water Hyacinth Eichhornia crassipes 102:96–104

Wirth B, Krebs M, Andert J (2015) Anaerobic degradation of increased phenol concentrations in batch assays. Environ Sci Pollut Res 22:19048–19059. https://doi.org/10.1007/s11356-015-5100-8

Wojcieszak M, Pyzik A, Poszytek K, Krawczyk PS (2017) Adaptation of Methanogenic Inocula to Anaerobic Digestion of Maize Silage. Front Microbiol 8:1–12. https://doi.org/10.3389/fmicb.2017.01881

Wolfe RS (2011) Chapter one - Techniques for Cultivating Methanogens. In: Rosenzweig AC, Ragsdale SWBT-M in E (eds) Methods in Methane Metabolism, Part A. Academic Press, pp 1–22

Wolverton BC, McKown MM (1976) Water hyacinths for removal of phenols from polluted waters. Aquat Bot 2:191–201

Wyk E, Wilgen B (2002) The cost of water hyacinth control in South Africa: A case study of three options. African J Aquat Sci 27:141–149. https://doi.org/10.2989/16085914.2002.9626585

Wyman CE (2013) Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals. John Wiley & Sons, Noida, India

Xia A, Cheng J, Song W, et al (2013) Enhancing enzymatic sacchari fi cation of water hyacinth through microwave heating with dilute acid pretreatment for biomass energy utilization. Energy 61:158–166

Xu N, Liu S, Xin F, et al (2019) Biomethane Production From Lignocellulose : Biomass Recalcitrance and Its Impacts on Anaerobic Digestion. Front Bioeng Biotechnol 7:191. https://doi.org/10.3389/fbioe.2019.00191

Yang H, Yan R, Chen H, et al (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86:1781–1788. https://doi.org/10.1016/j.fuel.2006.12.013

Yangin-gomec C, Sapmaz T, Aydin S (2018) Impact of inoculum acclimation on energy recovery and investigation of microbial community changes during anaerobic digestion of the chicken manure. Environ Technol 1–10. https://doi.org/10.1080/09593330.2018.1551434

Yao Z, Ma X, Xiao Z (2020) The effect of two pretreatment levels on the pyrolysis characteristics of water hyacinth. Renew Energy 151:514–527. https://doi.org/10.1016/j.renene.2019.11.046

Zaman CZ, Pal K, Yehye WA, et al (2017) Pyrolysis: A Sustainable Way to Generate Energy from Waste. In: Samer M (ed) Pyrolysis. Books on Demand, p 350

Zeng S, Yuan X, Shi X, Qiu Y (2010) Effect of inoculum/substrate ratio on methane yield and orthophosphate release from anaerobic digestion of Microcystis spp. J Hazard Mater 178:89–93

Zhang Q, Wei Y, Han H, Weng C (2018) Enhancing bioethanol production from water hyacinth by new combined pretreatment methods. Bioresour Technol 251:358–363. https://doi.org/10.1016/j.biortech.2017.12.085

Zhang Y, Liu H, Yan S, et al (2019) Phosphorus removal from the hyper-eutrophic Lake Caohai (China) with large-scale water hyacinth cultivation. Environ Sci Pollut Res 26:12975–12984

Zhao B, Xu H, Ma F, et al (2019) Effects of dairy manure biochar on adsorption of sulfate onto light sierozem and its mechanisms. RSC Adv 9:5218–5223. https://doi.org/10.1039/C8RA08916G

Zhao J, Liu Y, Wang D, et al (2017) Potential impact of salinity on methane production from food waste anaerobic digestion _ Elsevier Enhanced Reader.pdf. Waste Manag 67:308–317

Zhou Y, Zhang Z, Nakamoto T, et al (2010) Effect of Substrate-to-Inoculum Ratio on Methane Production with a Batch Anaerobic Digestion of Bean Curd Residue. Japanese J Water Treat Biol Vol46 46:161–169

Zhuang X, Wang W, Yu Q, et al (2016) Liquid hot water pretreatment of lignocellulosic biomass for bioethanol production accompanying with high valuable products. Bioresour Technol 199:68–75. https://doi.org/https://doi.org/10.1016/j.biortech.2015.08.051

Zoghlami A, Paës G (2019) Lignocellulosic Biomass : Understanding Recalcitrance and Predicting Hydrolysis. Front Chem 7:. https://doi.org/10.3389/fchem.2019.00874

APPENDICES

Appendix A. Map of Sampling Points

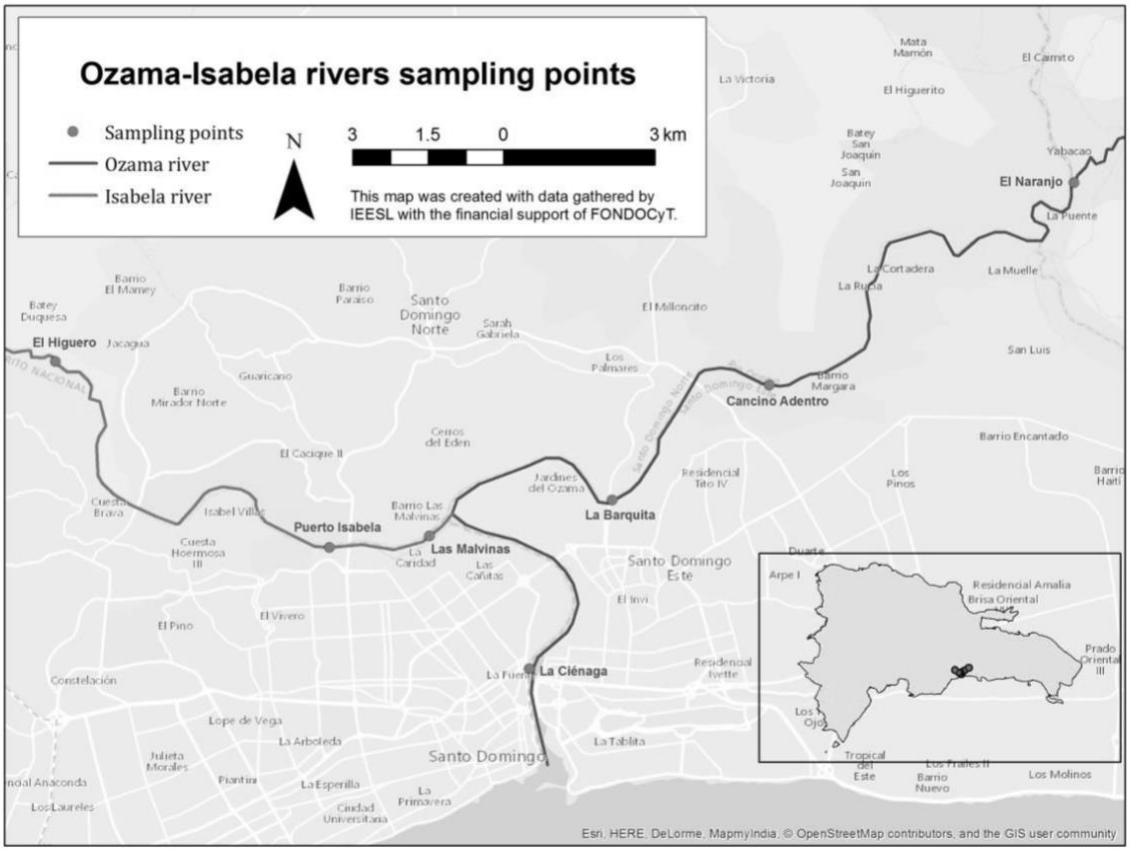

Fig. A-1 Map of Ozama River and its contributory, Isabela River, within Santo Domingo. The sampling points that are considered in this study are La Ciénaga and El Naranjo.

Appendix B. Energy Analysis for F/I and Temperature Effects on Batch Systems

1. **Volume (V) and mass (m) calculation for the feed (F) and inoculum (I).** The solid (S) and the liquid (S) portion of the inoculum (sludge) is considered for the calculations. The density of fresh feedstock was 96 kg/m3. The dry density and the total solids (TS) of the sludge were 560 kg/m3 and 2.5%. Water density is 1000 kg/m3.

$V = 5\ m^3$

$V_F + V_I = 5\ m^3$;

$M_F/V_F = 96.0\ Kg/m^3$

$M_F/M_S = F/I$

$V_I = V_S + V_L$

$M_L/V_L = 1000\ Kg/m^3$

$M_S/V_S = 560\ Kg/m^3$

$M_S/(M_L + M_S) = \%TS/100\%$; $M_S/(M_L + M_S) = 0.025$

$M_L = 39M_S$

$39M_S/V_L = 1000\ Kg/m^3;\ V_L = 0.039M_S$

$V_I = V_S + 0.039M_S$

a. F/I= 5.0

$M_F/M_S = 5.0$

$96\ V_F\ /560\ V_S = 5.0$; $V_F = 29.2\ V_S$

$30.2\ V_S + 0.039M_S = 5\ m^3$

$30.2\ V_S + 0.039(560\ V_S) = 5\ m^3$; $52.04\ V_S = 5\ m^3$;

$\boldsymbol{V_S = 0.096\ m^3;\ M_S = 53.8\ Kg}$

$V_I = 0.096 + 0.039\ (53.8)$; $\boldsymbol{V_I = 2.2\ m^3}$

$M_F = 53.8\ Kg * 5$; $\boldsymbol{M_F = 269\ Kg}$

$\boldsymbol{V_F = 2.8\ m^3}$

$M_L = 39\ (53.8\ Kg)$; $M_L = 2098\ Kg$

b. F/I= 10.0

$M_F/M_S = 10.0$

$96\ V_F\ /560\ V_S = 10.0$; $V_F = 58.3\ V_S$

$59.3\ V_S + 0.039 M_S = 5\ m^3$

$59.3\ V_S + 0.039(560\ V_S) = 5\ m^3$; $81.14\ V_S = 5\ m^3$;

$\boldsymbol{V_S = 0.062\ m^3;\ M_S = 34.7\ Kg}$

$V_I = 0.062 + 0.039\ (34.7)$; $\boldsymbol{V_I = 1.4\ m^3}$

$M_F = 34.7\ Kg * 10$; $\boldsymbol{M_F = 347\ Kg}$

$\boldsymbol{V_F = 3.6\ m^3}$

$M_L = 39\ (34.7\ Kg)$; $M_L = 1354\ Kg$

c. F/I=30.0

$M_F/M_S = 30.0$

$96\ V_F\ /560\ V_S = 30.0$; $V_F = 175\ V_S$

$176\ V_S + 0.039 M_S = 5\ m^3$

$176\ V_S + 0.039\ (560\ V_S) = 5\ m^3$; $197.8\ V_S = 5\ m^3$;

$\boldsymbol{V_S = 0.025\ m^3;\ M_S = 14.2\ Kg}$

$V_I = 0.025 + 0.039\ (14.2)$; $\boldsymbol{V_I = 0.6\ m^3}$

$M_F = 14.2\ Kg * 30$; $\boldsymbol{M_F = 425\ Kg}$

$\boldsymbol{V_F = 4.4\ m^3}$

$M_L = 39\ (14.2\ Kg)$; $M_L = 552\ Kg$

2. Heat capacity

$$C_p = (m_{Feed}/m)C_{p\ Feed} + (m_{Sludge}/m)C_{p\ Sludge} + (m_{Water}/m)C_{p\ Water}$$

a. F/I= 5.0

$C_p[\text{KJ/ Kg °C}] = (269\ /2421)(1.75) + (53.8/2421)(1.35) + (2098/2421)(4.19)$

$C_p[\text{KJ/ Kg °C}] = 0.19 + 0.03 + 3.63$; $\boldsymbol{C_p = 3.85\ \text{KJ/ Kg °C}}$

b. F/I= 10.0

$C_p[\text{KJ/ Kg °C}] = (347/1736)(1.75) + (34.7/1736)(1.35) + (1354/1736)(4.19)$

$C_p[\text{KJ/ Kg °C}] = 0.35 + 0.03 + 3.27$; $\boldsymbol{C_p = 3.65\ \text{KJ/ Kg °C}}$

c. F/I=30.0

$C_p[\text{KJ/ Kg °C}] = (425/991)(1.75) + (14.2/991)(1.35) + (552/991)(4.19)$

$C_p[\text{KJ/ Kg °C}] = 0.75 + 0.02 + 2.33$; $\boldsymbol{C_p = 3.10\ \text{KJ/ Kg °C}}$

3. Heating Energy (Q) and Produced Energy (E_p)

$Q = m \cdot c_p \cdot \Delta T$

$E_p = m \cdot BMP \cdot HHV_{CH_4}(TS/100)$

Anaerobic digestion at 30 °C

a. F/I =5.0

$Q = m \cdot c_p \cdot \Delta T$

$Q = 2421\ Kg\ (3.85\ KJ/\ Kg\ °C)(\ 10\ °C)\ (MJ/1000\ KJ)$

$\boldsymbol{Q = 93.2\ MJ}$

$E_p = (269\ \cancel{Kg})\ (328.0 \pm 16.3\ \cancel{L}/\cancel{Kg})(0.0398\ MJ/\cancel{L})\ (0.09)$

$E_p = 316.0 \pm 15.7\ MJ$

b. F/I =10.0

$Q = m \cdot c_p \cdot \Delta T$

$Q = 1736\ Kg\ (3.65\ KJ/\ Kg\ °C)(\ 10\ °C)\ (MJ/1000\ KJ)$

$\boldsymbol{Q = 63.4\ MJ}$

$E_p = (347\ \cancel{Kg})\ (330.3 \pm 5.2\ \cancel{L}/\cancel{Kg})(0.0398\ MJ/\cancel{L})\ (0.09)$

$\boldsymbol{E_p = 410.5 \pm 6.5\ MJ}$

c. F/I =30.0

$Q = m \cdot c_p \cdot \Delta T$

$Q = 991\ Kg\ (3.10\ KJ/\ Kg\ °C)(\ 10\ °C)\ (MJ/1000\ KJ)$

$\boldsymbol{Q = 30.7\ MJ}$

$E_p = (425\ \cancel{Kg})\ (263.6 \pm 23.0\ \cancel{L}/\cancel{Kg})(0.0398\ MJ/\cancel{L})\ (0.09)$

$\boldsymbol{E_p = 400.4 \pm 34.8\ MJ}$

Anaerobic digestion at 40 °C

d. F/I =5.0

$Q = m \cdot c_p \cdot \Delta T$

$Q = 2421\ Kg\ (3.85\ KJ/\ Kg\ °C)(\ 20\ °C)\ (MJ/1000\ KJ)$

$\boldsymbol{Q = 186.4\ MJ}$

$E_p = (269\ \cancel{Kg})\ (346.3 \pm 20.6\ \cancel{L}/\cancel{Kg})(0.0398\ MJ/\cancel{L})\ (0.09)$

$\boldsymbol{E_p = 333.7 \pm 19.8\ MJ}$

e. F/I =10.0

$Q = m \cdot c_p \cdot \Delta T$

$Q = 1736\ Kg\ (3.65\ KJ/\ Kg\ °C)(\ 20\ °C)\ (MJ/1000\ KJ)$

$\boldsymbol{Q = 126.8\ MJ}$

$E_p = (347\ \cancel{Kg})\ (308.4 \pm 0.6\ \cancel{L}/\cancel{Kg})(0.0398\ MJ/\cancel{L})\ (0.09)$

$\boldsymbol{E_p = 383.3 \pm 0.7\ MJ}$

f. F/I =30.0

$Q = m \cdot c_p \cdot \Delta T$

$Q = 991\ Kg\ (3.10\ KJ/\ Kg\ °C)(\ 20\ °C)\ (MJ/1000\ KJ)$

$\boldsymbol{Q = 61.4\ MJ}$

$E_p = (425\ \cancel{Kg})\ (284.3 \pm 15.9\ \cancel{L}/\cancel{Kg})(0.0398\ MJ/\cancel{L})\ (0.09)$

$$E_p = 432.8 \pm 24.2\ MJ$$

Appendix C. ANOVA for the Biochar, Alkali and Temperature Effects on the Biomethanation Kinetics of AWAO Water Hyacinth

a. 21 Days of Digestion

```
> summary(aov.Methane_AWAO_BC_21)
               Df Sum Sq Mean Sq F value  Pr(>F)
Alkali_21       2   1078     539   0.844 0.45054
Biochar_21      2   1437     719   1.126 0.35200
Temperature_21  2  11796    5898   9.243 0.00276 **
Residuals      14   8934     638
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
> summary(aov.Kz_AWAO_BC_21)
               Df Sum Sq Mean Sq F value   Pr(>F)
Alkali_21       2  19.81    9.90   2.904 0.088114 .
Biochar_21      2   1.65    0.82   0.242 0.788504
Temperature_21  2  90.21   45.11  13.226 0.000595 ***
Residuals      14  47.75    3.41
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
> summary(aov.Tlag_AWAO_BC_21)
               Df Sum Sq Mean Sq F value Pr(>F)
Alkali_21       2   1.62   0.811   0.188  0.831
Biochar_21      2  11.79   5.895   1.366  0.287
Temperature_21  2   8.53   4.267   0.989  0.397
Residuals      14  60.41   4.315
> TukeyHSD(aov.Methane_AWAO_BC_21)
  Tukey multiple comparisons of means
    95% family-wise confidence level

Fit: aov(formula = Methane_yield_21 ~ Alkali_21 + Biochar_21 + Temperat
ure_21, data = df_AWAO_BC_21)

$Alkali_21
                diff       lwr      upr     p adj
0.07-0      4.213333 -39.86351 48.29017 0.9661658
0.14-0    -11.045556 -55.12240 33.03129 0.7921419
0.14-0.07 -15.258889 -46.42592 15.90814 0.4280294

$Biochar_21
              diff       lwr      upr     p adj
0.05-0   14.204286 -21.13581 49.54438 0.5578734
0.1-0    19.617143 -15.72295 54.95724 0.3422249
0.1-0.05  5.412857 -29.92724 40.75295 0.9157521

$Temperature_21
              diff        lwr        upr     p adj
```

```
80-22    35.074444  -16.84342  86.992304 0.2474257
100-22   -9.767222  -61.68508  42.150638 0.9458873
170-22  -25.307222  -77.22508  26.610638 0.5099297
100-80  -44.841667  -87.23242  -2.450912 0.0366618
170-80  -60.381667 -102.77242 -17.990912 0.0048886
170-100 -15.540000  -57.93076  26.850755 0.7151103

> TukeyHSD(aov.Kz_AWAO_BC_21)
  Tukey multiple comparisons of means
    95% family-wise confidence level

Fit: aov(formula = CH4_rate_21 ~ Alkali_21 + Biochar_21 + Temperature_2
1, data = df_AWAO_BC_21)

$Alkali_21
                diff       lwr       upr     p adj
0.07-0     1.8777778 -1.344500 5.1000551 0.3095319
0.14-0    -0.1111111 -3.333388 3.1111662 0.9955210
0.14-0.07 -1.9888889 -4.267383 0.2896052 0.0913231

$Biochar_21
              diff       lwr      upr     p adj
0.05-0   0.5000000 -2.083569 3.083569 0.8693943
0.1-0    0.6571429 -1.926427 3.240712 0.7866848
0.1-0.05 0.1571429 -2.426427 2.740712 0.9861397

$Temperature_21
         diff       lwr        upr     p adj
80-22    2.55 -1.245502  6.3455020 0.2514720
100-22   0.35 -3.445502  4.1455020 0.9929542
170-22  -2.90 -6.695502  0.8955020 0.1653826
100-80  -2.20 -5.299014  0.8990144 0.2124585
170-80  -5.45 -8.549014 -2.3509856 0.0008071
170-100 -3.25 -6.349014 -0.1509856 0.0385070
```

b. 55 Days of Digestion

```
> aov.Methane_AWAO_BC <- aov(Methane_yield~ Alkali + Biochar + Temperat
ure + Pretreatment, data = df_AWAO_BC)
>  summary(aov.Methane_AWAO_BC)
            Df Sum Sq Mean Sq F value Pr(>F)
Alkali       2    922     461   0.548 0.5901
Biochar      2   1221     610   0.726 0.5014
Temperature  2   9559    4779   5.681 0.0156 *
Residuals   14  11778     841
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
> aov.Methane_AWAO_BC <- aov(Methane_yield~ Alkali + Biochar + Temperat
ure + Pretreatment, data = df_AWAO_BC)
> summary(aov.Methane_AWAO_BC)
            Df Sum Sq Mean Sq F value Pr(>F)
Alkali       2    922     461   0.548 0.5901
Biochar      2   1221     610   0.726 0.5014
Temperature  2   9559    4779   5.681 0.0156 *
```

```
Residuals   14  11778     841
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1


> aov.Kz_AWAO_BC <- aov(CH4_rate~ Alkali + Biochar + Temperature + Pret
reatment, data = df_AWAO_BC)
> summary(aov.Kz_AWAO_BC)
            Df Sum Sq Mean Sq F value Pr(>F)
Alkali       2   4.59   2.293   1.192 0.3327
Biochar      2   1.52   0.760   0.395 0.6808
Temperature  2  31.93  15.965   8.297 0.0042 **
Residuals   14  26.94   1.924
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
> aov.Tlag_AWAO_BC <- aov(T_lag~ Alkali + Biochar + Temperature + Pretr
eatment, data = df_AWAO_BC)
> summary(aov.Tlag_AWAO_BC)
            Df Sum Sq Mean Sq F value Pr(>F)
Alkali       2  49.64  24.820   2.912 0.0876 .
Biochar      2  35.90  17.949   2.106 0.1587
Temperature  2  57.28  28.641   3.360 0.0643 .
Residuals   14 119.34   8.525
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
> Int_aov.Tlag_AWAO_BC <- aov(T_lag~ Alkali * Temperature +  Biochar +
Pretreatment, data = df_AWAO_BC)
> summary(Int_aov.Tlag_AWAO_BC)
                  Df Sum Sq Mean Sq F value Pr(>F)
Alkali             2  49.64  24.820   2.760 0.1033
Temperature        2  57.28  28.641   3.185 0.0777 .
Biochar            2  35.90  17.949   1.996 0.1786
Alkali:Temperature 2  11.42   5.711   0.635 0.5469
Residuals          12 107.92   8.994
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
> summary(aov(T_lag~ Alkali, data = df_AWAO_BC))
            Df Sum Sq Mean Sq F value Pr(>F)
Alkali       2  49.64   24.82   2.102  0.151
Residuals   18 212.52   11.81
> Int_aov.Tlag_AWAO_BC <- aov(T_lag~ Alkali * Temperature + Biochar, da
ta = df_AWAO_BC)
> summary(Int_aov.Tlag_AWAO_BC)
                  Df Sum Sq Mean Sq F value Pr(>F)
Alkali             2  49.64  24.820   2.760 0.1033
Temperature        2  57.28  28.641   3.185 0.0777 .
Biochar            2  35.90  17.949   1.996 0.1786
Alkali:Temperature 2  11.42   5.711   0.635 0.5469
Residuals          12 107.92   8.994
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
>
> TukeyHSD(aov.Methane_AWAO_BC, "Temperature", ordered = TRUE)
  Tukey multiple comparisons of means
    95% family-wise confidence level
    factor levels have been ordered
```

```
Fit: aov(formula = Methane_yield ~ Alkali + Biochar + Temperature + Pre
treatment, data = df_AWAO_BC)

$Temperature
             diff        lwr       upr     p adj
22-170  31.535251 -28.076153  91.14665 0.4427930
100-170 40.182946  -8.489562  88.85545 0.1228257
80-170  54.422807   5.750299 103.09531 0.0264147
100-22   8.647695 -50.963709  68.25910 0.9738353
80-22   22.887556 -36.723848  82.49896 0.6860506
80-100  14.239861 -34.432646  62.91237 0.8296760

> TukeyHSD(aov.Kz_AWAO_BC, "Temperature", ordered = TRUE)
  Tukey multiple comparisons of means
    95% family-wise confidence level
    factor levels have been ordered

Fit: aov(formula = CH4_rate ~ Alkali + Biochar + Temperature + Pretreat
ment, data = df_AWAO_BC)

$Temperature
             diff        lwr      upr     p adj
100-170 1.0500000 -1.2778541 3.377854 0.5712676
22-170  1.4166667 -1.4343607 4.267694 0.4943389
80-170  3.2000000  0.8721459 5.527854 0.0064285
22-100  0.3666667 -2.4843607 3.217694 0.9814584
80-100  2.1500000 -0.1778541 4.477854 0.0747339
80-22   1.7833333 -1.0676940 4.634361 0.3059060
```

Appendix D. Energy Analysis for the Biomethanation of Low Temperature Wet Air Oxidized Water Hyacinth

31 days of digestion

1. Mass balance/ Heat capacity

1000 kg (m_{Feed}) of fresh water hyacinth has 910 kg of water, and 90 kg of solids. To reach 50 g/L (5% w/v), 1800 kg of water is required in total and 890 kg of water (m_{Water}) would be added to 1 ton (1000 kg) of fresh water hyacinth. The total mass (m) would be 1890 kg.

Since adding water to the system is not practical, $m = 1000$ kg and $C_p = 1.75 KJ/\ Kg\ °C$ will be assumed, which means that the system would have 9.9% solids.

2. Heating Energy (Q) and Produced Energy (Ep)

AWAO

$$Q = m \cdot c_p \cdot \Delta T$$

$$Q = 1000\ Kg\ (1.75\ KJ/\ Kg\ °C)(\ 60\ °C)\ (MJ/1000\ KJ)$$

$$Q = 105.0\ MJ$$

$$E_p = m \cdot BMP \cdot HHV_{CH_4}(TS/100)$$

$$E_p = (1000\ Kg)\ (129.7 \pm 5.3\ L/Kg)(0.0398\ MJ/L)\ (0.09)$$

$$E_p = 464.6 \pm 19.0\ MJ$$

$$E_{net} = (464.6 \pm 19.0) - (105.0\ )MJ$$

$$E_{net} = 359.6 \pm 19.0\ MJ$$

Unpretreated

$$E_p = (1000\ Kg)\ (94.8 \pm 11.8\ L/Kg)(0.0398\ MJ/L)\ (0.09)$$

$$E_p = 339.6 \pm 42.3\ MJ$$

$$E_{net} = 339.6 \pm 42.3\ MJ$$

CURRICULUM VITAE

Yessica A. Castro

Education

Ph.D., Biological Engineering — Dec 2020
Utah State University (USU), Logan, Utah, US. — GPA 3.73
Proposal: "Biomethanation and alkaline wet air oxidation of water hyacinth (*Pontederia crassipes*) from eutrophic rivers"
Adviser: Dr. F. Agblevor.

M.Sc., Biological Engineering — Nov 2014
Utah State University (USU), Logan, Utah, US. — GPA 3.67
Thesis: "Optimization of Wastewater Microalgae Pretreatment for Acetone, Butanol, and Ethanol Fermentation"
Adviser: Dr. R. Sims.

B.E., Industrial Engineering — Jun 2010
Universidad Autónoma de Santo Domingo (UASD), Santo Domingo, DO — GPA 3.52
" Process Improvement Techniques"

Research Experience

Research Associate
Instituto Especializado de Estudios Superiores Loyola (IEESL), San Cristóbal, DO. — 2016-2020

- Gained funds for research to contribute with the solution of an environmental problem in the Dominican Republic by bioconversion of invasive aquatic plants into bioenergy.
- Collaborated with a multidisciplinary team on the design of physical-chemistry, molecular biology, microbiology, entomology, and bioenergy integrated laboratory units.
- Divulgated research findings in conferences and scientific journals after conducting statistically designed experiments.

Teaching Experience

Lecturer (Mechanics, Engineering Economics)

Universidad APEC (UNAPEC), Santo Domingo, DO 2015-2016

Developed curriculum in all areas including instruction, grading, preparing tests (quizzes, midterms, and finals), and assigning final grades assisted by instructional technology tools (i.e. MOODLE).

Teacher Assistant (General Physics)

Universidad Autónoma de Santo Domingo (UASD), Santo Domingo, DO 2009-2010

Facilitated theoretical and experimental instruction and evaluation including assigning final laboratory grades.

Consulting Experience

Junior Consultant

Serviguide Dominicana, Santo Domingo, DO 2010-2011

- Participated in the initial assessment on Good Manufacturing Practices (GMP), Hazard Analysis Control of Critical Points (HACCP), ISO 9001, ISO 22000, and ISO 14000 standards of 18 exporting companies.
- Assisted 8 companies on the successful implementation of GMP, HACCP, ISO 9001, or ISO 22000, including the preparation of documentation required for certification.
- Audited internally 7 exporting companies against Good Manufacturing Practices (GMP), Hazard Analysis Control of Critical Points (HACCP), ISO 9001, and ISO 22000 standards.

Industry Experience

Project Engineer

Alimentos Fortuna, S.R.L, Santiago Rodríguez, DO 2011-2012

- Prepared documentation for manufacturing processes and engineering procedures adhering applicable regulations for food safety and environmental compliance.
- Designed the layout of a new production plant to achieve maximum efficiency.

Publications

Castro, Y.A., Agblevor, F.A., 2020. Effect of high feed to inoculum ratio (F/I), temperature, and inoculum acclimatization on the biomethanation kinetics of water hyacinth. SN Appl. Sci. https://doi.org/10.1007/s42452-020-03626-w

Castro, Y.A., Agblevor, F.A., 2020. Effect of wet air oxidation on the composition and biomethanation of water hyacinth. Biomass Convers. Biorefin. https://doi.org/10.1007/s13399-020-00825-8

Castro, Y.A., Agblevor, F.A., 2020. Biomethanation of invasive water hyacinth from eutrophic waters as a post weed management practice in the Dominican Republic, a developing country. Environ. Sci. Pollut. Res. https://doi.org/10.1007/s11356-020-07927-w

Castro, Y.A., Ellis, J.T., Miller, C.D., Sims, R.C., 2015. Optimization of wastewater microalgae saccharification using dilute acid hydrolysis for acetone, butanol, and ethanol fermentation. Appl. Energy 140, 14–19. https://doi.org/10.1016/j.apenergy.2014.11.045

Skills

Computer/ Statistics: R Studio, MOODLE, ArcGIS, Microsoft Office (Excel, Visio, PowerPoint)

Analytical Instruments: High-Pressure Liquid Chromatography (HPLC), Gas Chromatography (GC), Fourier Transform Infrared Spectroscopy (FTIR), Thermal gravimetric analysis (TGA), Elemental Analyzer (CHNSO), Scanning Electron Microscopy (SEM), and calorimeter.

Field/Research Techniques: microalgae cultivation, environmental quality analysis, plant collection and preparation, biomass characterization, media preparation, anaerobic fermentation, gas sampling, thermochemical pretreatment of biomass, distillation, and soxhlet extraction.

Languages: Spanish - native speaker , English - Fluent