Schriftenreihe Umweltingenieurwesen

Band 102

Dissertation

Edward Antwi

Pathways to sustainable bioenergy production from cocoa and cashew residues from Ghana

Professur

Abfall-
und Stoffstromwirtschaft

Agrar- und Umweltwissenschaftliche Fakultät

Universität
Rostock

Traditio et Innovatio

Dissertation

HERAUSGEBER

Prof. Dr. mont. Michael Nelles
Universität Rostock
Agrar- und Umweltwissenschaftliche Fakultät
Professur Abfall- und Stoffstromwirtschaft
18051 Rostock

CIP-KURZTITELAUFNAHME

Dissertation Edward Antwi
Universität Rostock
Agrar- und Umweltwissenschaftliche Fakultät
Rostock, 2020

BEZUGSMÖGLICHKEITEN

Universität Rostock
Universitätsbibliothek, Schriftentausch,
18051 Rostock
Tel.: 0381/498-8639, Fax: 0381/498-8632
E-Mail: tausch.ub@uni-rostock.de

Universität Rostock
Agrar- und Umweltwissenschaftliche Fakultät
Professur Abfall- und Stoffstromwirtschaft
Justus-von-Liebig-Weg 6, 18059 Rostock
Tel.: 0381/498-3401, Fax: 0381/498-3402

ISBN 978-3-86009-520-1
https://doi.org/10.18453/rosdok_id00002818

Universität Rostock
Professur Abfall- und Stoffstromwirtschaft

Gedruckt in Deutschland auf Recyclingpapier.

Vorwort

Deutschland hat in den letzten Jahren das Engagement in Afrika verstärkt und fast alle Bundesministerien haben eigene Afrikastrategien entwickelt, die derzeit im Rahmen der jeweiligen Ressortzuständigkeiten umgesetzt werden. In diesen Programmen spielen die Themen Umwelt- und Klimaschutz sowie erneuerbare Energien eine zentrale Rolle und Ghana gehört zu den regionalen Schwerpunktländern der Aktivitäten. Ghana hat sich in den letzten Jahren gut entwickelt und im Rahmen der Zusammenarbeit mit Deutschland werden derzeit eine ganze Reihe von Kooperationsvorhaben bearbeitet. Vor diesem Hintergrund engagiert sich auch unsere Professur für Abfall- und Stoffstromwirtschaft in Ghana und unterstützt u.a. bei dem Aufbau abfallwirtschaftlicher Strukturen. Ein Schwerpunkt ist dabei die Sammlung und umweltverträgliche Verwertung von biogenen Abfällen und Reststoffen, die in Ghana in großen Mengen u.a. in der Landwirtschaft anfallen.

So werden z.B. Kakao- und Cashew-Bohnen im großen Stil für die Versorgung des Weltmarktes angebaut, wo bei der Ernte und Weiterverarbeitung bis zum Transport der eigentlichen Kakao- und Cashew-Bohnen bis zu 90 M-% als biogener Abfall anfallen und dafür eine geordnete Entsorgung fehlt. Hier setzt das Promotionsvorhaben von Herrn Antwi an und damit hat er ein sehr praxisrelevantes Forschungsthema gewählt.

Das übergeordnete Ziel des Promotionsvorhabens ist es, für die biogenen Reststoffe aus der landwirtschaftlichen Produktion von Kakao- und Cashew-Bohnen eine umweltverträgliche Verwertungsoption zu konzipieren und dabei gleichzeitig einen Beitrag zur nachhaltigen Energieversorgung zu leisten.

Das Vorhaben von Herrn Antwi wurde im Rahmen des Promotionsprogramms „Stoffliche und energetische Verwertung von Abfälle und Biomasse“ bearbeitet, das von der Professur Abfall- und Stoffstromwirtschaft an der Uni Rostock koordiniert wird. Finanziell unterstützt wurde das Promotionsvorhaben vom DAAD mittels eines PhD-Stipendiums über insgesamt 3,5 Jahre, was sehr hilfreich war. Die Ergebnisse wurden in der vorliegenden Dissertation in Form einer Monografie ausgewertet und Herr Antwi hat die Arbeit im Sommer 2020 an der Agrar- und Umweltwissenschaftlichen Fakultät eingereicht.

Die wissenschaftliche Bedeutung der vorliegenden Arbeit ergibt sich aus Sicht der Gutachter insbesondere aus folgenden Punkten:

- Herr Antwi hat sich in den letzten 4 Jahren sehr intensiv mit den Möglichkeiten und Grenzen der kombinierten stofflichen und energetischen Verwertung von biogenen Reststoffen aus der landwirtschaftlichen Produktion von Kakao- und Cashew-Bohnen beschäftigt und hierzu u.a. wissenschaftlich fundierte Abschätzungen zu den anfallenden Mengen vorgenommen.

Damit liegen für Ghana erstmals fundierte Zahlen vor, die für die Realisierung von umweltverträglichen Entsorgungslösungen eine Grundvoraussetzung darstellen. Insgesamt fallen hier jährlich rund 2 Mio. Mg Trockenmasse an, für die eine nachhaltige Verwertungslösung gefunden werden muss.

- Hierzu werden von Herrn Antwi konkrete technische Verwertungskonzepte auf Basis der prinzipiell geeigneten Behandlungsverfahren (hydrothermale Karbonisierung und Biogastechnik) entwickelt und umfangreiche praktische Versuche im Labormaßstab durchgeführt. Die Ergebnisse belegen, dass beide Verfahrensoptionen zur Lösung des Entsorgungsproblems technisch realisierbar und auch wirtschaftlich darstellbar sind. Darüber hinaus kann ein erheblicher Beitrag zum Klimaschutz und zur nachhaltigen regionalen Energieversorgung in Ghana geleistet werden. Nun geht es darum, die wissenschaftlichen Erkenntnisse in die Praxis der landwirtschaftlichen Produktion und Aufbereitung von Kakao- und Cashew-Bohnen in Ghana zu integrieren.

Abschließend wünschen wir Ihnen nun interessante fachliche Anregungen und viel Spaß beim Lesen der Dissertation von Herr Dr.-Ing. Edward Antwi.

Herzliche Grüße aus Kumasi, Göttingen und Rostock senden

Prof. Dr. Ahmad Addo
Kwame Nkrumah University of
Science and Technology Kumasi

Achim Loewen

Prof. Dr.-Ing. Achim Loewen
Hochschule für Angewandte
Wissenschaften und Kunst
Hildesheim/Holzminden/Göttingen

M. Nelles

Prof. Dr. mont. Michael Nelles
Universität Rostock und
Deutsches Biomasseforschungszentrum gGmbH (DBFZ) Leipzig

Preface

Germany has increased its engagement in Africa in recent years and almost all federal ministries have developed their own Africa strategies, which are currently being implemented within the scope of the respective departmental responsibilities. In these programs, the topics of environmental and climate protection as well as renewable energies play a central role and Ghana is one of the regional focus countries of the activities. Ghana has developed well in recent years and a whole series of cooperation projects are currently being worked on within the framework of cooperation with Germany. Against this background, our professorship for waste and resource management is also involved in Ghana and supports, among other things in the development of waste management structures. One focus is the collection and environmentally friendly recycling of biogenic waste and residues, which are produced in large quantities e.g. in agriculture in Ghana.

As an example, cocoa and cashew beans are grown on a large scale to supply the world market. During harvesting, processing and transport, up to 90 w.-% of the actual cocoa and cashew beans end up as biogenic waste and for this there is no proper disposal yet. This is where Mr. Antwi's PhD project comes in and he has thus chosen a very practice-relevant research topic.

The overarching goal of the PhD project is to design an environmentally friendly recycling option for the biogenic residues from the agricultural production of cocoa and cashew beans, while at the same time making a contribution to sustainable energy supply.

The project of Mr. Antwi was worked on within the framework of the PhD program "Material and energetic utilization of waste and biomass", which is coordinated by the professorship of waste and resource management at the University of Rostock. The PhD project was financially supported by the DAAD through a PhD scholarship for a total of 3.5 years, which was very helpful. The results were evaluated in the present dissertation in the form of a monograph and Mr. Antwi submitted the work to the Faculty of Agricultural and Environmental Sciences in summer 2020.

From the perspective of the reviewers, the scientific significance of the present work results in particular from the following points:

- In the last 4 years, Mr. Antwi has dealt very intensively with the possibilities and limits of the combined material and energetic utilization of biogenic residues from the agricultural production of cocoa and cashew beans and made scientifically based estimates of the quantities produced. This is the first time that well-founded figures are available for Ghana, which represent a basic requirement for the implementation of environmentally friendly disposal solutions. In total, around 2 million Mg of dry matter are produced here every year, for which a sustainable recycling solution must be found.

- For this purpose, Mr. Antwi develops specific technical recycling concepts based on the treatment processes that are technically suitable (hydrothermal carbonation and biogas technology) and extensive practical tests are carried out on a laboratory scale. The results show that both process options are technically and economically feasible for solving the disposal problem. In addition, a significant contribution to climate protection and sustainable regional energy supply in Ghana can be made. The task now is to integrate the scientific findings into the practice of agricultural production and processing of cocoa and cashew beans in Ghana.

Finally, we wish you interesting technical suggestions and a lot of fun reading the dissertation of Dr.-Eng. Edward Antwi.

Sending warm greetings from Kumasi, Göttingen and Rostock

Prof. Dr. Ahmad Addo
Kwame Nkrumah University of
Science and Technology Kumasi

Achim Loewen

Prof. Dr.-Ing. Achim Loewen
Hochschule für Angewandte
Wissenschaften und Kunst
Hildesheim/Holzminden/Göttingen

M. Nelles

Prof. Dr. mont. Michael Nelles
Universität Rostock und
Deutsches Biomasseforschungszentrum gGmbH (DBFZ) Leipzig

Universität Rostock Traditio et Innovatio

Professorship for Waste and Resource Management
Faculty of Agriculture and Environmental Science

Pathways to sustainable bioenergy production from cocoa and cashew residues from Ghana

Dissertation

Submitted in fulfillment for the award of Doctor of Engineering (Dr.-Ing)

At the Faculty of Agriculture and Environmental Science
University of Rostock

Presented by

Edward Antwi (M.Sc.)

Rostock

Rostock, 2020

Gutacher:

Prof. Dr. Michael Nelles
Universität Rostock, AUF, Abfall- und Stoffstromwirtschaft

Prof. Dr. Achim Loewen
Hochschule für Angewandte Wissenschaft und Kunst Hildesheim/Holzminden/Göttingen, Fakultät Ressourcenmanagement,
Fachgebiet Nachhaltige Energie- und Umwelttechnik NEUTec

Prof. Ahmad Addo
Kwame Nkrumah University of Science and Technology,

Tag der Einreichung: 26. Juni 2020
Tag der Verteidigung: 06. November 2020

This thesis was printed with the support of the German Academic Exchange Service

Declaration of independence

I hereby solemnly declare this work was prepared and submitted independently by me without the assistance of any other person except those duly cited and acknowledged.

Signature Date:

Dedication

This thesis is dedicated to Abena Adepa my sweet wife, and children – John Marvel Tutu, Jesse Jackson and Gracie-Mariah Adepa

Acknowledgment

My sincerest gratitude goes first to Prof. mont Michael Nelles who went the extra mile to accept me into his workgroup to carry out this work and for supervising the completion of this thesis. I wish to also acknowledge and thank Dr. Andrea Schüch with whom I have been working directly for the past three and a half years. Her useful advice, comments, and suggestions have contributed immensely to shape the direction of this thesis as well as improve on the quality of the presentation. She has been a great de-facto supervisor with whom I have had great pleasure working with. I am immensely grateful to Dr. Nils Engler who supervised almost all the laboratory work and assisted me in times of difficulty not to mention his generosity to allow me to work sometimes on Saturdays and Sundays in the laboratory. To his wonderful technical staff in the persons of Mrs. Kersten Eckermann and Mrs. Peggy Wefers who were always ready to assist me in all my experiments, I say thank you very much. I am very grateful for your time and effort in helping me achieve this lifetime goal. I wish to also acknowledge Dr. habil Satyanarayana Narra, Dr. habil Nassour, Dr. Gert Morsheck, and Dr. Ruth Gebauer who in one way or the other have inspired and brought out the best in me. Often when the going gets tough, there is always a shoulder to fall on for advice and counseling. And not to forget Mrs. Christine Herz, our indefatigable administrator who assisted me with all the complex administrative process during my studies. Thank you very much, madam. My sincerest gratitude also goes to all my PhD colleagues some of whom I shared an office with, in the persons of Wassim Chaabane and Qahtan Thabit, Jan Sprafke who took time off his busy schedule to assist me in bringing samples from Ghana and Vicky Shettigondahalli Ekanthalu for your inputs, suggestions and useful discussions over the last three and half years. Not to forget the contributions of Isabell Eickhoff, Ying Zhou, Mona-Maria Narra, Nour Chaher, Sebastian Foth, and Jan Klein, most especially for your friendship and productive academic discussions. I strongly believe through our shared common interest in making the world a better place through waste and resource management, we have built both professional and personal relationships that can last a lifetime. My PhD colleagues from other departments in persons of Charles Ayensu Okai with whom I journeyed together to Rostock from Ghana to begin our studies, Bright Danquah our senior colleague, all my DAAD 2016 batch scholars and Dr. Kay have all been a solid rock of comfort and advice. Thank you for your friendship. Special thanks also go to Benjamin Boahen who organized all my samples in Ghana and Nana Kwame Gyamfi who assisted me under very difficult and challenging circumstances. The spiritual support by Pastor Daniels Weimer and the entire congregation of Christliches Zentrum, Rostock is also acknowledged. Through you, I have come to know some very warm hearts and fantastic people of great faith in Rostock. Every worship meeting was savored. Thank you.

The financial support obtained through the German Academic Exchange Services (DAAD) and the Government of Ghana through the Ministry of Education partnership and the Federal Ministry of Education and Research for the completion of this thesis is acknowledged and deeply appreciated.

Lastly, my greatest gratitude goes to Jehovah who has kept faith with me and showed me greater mercies and favor.

Abstract

This thesis evaluated the potential of bioenergy production from cocoa pods residues and cashew peduncle residues using two pathways – anaerobic digestion process and hydrothermal carbonization process. Bench-scale anaerobic digestion studies were conducted to determine the kinetic parameters of the digestion process, while a large-scale reactor experiment was conducted to validate the kinetic models. The potential of using hydrothermal treatment as a pretreatment step to hydrolyze the substrate leading to enhanced biogas yield was also investigated. Further studies were conducted to determine the digestibility of residues during anaerobic digestion under mesophilic conditions in semi-continuous mode in a continuous stirred tank reactor as mono substrates and as co-substrates with maize silage. The effect of varying process parameters on the yield, higher heating value, ash content, and Chemical Oxygen Demand (COD) of the hydrolysate during hydrothermal carbonization of the residues were investigated. In addition, the possibility of multiple interactive effects of the process parameters on the yield, heating value, ash content, and the COD of hydrolysate was also investigated.

The result of the anaerobic digestion studies showed that cocoa pods and cashew peduncles were digestible with a specific biogas yield of 357 l(N)/kgVS. The kinetic parameters obtained for cocoa pods (Kl = 0.08/day, α = 0.7, Kf = 11.0 /day, S = 408.7 l(N)/kgVS and Kvfa = 0.42/day) were successfully used to predict the biogas yield in a larger reactor (30 l). The biodegradability of cocoa pods could be enhanced through mild hydrothermal pretreatment at an optimum temperature of 150 ºC and 15 minutes reaction time resulting in a specific biogas yield of 526 l(N)/kgVS. Semi-continuous mono substrate digestion of cocoa pods studies showed that the digestion of cocoa pods was stable between the OLR of 2.5 – 5.0 kgVS/m^3.day considered. However, biogas yield reduced linearly with increasing OLR. The studies confirmed that the biogas potential of the cashew peduncles was affected by the inoculum used. Exceeding OLR of 3.0 kgVS/m^3.day in a continuous stirred tank reactor led to excessive process inhibition. Phase separation and subsequent digestion of the cashew bagasse resulted in a stable anaerobic digestion process up to 4.0 kgVS/m^3.day. It was established further that the cashew peduncle can serve as a biogas promoter when it is co-digested with maize silage. However, this synergetic effect of the cashew peduncles is strongly dependent on the feed composition or the percentage of cashew peduncles in the feed composition. The result of the hydrothermal carbonization (HTC) study showed that the effect of process parameters on the fuel properties of the hydrochar produced was strongly dependent on the substrate used. The yield of cashew peduncle hydrochar was influenced by the process temperature and reaction time, the hydrochar yield of cocoa pods was influenced by all three process parameters investigated. Significant multiple interactive effects were observed between the process temperature and heating rate. The Higher heating value (HHV) correlated well with the process severity for both substrates. The HHV of cashew peduncle hydrochar was largely influenced by the temperature and reaction time without any interactive effect observed. On the contrary, the higher heating value of cocoa pods hydrochar was largely influenced by all three process parameters investigated with significant interactive effective observed between the process temperature and the heating rate. The ash content of the hydrochar from both residues was similar and both could be described with linear equations. The dominant process parameters were process temperature and reaction time with the heating rate having little or no effect on the ash content of the fuel. Significant interactive effects were observed in both cases between the process temperature and the reaction time.

Zusammenfassung

In dieser Arbeit wurde das Potenzial der Bioenergieproduktion aus Kakaofrucht- und Cashewstielresten auf zwei Wegen – dem anaeroben Aufschlussprozess und dem hydrothermalen Karbonisierungsprozess – untersucht. Fermentationstests im Labormaßstab wurden durchgeführt, um die kinetischen Parameter des Aufschlussprozesses zu bestimmen, und ein Reaktorexperiment im großen Maßstab wurde durchgeführt wurde, um die daraus entstandenen kinetischen Modelle zu validieren. Ferner wurde die die Nutzung einer hydrothermalen Behandlung als Vorbehandlungsschritt zur Hydrolyse des Substrats, was zu einer erhöhten Biogasausbeute führen kann, untersucht. Weitere Studien wurden durchgeführt, um die Abbaubarkeit der Gärreste während des anaeroben Aufschlusses unter mesophilen Bedingungen im halbkontinuierlichen Modus in einem kontinuierlichen Rührkesselreaktor als Monosubstrate und als Co-Substrate mit Maissilage zu bestimmen. Die Auswirkung variierender Prozessparameter auf die Gasausbeute, den höheren Heizwert, den Aschegehalt und den chemischen Sauerstoffbedarf (CSB) des Hydrolysats während der hydrothermalen Carbonisierung der Gärreste wurde ebenfalls untersucht. Darüber hinaus wurde die Möglichkeit mehrerer interaktiver Effekte der Prozessparameter auf die Gasausbeute, den Heizwert, Aschegehalt und CSB des Hydrolysats untersucht.

Das Ergebnis der anaeroben Aufschlussstudien zeigte, dass Kakaofrüchte und Cashewstiele mit einer spezifischen Biogasausbeute von 357 l (N) / kgVS abbaubar waren. Die für Kakaofrüchte erhaltenen kinetischen Parameter (Kl = 0,08/d; α = 0,7; Kf = 11,0/d; S = 408,7 l (N)/kgVS und Kvfa = 0,42/d) wurden erfolgreich verwendet, um die Biogasausbeute in einem größeren Reaktor vorherzusagen (30 l). Die biologische Abbaubarkeit von Kakaofrüchten konnte durch moderate hydrothermale Vorbehandlung bei einer optimalen Temperatur von 150 °C und einer Reaktionszeit von 15 Minuten verbessert werden, was zu einer spezifischen Biogasausbeute von 526 l(N)/kgVS führte. Studien zum semikontinuierlichen Monosubstratverdau von Kakaofrüchten zeigten, dass der Abbau von Kakaofrüchten zwischen dem betrachteten OLR von 2,5 - 5,0 kgVS/m^3*d stabil war. Die Biogasausbeute nahm jedoch mit zunehmender OLR linear ab. Die Studien bestätigten, dass das Biogaspotential der Cashewstiele durch das verwendete Inokulum beeinflusst wurde. Das Überschreiten der OLR von 3,0 kgVS/m^3*d in einem kontinuierlichen Rührkesselreaktor führte zu einer übermäßigen Prozesshemmung. Die Phasentrennung und der anschließende Aufschluss der Cashewbagasse führten zu einem stabilen anaeroben Aufschlussprozess bis zu 4,0 kgVS/m^3*d. Es wurde ferner festgestellt, dass der Cashewstiel als Biogaspromotor dienen kann, wenn er zusammen mit Maissilage verdaut wird. Diese synergetische Wirkung der Cashewstiele hängt jedoch stark von der Futterzusammensetzung oder dem Prozentsatz der Cashewstiele in dieser ab. Das Ergebnis der Studie zur hydrothermalen Karbonisierung (HTC) zeigte, dass die Auswirkung von Prozessparametern auf die Kraftstoffeigenschaften des hergestellten Hydrochars stark vom verwendeten Substrat abhängt. Die Ausbeute an Cashewstiel-Hydrochar wurde durch die Prozesstemperatur und Reaktionszeit beeinflusst; die Hydrochar-Ausbeute aus Kakaofrüchten wurde durch alle drei untersuchten Prozessparameter beeinflusst. Es wurden mehrere signifikante Synergien zwischen der Prozesstemperatur und der Heizrate beobachtet. Der höhere Heizwert (HHV) korrelierte gut mit der Prozessintensität für beide Substrate. Der HHV des Cashewstiel-Hydrochars wurde weitgehend von der Temperatur und der Reaktionszeit beeinflusst, ohne dass ein synergetischer Effekt beobachtet wurde. Im Gegensatz dazu wurde der höhere Heizwert von Kakaofrucht-Hydrochar weitgehend durch alle drei untersuchten Prozessparameter beeinflusst, wobei eine

signifikante Synergie zwischen der Prozesstemperatur und der Heizrate beobachtet wurde. Der Aschegehalt des Hydrochars aus beiden Rückständen war ähnlich und beide konnten mit linearen Gleichungen beschrieben werden. Die dominierenden Prozessparameter waren Prozesstemperatur und Reaktionszeit, wobei die Heizrate den Aschegehalt des Brennstoffs kaum oder gar nicht beeinflusste. In beiden Fällen wurde ein signifikanter synergetischer Effekt zwischen der Prozesstemperatur und der Reaktionszeit beobachtet.

Table of content

Table of figures

List of tables

List of abbreviations

AD	Anaerobic digestion
ADF	Acid Detergent Fibers
ADL	Acid Detergent Lignin
BD	Biodegradability Index
BET	Brunauer – Emmett – Teller
BMP	Biomethane Potential
C	Carbon
C/N	Carbon to Nitrogen Ratio
COD	Chemical Oxygen Demand
COMCashew	Competitive Cashew Initiative
CP	Annual Crop Production
CRIG	Cocoa Research Institute of Ghana
CSTR	Continous Stirred Tank Reactor
DOC	Degradable Organic Carbon
FOS	Volatile Organic Acids
GDP	Gross Domestic Product
GIS	Geographical Information system
GIZ	Gesellschaft für Internationale Zusammenarbeit
H	Hydrogen
H/C	Hydrogen to Carbon ratio
HHV	Higher Heating Value
HMF	Hydroxymethylfurfural
HRT	Hydraulic Retention Time
HTC	Hydrothermal Carbonization
IPCC	Intergovernmental Panel on Climate Change
LCOE	levelized Cost of Electricity
MCF	Methane Conversion Fraction
N	Nitrogen
NDF	Neutral Detergent Fibers
O	Oxygen
O/C	Oxygen to Carbon ratio
O/C	Oxygen to Carbon ratio
OLR	Organic Loading Rate
OS	Original Substances
r	Heating rate
R	Residues
RCN	Raw Cashew Nuts
RCR	Residue to Crop Ratio
RSM	Response Surface Methodology
S	Sulfur
S/I	Substrate to Inoculum Ratio
SI	Synergetic Index
t	Reaction time

T	Temperature
TAC	Total Alkalinity
TS	Total solids
VDI	Verein Deutscher Ingenieure
VFA	Volatile Fatty Acid
VS	Volatile Solids

1. Introduction

1.1 Background

Bioenergy continues to play a leading role in the global energy matrix. As of 2016, bioenergy accounted for 70% of all primary energy supply from renewable sources globally. This figure translates into about 56.5 EJ [1]. Even though the percentage share of bioenergy in the renewable energy matrix is expected to decrease marginally to 60% according to IRENA [2], strong growth is anticipated in the dependence on bioenergy globally reaching about 108 EJ by 2030 and accounting for nearly 20% of total primary energy supply globally. The projected increase in bioenergy consumption in the global primary energy supply is partly driven by environmental concerns associated with the exploitation of fossil fuels and the need to cut back on the dependence on fossil-derived fuels and partly due to energy security concerns in a highly volatile energy space where price fluctuation and uncertainties driven by political instabilities have a cascading effect on the economies of energy-dependent countries.

In Sub-Sahara Africa, dependence on bioenergy is still very strong and is estimated to account for nearly 60% of the primary energy supply [3]. This is especially so, as most of the continent is highly dependent on raw biomass in the form of woodfuels and charcoal to meet their domestic energy needs [4]. The situation is not different in Ghana. Even though the share of bioenergy in the primary energy supply matrix has seen a decline from about 51.8% in 2009 to about 36.9% in 2018 (Figure 1.1), in nominal terms, dependence on bioenergy has increased from 3,127 ktoe to 3,881 ktoe within the same period [5]. The percentage reduction in bioenergy's share of the primary energy supply is largely driven by an increase in dependence on oil and gas as shown in Figure 1.1. Ghana has over the last decade seen a significant shift from dependence on hydroelectric energy to thermal energy fueled with light crude oil and in some cases natural gas. As a result, Ghana has increased its carbon footprint with increasing and worrying signals of non-abatement. Greenhouse emissions have increased by about 67% above the levels in 1990 from 26.4 to 42.2 million tons of carbon dioxide equivalent in 2016 [6]. The emissions are disaggregated as follows;

1. The waste sector is driven by poor waste management practices accounting for nearly 7.5% of the total emissions,
2. The Agricultural and land-use sector which is the largest contributor to greenhouse gas emissions accounting for more than half (54%) of the total emissions,
3. The energy sector accounting for about 35.6% of the total emissions, and
4. The industrial process and product use accounting for the remaining 2.5% of the total emissions.

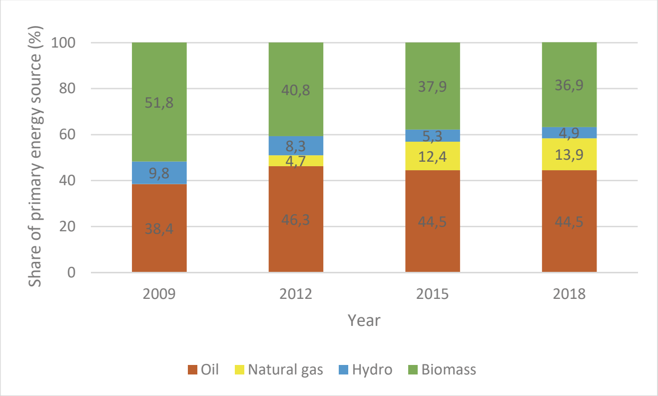


Figure 1.1: Primary energy supply in Ghana [7].

In recent times, sources to produce modern biofuels have evolved from food crops (1st generation biofuels) to agricultural residues and biogenic waste (2nd generation), and lately algae (3rd generation) [8,9]. However, according to Bentsen et al. [10], agricultural residues are by far the most abundant and fairly distributed bioenergy resources globally. This means every country has a fair share of resources for the exploitation of bioenergy. Secondly, the inherent contribution of agricultural residues to global emission of greenhouse gases present a very good opportunity for mitigation. According to Heidecke et al. [11], the EU identified crop residues as the third-largest contributor to direct N_2O emissions from agricultural soils. Further, the direct combustion of crop residues that takes place in tropical agricultural fields is also a leading contributor to greenhouse emissions. For instance, according to Bhattacharyya and Barman [12], if only 20% of rice residues are used for ethanol production, about 70 million tons of CO_2 equivalence could be saved. Additionally, crop residues present a unique opportunity to sequester carbon when they are converted to char. Nonetheless, the sheer abundance of agricultural residues also presents a formidable challenge in the choice of conversion pathway in that the resources are not homogenous even in the same country. Crops residues are so diverse in their physical structure, chemical composition, and mineral content. The physical structure and chemical diversity of the residues thus affect the treatment pathway, energy yield, and quality in terms of the characteristics of the final energy produced. The choice of agricultural residue as bioenergy feedstock does not only depend on the physical and chemical characteristics of the feedstock but also its availability.

Even though Ghana has moved from an agrarian driven economy to a service-driven economy, agriculture contributes a significant fraction of Ghana's Gross Domestic Product (GDP). In 2013 for instance, agriculture contributed about 22% of Ghana's GDP [13]. Aside from contributing significantly to the GDP of Ghana, agribusiness employs nearly 46.1% of the labor force in Ghana [14]. Crops production accounted for the bulk (77%) of the GDP from agriculture. As a result of the diversity of crops cultivated as shown in Figure 1.2, there is a high potential of generating huge quantities of agricultural residues that could serve as feedstock to produce modern biofuels. Indeed previous estimates of bioenergy potential have established a huge resource base for bioenergy generation in Ghana [15–17]. Among the crops cultivated in Ghana is cocoa. Cocoa is mainly cultivated for the beans which are an essential raw material in the confectionery and cosmetic industry globally. Even though cassava, yam, and plantain crop production far outweigh cocoa beans production, these food crops are not industrial crops in Ghana and are at present grown for only domestic consumption. Thus, cocoa beans production is such an important industrial crop for Ghana because of its huge foreign exchange earnings potential. It further doubles as having the greatest impact in terms of contribution to the GDP of Ghana. Cocoa beans single-handedly accounted for 2.2% of Ghana's GDP in 2013 [14].

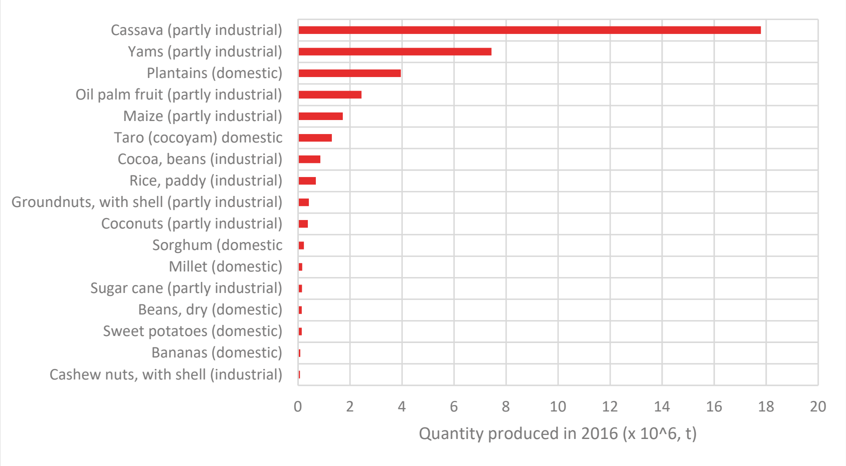


Figure 1.2: Crop production in Ghana [18].

Worldwide, the production of cocoa beans has been very strong, averaging about 4.3 x 10^6 t/a in the last decade [19]. West Africa accounts for more than 2/3rd of the total annual global production (Figure 1.3). Cocoa pods are the main residues generated at the harvesting stage of the cocoa beans [20]. It is estimated that about 40 x 10^6 t/a of cocoa pods are generated globally of which a greater majority is underutilized [21]. By implication, Africa also carries the burden of generating more than 28 x 10^6 t/a of cocoa pods annually which is not utilized. The huge quantum of cocoa pods generation worldwide presents a challenge but more importantly an opportunity to utilize it as a feedstock for bioenergy production. The case of Ghana is not different. The underutilization of cocoa pods have featured in bioenergy potential estimation carried out by Duku et al. [15] and Kemausuor et al. [17].

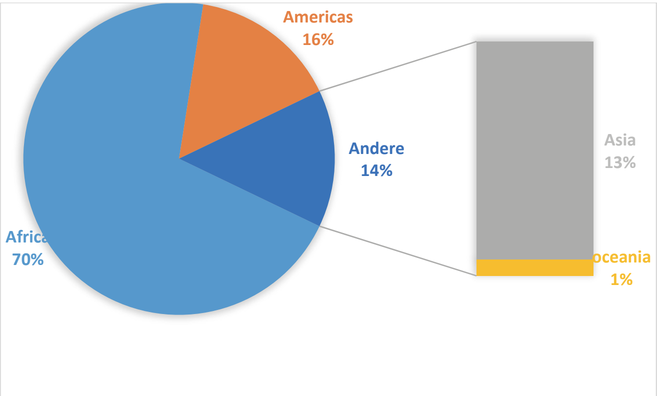


Figure 1.3: Regional production of cocoa beans worldwide [19].

Aside from cocoa, interest in cashew (Anacardium occidentale) cultivation has been growing across Africa in recent times not only because of their potential to earn foreign exchange at the national level but also to support household income at the family level. Thus, cashew nuts have now become the second most important cash crop after cocoa beans in West Africa [22]. Global production of cashew nut stood at about 4.9 x 10^6 tons as of 2016, with West and Eastern Africa accounting for about 52% [19]. Interestingly, West Africa increased its share of the global production of cashew nuts from 36% in 2013 [23] to about 45% in 2016 [19]. Until now, only the nuts have commercial value due to their nutritional content [24,25], leaving behind the peduncle which constitutes a significant mass of the entire fruit. Though the peduncle is reported to be rich in nutrients (protein, fat, and carbohydrates), vitamins (Vitamin C and beta carotene), and antioxidants [23,26,27], it has hardly found substantial commercial value, especially in Africa. This could be due to the short shelf life of the peduncle, which makes it difficult to store, transport, and process as well as its astringency. In Brazil and India, however, the peduncle has found limited commercial value in the processing of juice and alcoholic beverages. This is however not the case in West and Eastern Africa where apart from the nuts being collected for export, the peduncle is highly underutilized and in most cases left to decay on the farm [28]. Even in the limited use of the peduncle to produce fresh juice and gin, the bagasse, which is reported to consist of about 15% (w/w) of the peduncle, has no commercial value and as such discarded [29].

To enable the treatment and effective utilization of the cocoa pods and cashew peduncles residues, several valorization pathways including direct combustion [30], carbonization [31], and fermentation have been investigated with limited success in some cases. Syamsiro et al. [30], identified high potash content in the ash of the combusted cocoa pods as an indicator of its unsuitability as fuel for direct combustion. Thomsen et al. [32], did not include cocoa pods in their final four most promising agricultural residues feedstock from West Africa to produce bioethanol. In the view of the authors, other agricultural residues had higher ethanol production potential than cocoa pods. Thus, any choice of feedstock for ethanol production could exclude cocoa pods because of its comparative low ethanol yield. This still leaves us with the question of the appropriate technology to treat or energetically valorize this type of waste open. Notwithstanding

the above statement, Maleka [33] conducted a techno-economic analysis of 5 treatment pathways for the energetic valorization of cocoa pods and concluded on anaerobic digestion and hydrothermal carbonization as the most effective treatment technologies. This notwithstanding previous studies on cocoa pods utilization was limited in scope to using the Buswell and COD equation to estimate the biogas potential [17,34]. Actual laboratory-scale anaerobic digestion studies to determine the kinetics of the digestion process, actual biogas yield, and performance characteristics in semi-continuous operation mode has not been previously determined. More so, the characteristics of the hydrothermally carbonized fuel in terms of the thermal stability and fuel properties are currently unknown. This is also the case for the cashew peduncle. Even though no techno-economic studies have been conducted, studies on the energetic valorization pathway of cashew peduncle have been limited to ethanol production. This is apparently due to the high amount of fermentable sugars in the juice of the peduncle and the possibility of pretreating the bagasse to release more fermentable sugars. However, anaerobic digestion and hydrothermal carbonization also present viable pathways to energetic valorization of the peduncle.
This thesis thus seeks to address the following questions in the energetic valorization of cocoa pods and cashew peduncles.

1) How much cocoa pods and cashew peduncle residues are generated in Ghana and what is their regional distribution?
2) What is the anaerobic degradability of cocoa pods and cashew peduncle residues?
3) What is the effect of hydrothermal pretreatment on the biogas yield of the cocoa pods?
4) How does increasing the organic loading rate during mono digestion of the cocoa pods and cashew residues affect the biogas yield and process stability?
5) What is the effect of feed composition on biogas yield from co-digested cocoa pods and cashew peduncle residues with maize silage?
6) What is the effect of process parameters on energy intensification through hydrothermal carbonization?
7) What is the potential effect of energetically valorizing cocoa pods and cashew peduncle residues on Ghana's energy sector?

1.2 Aim of the study

The main objective of this research was to determine the energetic valorization pathway for cocoa pods and cashew peduncles from Ghana using anaerobic digestion and hydrothermal carbonization process.

To provide answers to the research questions, the following were the specific objectives of the study;

1. Investigate and map out at the regional level cocoa pods and cashew peduncle residues generated,
2. Investigate the BMP of cashew peduncle and cocoa pods in batch and semi-continuous reactions,
3. Investigate the combined effect of process temperature and residence time on the hydrolysis of cocoa pods to enhance biogas yield,

4. Investigate the effect of process temperature, reaction time and heating rate on the yield and fuel properties of the char produced during hydrothermal carbonization and determine the optimum operating conditions to produce hydrochars from cocoa pods and cashew peduncle residues.

2. State of knowledge

2.1 Bioenergy usage in perspective

Bioenergy is defined as the energy derived from biogenic sources such as biomass. The broad-spectrum of bioenergy fuels or biofuels exist in solid (carbonized and uncarbonized), liquid, or gaseous form. Due to its versatility, bioenergy is utilized in several applications such as electricity generation, space heating, transportation fuel, and as a domestic fuel for heating and cooking. Bioenergy The global disaggregation of deployed renewable energy pointed to bioenergy accounting for close to 50% of the total [4].

With a combined population of about 1.3 billion, Africa is the second largest most populated continent in the world. However in terms of energy demand and consumption, Africa accounts for just about 6% of the global energy demand and only 3% of the global electricity demand [3]. This is primarily due to the low level of industrialization in Africa, poor access to electricity and low level of per capita consumption of electricity. Due to the overreliance on traditional cookstoves for domestic heating purposes, the use of unprocessed bioenergy is prevalent in Africa [35]. Thus, bioenergy accounts for about 45% of the primary energy demand in Africa [3]. When the data on primary energy source is further disaggregated, bioenergy accounts for 61% of the primary energy source in Sub Sahara Africa and when south Africa is taken out then bioenergy accounts for 81% of the primary energy in the remaining countries put together. An estimation of bioenergy potential in Africa reported huge but varied potential due to the lack of reliable data [36]. The exploitation of the huge biomass resources to produce modern biofuels have been limited. These could be due to the lack of policy framework in the individual countries, lack of institutional support, energy food nexus, and the lack of strong legislature and enforcement of existing legislatures. In an attempt to address some these challenges, the African Union drew up a non-binding Africa bioenergy policy framework and guidelines to serve as a useful guide to member countries to develop their own bioenergy policies [35].

The case of Ghana is not quite different from that of many countries in Africa despite the huge bioenergy resource potential. Production and utilization of modern bioenergy fuels have not quite taken off in Ghana yet. Demand for woodfuel as firewood was projected to increase from about 10 million tons in 2008 to about 16.2 million tons by 2020. Likewise, the wood used for charcoal production was expected to increase from 6.8 – 10.2 million in 2008 to 10.8 – 16.3 million tons by 2020 [37]. These estimates were based on a business as usual scenario national GDP growth rate. To date apart from charcoal which is generally produced from woody biomass and the direct use of woody biomass as fuel (firewood), the production of modern biofuels is yet to fully take off in Ghana. This is notwithstanding the legal and regulatory framework for the production and utilization of modern biofuels which has been in place since 2007. A draft bioenergy policy was drawn-up in 2007 to drive the production and utilization of modern biofuels in Ghana. The policy was largely skewed towards the penetration of liquid biofuels into the transportation energy mix. This is seen in the policy objective which was to increase the penetration of biofuels by 10% in the transportation fuel mix by 2020 and 20% by 2030 [38]. Driven by this ambitious target, several biofuels specific projects took off especially in the area of biodiesel production. As noted by Ahmed et al. [39] and Nygaard and Bolwig [40], a number of biodiesel initiative using jatropha as the feedstock took off in Ghana. However, sooner than later most of these initiatives died out due

to a multiplicity of factors. One key reason identified by the authors was the lack of institutional supports. Nygaard and Bolwig [40] for instance, argued that the government lost interest early after one of the pioneers of biodiesel production died. Further, the fact that the policy remains as a draft and not finalized to date speaks volumes about the weight placed on bioenergy development especially immediately after Ghana discovered oil in commercial quantities. The furthest Ghana has gone in terms of achieving the policy goals is the development of technical standards on biodiesel and bioethanol as a transportation fuel. However, the development of the standards did not necessarily lead to its adoption [41]. The draft policy even though it was arguably good, failed to achieve its target of spurring the production of modern biofuels in Ghana.
The failure of Ghana's modern biofuel productions can be attributed mainly to the following reasons;

1. The overdependence on energy crops as the main feedstock for bioenergy production was also a critical failure factor. The cultivation of energy crops was and is still a thorny issue in Ghana. As reported by Ahmed et al. [39], land is vested mainly in the traditional rulers and family heads. The tacit support of chiefs and family heads is needed in acquiring large tracts of land for energy cultivation. The uncooperative nature of chiefs to release their land for energy crop cultivation was thus one of the major causes of failure
2. The boom and fall of jatropha significantly affected Ghana's drive to integrate modern biofuel production into its energy mix.
3. Equally important was the discovery of oil in commercial quantities in Ghana. Obviously, the attention of the government quickly shifted to making the best out of the oil discovery than focusing its attention on biofuel production.

Notwithstanding these developments, the biogas sector thrived albeit at the domestic level. Even though biogas is a potential transportation fuel, the government's attention has not been directed at its production and utilization as such. At present, most of the biogas installations in Ghana are for domestic treatment of fecal sludge and are thus seen more as an environmental solution rather than as energy carriers. According to Kemausour et al. [42], a few industrial or commercial biogas plants can be found in Ghana. The most pressing challenge to the deployment of industrial biogas plant is the huge capital investment required according to the same authors.

In overcoming some of the critical failures in the future, the choice of feedstock for bioenergy production must be concentrated on readily available agricultural residues that can be obtained through the existing farming practices and cultivation of food and cash crops. This brings into sharp focus the readily available crop residues due to the extensive crop cultivation practices in Ghana. A number of different crops are cultivated in Ghana as food crops and some as cash crops. The main cash crops are cocoa and palm oil but in recent times cashew peduncle is coming up as a very important cash crop. Recently, the government in recognizing the huge economic potential of cashew nuts launched a masterplan to boost its production. The masterplan is expected to drive the production of cashew nuts to about 300,000 nuts by 2025. The residues generated during the value chain of the cash crops such as cocoa beans and cashew nut especially could serve as readily available feedstock to produce modern biofuels.

2.2 Cocoa pods

Theobroma cocoa L. is a cash crop grown mainly in the tropics. The main fruit consists of the beans which are housed in a shell and the main product and the pod that houses it as shown in Figure 2.1. The fruit is harvested for the beans with the pod coming out as the main waste product on the farm. The beans are mainly dried and fermented after which it is processed into end products like butter and chocolate. The pod is reported by Vriesmann et al. [43] to form about 90% of the weight of the cocoa fruit respectively. This makes the pod constitutes a major component of the cocoa fruit.

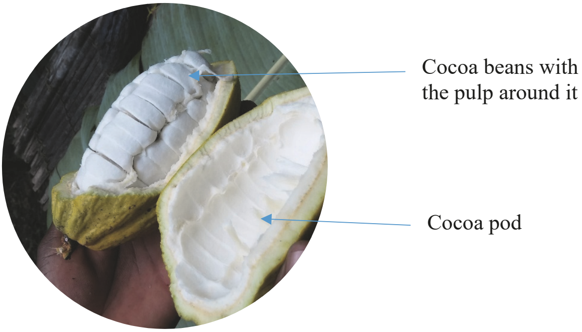


Figure 2.1: The cocoa pods with the beans.

In terms of nutrient recovery, several scientific studies in the past have been focused mainly on the utilization of cocoa pods as feed for ruminants [44–47]. Even though this has been projected as one of the possible uses of the waste products, it has been reported that ruminating animals have problems digesting the pods effectively due to its high Theobromine content according to Ofori-Boateng and Lee [48]. Other scientific studies have investigated the possibility of producing caustic potash from cocoa pods since local farmers started using burnt cocoa pods ash as the main base in saponification reaction reactions [49,50]. Aside from the extraction and use of caustic potash for soap making, other scientists have investigated the use of caustic potash from cocoa pods as a catalyst for biodiesel production due to its high magnesium and potassium content. Even though the biodiesel yields as reported by Ofori-Boateng and Lee were high, not much has been done in terms of setting up a plant even at the pilot-scale level to produce caustic potash from the pods. Similarly, Khanahmadi et al. [51], reported a high yield of 93% when Lipase extracted from cocoa pods was used to catalyze the transesterification reaction of Jatropha oil to produce biodiesel. Aside from the results presented, there was no discussion on the potential waste after the caustic potash extraction process given room for concern as to whether this is the best use to which the pods can be put. This is also because of concerns that the waste generated after the extraction process may not be tenable for further processing leading to further nutrient and energy loss. In terms of energetic use of the pods, recent studies by Adjin-Tetteh et al. [52], pointed to the extraction of bio-oils through fast pyrolysis, while Dahunsi et al. [53] and Ward-Doria [54] suggested anaerobic digestion as possible energetic valorization pathways.

Ghana has consistently been ranked as the second-largest producer of cocoa beans in the world and has maintained this position since 2006. Production levels in the last decade have averaged about 630,000 MT and earned the country close to $2 billion in foreign currency annually [13]. It is, therefore, a critical and important sector for the country. Currently, the only use to which cocoa pods are put is the artisanal production of caustic potash on exceedingly small scales in the villages for use as a base to produce traditional black soap. Aside this, the pods are left to naturally decay on the farms, a situation which is both environmentally unfriendly and has also been attributed to the spread of block bod diseases that eventually reduces the production of the cocoa beans as reported by Donkoh et al. [55] and more recently by Vriesmann et al. [43].

2.3 Cashew peduncle

The cashew tree (Anacardium occidentale L.) is widely believed to have emanated from South America and was propagated by the Portuguese merchants to Africa. The tree mainly thrives in the tropical regions of the world and is mostly grown for its nuts which is a delicacy around the world. The cashew peduncle is green when it is not mature but changes color to red, yellow, or orange when it is fully matured. The fruit consists of a fleshy peduncle apple which is edible and at the base of the peduncle is the nut/kernel concealed in a shell (Figure 2.2). The peduncle is reported to have of a mass of 50 – 140 g depending on the variety as shown in Table 2.1 below.

Table 2.1: Mass of different types of cashew peduncle [23].

Type of cashew peduncle	Mass (g)
Red cashew nut peduncle	50 – 120
Yellow cashew nut peduncle	100 – 130
Orange cashew nut peduncle	100 – 140

The nut which weighs about 5 g constitutes less than 10 % of the weight of the entire peduncle. After harvesting the nut, the peduncle can either be processed into valuable end products such as juice and alcohol by squeezing out the juice or left to rot on the farms of the farmers. The peduncle is fibrous with little liquid. According to Sivagurunathan et al. [56], 100 g of fresh peduncle will yield between 10.8 – 29.9 ml of syrup leaving behind 72.5 – 84.5 g of residue. This means that even when the peduncle is used for syrup production, a significant percentage of the peduncle is returned as waste material.

Figure 2.2: Cashew nut peduncles and nut.

2.4 Energetic valorization pathways

2.4.1 Thermochemical treatment

Conventional thermochemical treatment of agricultural waste to recover energy has been mainly focused on four treatment pathways – direct combustion of the waste product, pyrolysis, gasification, and hydrothermal process (Figure 2.3).

2.4.1.1 Direct Combustion

Direct combustion is an oxidation reaction that involves burning biomass directly in the presence of pure oxygen or air. The end products are usually CO_2 and H_2O if the combustion is complete and carried out in excess oxygen. Otherwise, the possibility of the formation of carbon monoxide (CO) in addition to CO_2 and H_2O is a possibility. The higher heating value (HHV) of the calorific value of the biomass is an indication of how much energy can be potentially recovered from the biomass through combustion. Direct combustion of biomass presents key challenges. The high mineral content of biomass present challenges such as agglomeration and sintering leading in some cases to slagging and fouling in canisters [57]. the presence of high moisture content requiring a drying pretreatment step also present a significant challenge due to the huge thermal load it present. A complete energy balance taking into consideration the pretreatment step negatively affects the thermal efficiency of the entire process.

Ortíz-Rodríguez et al. [57] used the elemental analysis of cocoa pods and the mineral composition of cocoa pods generated in Columbia to evaluate the potential of thermochemically energetic valorization of cocoa pods suing equilibrium models. The authors concluded that the direct combustion of cocoa pods may be challenging due to the high fouling and fusibility index which will lead to sintering and agglomeration.

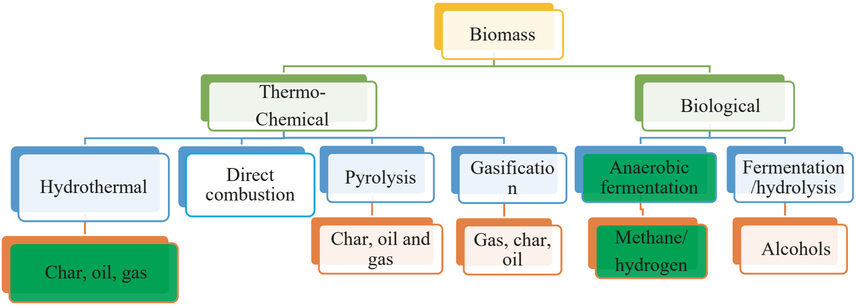


Figure 2.3: Pathways to the energetic valorization of biomass.

2.4.1.2 Pyrolysis

Pyrolysis of biomass is another thermochemical process that results in increasing the energy density of the fuel by carbonizing the biomass or transforming the solid fuel into gaseous, solid, or liquid fuel. Pyrolysis involves thermally treating the waste product in an oxygen-depleted environment. During the process, the waste product first goes through drying where all the moisture is evaporated. The second stage involves the chemical transformation of the biomass into pure carbon, syngas, and liquid products and it takes place between 200 – 800 ºC. Biomass precursors such as cellulose and lignin are known to degrade thermally above 200 ºC. During temperatures above 200 ºC, the biomass begins to undergo chemical deformation. This is characterized by the release of volatile organic matter from the long-chain hydrocarbons in the biomass. Pyrolysis can be classified as fast, slow, or flash pyrolysis depending on the heating rate and solid residence time [58]. Slow pyrolysis is characterized by long residence time (several hours) for the biomass which allows for slow degradation of the biomass and repolymerization of depolymerized monomers. This leads to the formation of more char and less gas [58]. Fast pyrolysis on the other hand is characterized by heating rate above 10 ºC/s and very short residence time (0.5 – 2) for the biomass [59]. The product distribution favors bio-oil yield 50 – 70% w/w [58]. When the heating rate is above 1000 ºC [58,59] an reaction time of less than 0.5 s resulting in a bio-oil yield of about 75 – 80% w/w [58].

The main drawback of pyrolysis just like direct combustion is its inability to effectively handle wet waste. When the waste is significantly wet, a lot of externally sourced energy is required to dry the waste before initiating the second stage of the process. Further, significantly higher operating temperatures are required to effectively carbonize the waste or produce syngas. Another drawback is using high ash content biomass might lead to lower heating values of the resultant char which is not a particularly good attribute. Poucke et al. [60] for instance reported that slow pyrolysis could only lead to a higher heating value char provided low ash content feedstock is used. Despite the drawback, pyrolysis is dynamic unlike direct combustion, and can lead to the production of crude bio-oils [61] and liquid fuels through the Fischer-Tropsch process.

In terms of pyrolysis' application to cocoa pods and cashew peduncles, not much was found in the literature. A preliminary study carried out by Symasiro et al. [30] on the use of cocoa pods as fuel after pyrolysis and pelleting, concluded that even though combustion was possible releasing about 17 MJ/kg, there was high ash content left after combustion and the process required a much higher fuel-air ratio to ensure complete combustion. During combustion, the mineral content of the waste, mainly potassium, oxidizes into potassium carbonate K_2CO_3 and is left behind in the ash [62]. The caustic nature of the ash due to the high potash content of the pods and the effect it could have on the canisters was not a subject of investigation for the authors. More recently, Adjin-Tetteh et al. [52] attempted to produce drop-in fuels through fast pyrolysis and reported 58% w/w bio-oil yield, 30% w/w char and 12% w/w non-condensable gas from cocoa pods from Ghana.

2.4.1.3 Gasification

Gasification of biomass is another thermochemical process that converts biomass into mainly gaseous fuels, liquid fuels, and solid fuels. Dasappa [63], describes gasification as a thermochemical process where biomass undergoes a series of sub-stochiometric oxidation and reduction reactions with different reactants that includes pure oxygen, steam, air, and CO_2 to produce a gaseous mixture of combustible and incombustible gases comprised of CO, H_2, CH_4 and CO_2, solid fuel (char) and tar. In addition to the fuels, soot and ash are also generated. Temperature plays an important role in the final products obtained. Depending on the final gasification temperature, the combustible gases produced at the end of the gasification process can be referred to as producer gas or synthetic gas as reported by Motta et al. [64]. When the gasification is carried out at lower temperatures the combustible gas produced is called producer gas, while the combustible gas is referred to as syngas when the reaction is carried out at higher temperatures.

The entire reaction mechanism can be divided into five stages – drying, pyrolysis, oxidation (combustion), cracking and reduction [65] (see Figure 2.4) or in some cases some researchers have reported 4 stages omitting the cracking step which is seen as an integral part of the pyrolysis stage [63,66,67].

1. The drying process is mainly mechanical and does not involve any chemical reaction. The biomass undergoes mechanical drying where moisture in the cells is heated and evaporated between the temperature of 100 – 200 °C [66]. The drying process is an endothermic reaction that requires an external energy source.
2. The pyrolysis stage usually starts at a temperature above 200 °C and it involves heating of the biomass in an oxygen-depleted atmosphere. This results in the decomposition of biomass leading to the release of the volatile organic compounds from the biomass and the charring of the biomass. The process can be classified into two – primary pyrolysis and

secondary pyrolysis. According to Motta et al. [64], the primary pyrolysis stage leads to the devolatilization of the biomass resulting in the release of synthetic gas and char from the biomass during the charring process. This takes place up to a temperature of about 600 ºC. Temperatures above 600 ºC result in the thermal cracking of the char into lighter hydrocarbons. This secondary pyrolysis stage is the difference between the two proposed reaction mechanisms. The entire pyrolysis stage is an endothermic reaction thus, it requires the input of energy.

3. The oxidation/combustion stage involves the supply of a non-stoichiometric amount of pure oxygen or air to initiate a series of reactions. The oxidation stage which is exothermic leads to the release of energy. The reactions taking place involves the partial oxidation of the char and the gaseous pyrolysis products.
4. Reduction stage involves the use of a gasifying agent such steam or CO_2 to initiate multiple complex reactions involving the char and the primary and secondary pyrolysis such as the water-gas reaction, methanation reaction, Boudouard reaction, and the water gas shift reaction to produce gaseous combustible and non-combustible products [54,56].

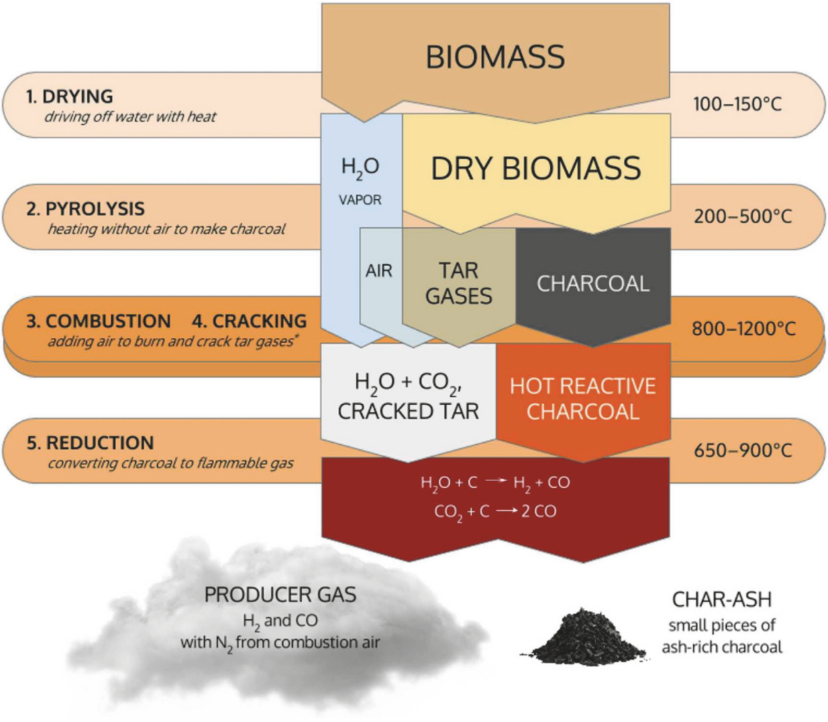


Figure 2.4: Gasification reaction mechanism [55].

Even though gasification of biomass is a promising technology for the processing of modern biofuels, the technology faces several key challenges. As pointed out by Wang et al. [69] and more recently Sansaniwal et al. [70], syngas quality remains a major challenge in gasification technology. The presence of tar and solid pollutants (char) in the syngas renders the syngas unusable in combustion engine. This requires an additional unit operation to clean the gas and rid it of the char and the tar either through physical separation techniques or through reduction reaction which may lead to the production of additional syngas.

The physical nature of the biomass feedstock is also major challenge. For instance, high moisture containing feedstock requires a pretreatment step that involves drying the feedstock to an acceptable equilibrium moisture content. The drying process is usually energy intensive due to the high latent heat of vaporization of water. External energy sources may be required or a complex energy integration process where excess energy generated during the combustion stage is used to dry the biomass to achieve higher thermal over thermal efficiency for the process. Additionally, the moisture content of the biomass influences the densification process prior to gasification just as it influences the long-term storage of the biomass before gasification. A 10% moisture content is recommended for long term storage of biomass, while the biomass is required to be dried before and after densification [71].

Aside from the moisture content, the particle size of the biomass is also a challenge. The particle size of bulky biomass must be reduced through grinding or pulverization to increase the particle surface area to enhance mass and heat transfer operations during the gasification process [71].

Lastly, the ash content of the inherent ash and mineral content of the biomass is also a challenge in biomass gasification. Ash agglomeration, sintering, position, erosion and corrosion are some of the challenges encountered when biomass with high ash content are used as gasification feedstocks [69]. The presence of alkali earth metals such as potassium in the feedstock is known to react with the silica to form alkali silica resulting in bed sintering and defluidization. Further, the corrosiveness of the alkali earth metals such as potassium has been reported as a major challenge in gasification even though effort to reduce the concentration of the alkali earth metals prior to gasification are ongoing [69].

Literature search for utilization of cocoa pods or cashew peduncle residues as biomass gasification feedstock did not yield much results in terms of completed experimental studies. Martínez-Ángel et al. [57], recommended gasification process as the better of direct combustion and pyrolysis despite the high agglomeration and slagging content of cocoa pods. The authors failed to address the problem of corrosion posed by the high alkali earth metals in cocoa pods. However, given the high concentration of potassium in cocoa pods, it can be posited straight away that it will be a challenging feedstock to deal with. This is beside the high moisture content and bulky nature both of which must be dealt with in a pretreatment step prior to gasification. In the case of cashew peduncle, the high moisture content and bulky nature may be the main challenges to deal with.

2.4.2 Hydrothermal process

Hydrothermal process in its various forms (carbonization, liquefaction, and gasification) relies on the unique properties of water at near its critical point (subcritical), at its critical point or above its critical point (supercritical) to hydrolyze, dehydrate, polymerize and aromatize biomass into more than 400 distinct bio-oils and compounds as well as methane and hydrogen gas and char [72]. Water at its critical temperature (375 ºC) and pressure (22 MPa) exhibits unique properties that make it possible to dissolve organic compounds. At elevated temperatures of water, the relative strength of the hydrogen bonds of the water molecules diminishes, while reducing the dielectric constant. The combine ionic product $[H^+][OH^-]$ is also known to increase considerably to a maximum of 6.34×10^{-12} at 250 ºC and then after decrease to 1.88×10^{-16} at the critical point [73] resulting in a lower dielectric constant and density, thereby making it a very potent organic solvent. Additionally, the huge heat capacity of water also makes it an effective heat transfer and storage medium during the hydrothermal process [74]. Further, water is one of the most abundant compounds on the planet and at the same time is also very environmentally friendly and neither toxic nor inflammable making it a unique solvent for diverse applications. These factors combine to make the hydrothermal process a potent tool for the treatment of biomass into useful products.

The Hydrothermal process can be classified into three groups depending on the severity of the operation and the end products [75].

1. Operating temperatures below 247 ºC are considered hydrothermal pyrolysis leading to the production of more biochars.
2. Operating temperatures between 247 – 374 ºC are called hydrothermal liquefaction leading to the production of more oils.
3. Operating temperatures above 374 ºC are termed as hydrothermal gasification leading to the production of more methane gas and or hydrogen gas.

A parallel classification put forward by Jin [73], classified the hydrothermal process into two main groups;

1. Hot temperature hydrothermal process between 150 – 374 ºC.
2. Supercritical Temperature process for operating temperatures above 374 ºC and pressure above 22.1 MPa.

Hydrothermal treatment of biomass holds great promise for the conversion of biomass into bio-crude or specific finished products. As compared to the thermal treatment and biological treatment technologies, hydrothermal liquefaction process is reported to utilize just about 2 % of the energy contained in the biomass and up to about 75% thermally efficient when designed properly, while hydrothermal gasification could be between 45 – 70 % thermally efficient [72]. After operating a commercial hydrothermal plant, the city of Berlin conducted an analytical study and reported that hydrothermal carbonization came out as the best treatment option for biological waste as compared to fermentation and composting as cited in Steurer and Ardisonne [76].

2.4.1.3.1 Hydrothermal carbonization

Hydrothermal carbonization is defined as a wet thermo-chemical process that converts biomass at sub-critical temperatures (180 – 250 ºC) and autogenous pressures of 2 – 10 MPa [74] into coal-like substance sometimes referred to as bio-coal or hydrochar. In this thesis, the coal-like solid material will be referred to as hydrochar to distinguish it from biochar which is produced through slow pyrolysis of biomass. The main advantage of hydrothermal carbonization of biomass is its ability to overcome some of the key challenges posed by the biological and some thermal treatment technologies where the presence of lignin, high moisture content, high reaction temperature and inhomogeneous feedstock become major technical barriers.

The hydrothermal carbonization process is complex with several side reactions taking place. This makes the entire reaction mechanism difficult to comprehend. Even more so when dealing with complex substrates like biomass which has chemically bound lignocellulosic fibers, sometimes high mineral content that can affect product selectivity and high amount of extractives. The large number of products especially in the liquid phase is a testament to the complex nature of the reaction mechanism. From a chemistry point of view, the reaction pathways can be generically grouped into five stages – hydrolysis, dehydration, decarboxylation, condensation polymerization, and aromatization [74,77] even though shorter reaction mechanisms depending on biomass precursor have been proposed elsewhere. A simplified reaction pathway based on the hydrolysis of cellulose has been proposed by Titirici [78] (see Figure 2.5).

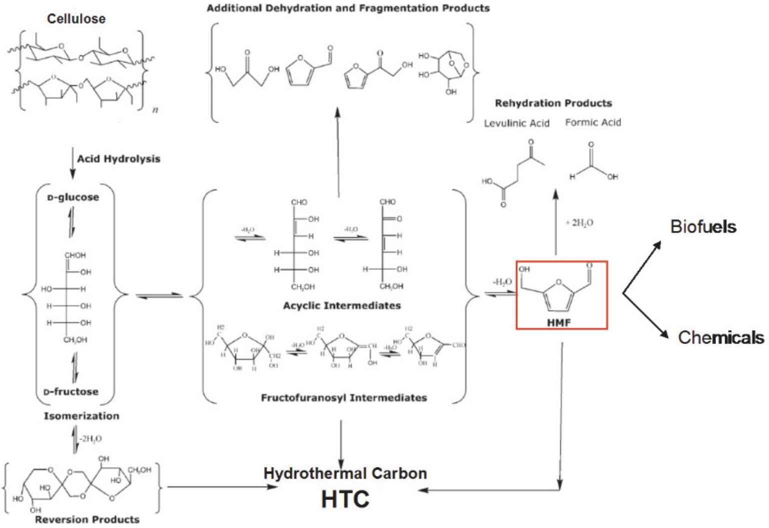


Figure 2.5: HTC reaction pathways [78].

Using biomass precursors (cellulose, hemicellulose, and lignin), researchers have sought to understand the reaction mechanism and pathways for the conversion of biomass to hydrochar. Analysis of the solid and liquid phase suggests hydrolysis of the precursors as the first step. The hydrothermal carbonization process is reported to first hydrolyze the biomass or complex carbohydrate into its basic oligomers and monomers. The degree of efficiency of hydrolysis is however dependent on the temperature and biomass precursor. For instance hydrolysis of hemicellulose into xylan, glucan and mannose have been reported to take place at temperatures below 180 ºC Wang et al. [79], while complete hydrolysis of hemicellulose at temperatures above 200 ºC is possible. Baruah et al. [80], reported the maximum hemicellulose derived sugars (180 ºC) during hydrothermal treatment of corn cobs at 160 ºC and 30 minutes. Sun et al. [81], also hypothesized that an increase in cellulose content of hydrothermally treated Eucalyptus urophylla at temperatures within the temperature range of 160 – 180 could be attributed to hydrolysis of hemicellulose. Degradation of pure cellulose into glucose and oligosaccharides is somehow limited due primarily to its crystalline nature and only takes place at temperatures above 220 ºC. Sun et al. [81], for instance, reported marginal hydrolysis of cellulose at 200 ºC. Several studies have confirmed the limited hydrolysis of cellulose at temperatures below 250 ºC. According to Jin [73], the hydrolysis of the cellulose could follow three paths – acid (H^+), base (OH^-), and water catalysed pathways. This is primarily driven by the autocatalytic properties of water near and above its critical point. As observed by Sasaki et al. [82] and Sasaki et al. [83], the hydrolysis of cellulose is more prominent near or above the critical point of water. Reported hydrolysis efficiency of about 75% was obtained at supercritical conditions. Thus, at subcritical conditions, a significant fraction of the cellulose remains unhydrolyzed, maintaining its crystalline morphology.

As a result, Sheng et al. [84] and Dinjus et al. [85], proposed 2 parallel pathways for the conversion of cellulose into hydrochar. Pathway 1 involves the limited hydrolysis at the cellulose water interphase leading to the release of glucose and oligosaccharides. Reaction mechanism 2 involves the direct conversion of the cellulose to hydrochar through intermolecular condensation, dehydration, and decarboxylation reactions.

Similarly, lignin hardly degrades and even when it does begin to degrade above 200 ºC, the rate of degradation is very slow [86]. For instance, Kim et al. [87] using pure cellulose, xylan, and lignin as biomass precursors to produce hydrochars reported that the decomposition of lignin only began at temperatures above 250 ºC. Dinjus et al. [85], also reported limited hydrolysis of lignin during hydrothermal carbonization when they studied the influence of lignin on the composition and structure of the hydrochar formed. From the foregoing, hydrolysis of biomass during hydrothermal carbonization under sub-critical conditions may be limited mainly to the hemicellulose component and partly to the cellulose component.

After hydrolysis, the monomers and oligomers undergo both physical and chemical dehydration [72–74,88]. For instance, the dehydration of fructose to form hydroxymethylfurfural (HMF) was reported [89,90]. Similarly, Wang et al. [79] reported the dehydration of xylose which is one of the main constituents of hemicellulose into furfural and retro -Aldo. Chemical dehydration leads to the lowering of H/C and O/C ratios through intense carbonization as pointed by Funke et al. [74]. According to Crocker [72], oxygen removal through decarboxylation or decarbonylation is essential to improve the fuel quality of the end product. The presence of oxygen in the hydrochar reduces its calorific value thus affecting the quality of the fuel. Decarboxylation and decarbonylation reactions result in the partial removal of carboxyl groups especially at 150 ºC resulting in the production of CO_2 and CO (Equation 2.1 and 2.2) respectively [74].

$$\mathrm{R-COOH} \rightarrow \mathrm{RH} + \mathrm{H_2} + \mathrm{CO_2} \tag{2.1}$$

$$\mathrm{R-COOH} \rightarrow \mathrm{RH} + \mathrm{H_2O} + \mathrm{CO} \tag{2.2}$$

As pointed out by Jin [73], the decarboxylation and decarbonylation reactions are better understood by the reaction mechanism of formic acid which is an intermediate of water-gas shift reaction. Additionally, formic acid is formed in a significant amount during the degradation of cellulose. Both the decarboxylation and carbonylation reactions (Equation 2.4) take place in the gas phase and liquid phase. However, it is generally believed that the decarboxylation reaction is dominant in the liquid phase due to the presence of water that acts as a homogenous catalyst for the reaction, while decarbonylation is dominant in the gas phase [73].

$$\mathrm{COOH} \rightarrow \mathrm{RH} + \mathrm{H_2} + \mathrm{CO_2} \tag{2.3}$$

$$\mathrm{COOH} \rightarrow \mathrm{RH} + \mathrm{H_2O} + \mathrm{CO} \tag{2.4}$$

The intermediate products such as furfural, 5-HMF, anhydroglucose, and 5-methyl furfural produced during the dehydration and decarboxylation and decarbonylation reactions are reported to very unstable and thus highly reactive [73]. The condensation and addition reaction which is reported to take place was confirmed. The intermediates formed from the hydrolysis, dehydration, decarboxylation, and polymerization condensation reaction of cellulose and hemicellulose have been confirmed to undergo some form of aromatization which depends significantly on temperature [74].

The effect of process parameters on the yield of the three main products – oils, gas, and char has long been of interest to many researchers. Several factors have been identified to influence product yield chief among them are; heating rate, temperature, reaction time, biomass particle size, biomass loading rate (% solids) catalyst concentration, and liquefaction atmosphere inert (N_2, Ar) or reducing (CO, H_2) [72]. For instance, using a batch reactor Donar et al. [91], investigated the effect of the reaction time and temperature on the yield of hydrochar from hazelnut waste and olive residue. By determining the carbon content of the product at different reaction conditions, they reported that reaction temperature had more influence on the yield of hydrochar than the reaction time, whereas the properties of the biochar also differed significantly at different reaction conditions. The combined effect of the two process parameters was however not investigated which makes it difficult to determine how the two process parameters could have a possible combined effect on the biochar yield. Prapaiwatcharapan [92], investigated the effect of a single step and two-step sequential semi-continuous hydrothermal treatment by changing the temperature, pressure, and the water flow rate in a univariate manner for 2 hrs using Coelastrum sp. microalgae as the main feedstock. They reported higher bio-crude yields using the two-step sequential approach but warned against higher temperatures greater than 320 ºC. Through the univariate analysis they reported, optimum operating conditions for the two-step sequential hydrothermal process at a temperature of 200 and 320 ºC, pressure of 7 – 20 MPa respectively, and water flow rate 0.5 mL/min for both. No attempt was made to design the experiment to study the interactive effect of the process parameters on the yield.

While studies on the effect of temperature and reaction temperature abound in the literature, other researchers have looked at the effect of mass concentration on the hydrochar yield. Sermyagina [93], studied the effect of temperature (180 – 250 ºC), the ratio of biomass to water (1:6 and 1:8) and reaction time on the mass yield of hydrochar and the heating value of the resulting biochar using coniferous biomass as the main raw material in a 1 L batch reactor. They reported about 20 % loss in mass at a higher operating temperature of about 250 ºC but an increase of about 36 – 40 % in heating values. Reaction time and the ratio of biomass to water were also reported to have a certain influence on the yield and the heating values of the resulting product. A higher quantity of water led to higher product yield as a result of higher hydrolysis intensification. Longer reaction time was also reported to have led to the loss of mass but higher heating values. The heating rate of the reactor is another process parameter of interest but has attracted little attention from researchers. The majority of the authors have placed more emphasis on the process temperature and reaction time than on heating rate. Apart from few studies that reported on the effect of heating rate on the hydrothermal liquefaction process as reported in Wang et al. [79], the literature on its effect on the carbonization process is very scarce. Generally, the residence time/holding time/reaction time as defined earlier is taken as the time the process reaches the set-point and the time the process begins to cool down. However, in most batch studies, the substrate is introduced at room temperature into the reactor, thus the total time the substrate spends in the reactor is dependent on the heating rate of the reactor. Jin [73], reported the possibility of degradation of biomass precursors before reaching the set-point leading to the initiation of the side reactions such as the onset of polymerization. Additionally, the influence of the thermal as well as the rheological properties of the substrate on the heat and mass transfer process could be affected by the heating as noted by [79]. Thus, the effect of heating rate on hydrochar yield could be significant.

In recent times, hydrothermal carbonization has moved from using biomass precursors to real biomass to elucidate on the carbonization process and gather additional data for design purposes. Some biomass feedstocks reported in the literature include but not limited to municipal solid waste [94,95], hazelnut waste and olive waste [91], microalgae [96] among others.

Other researchers have also focused their attention on the production of other chemical compounds from biomass using hydrothermal process. Song et al. [97], successfully produced cyclohexanol from biomass-derived cyclohexanone using Cu powder as a catalyst under hydrothermal in a 30 mL batch reactor. The yield of cyclohexanol was highest (100 %) during the in-situ production of hydrogen through the oxidation of Zn in water. Rasmussen et al. [98], successfully identified a previously unknown compound occurring in the aqueous phase of pretreated palm empty fruit bunches under hydrothermal conditions. Using a continuous feed reactor and palm empty fruit bunches as the substrate, they subjected it to the hydrothermal condition of 200 ºC for 18 minutes. The high percentage occurring previously unknown compound was identified as 4–hydroxybenzoic acid a base reactant to produce esters used in the cosmetic industry. Jain et al. [99], successfully produced activated carbon possessing high mesopores and Brunauer – Emmett – Teller (BET) surface area from coconut shell using hydrogen peroxide as an oxidizing agent.

A number of challenges and knowledge gaps in the hydrothermal carbonization process are outlined below.

- Product analysis

Analysis of products has been a major challenge given the diverse nature of the products, especially in the liquid phase. Jin [73] recommended further work to properly characterize and quantify the products in the aqueous phase and all the by-products from the reaction. The characterization of the products in the liquid phase will throw more light on the reaction mechanisms and pathways taking place. Additionally, it will inform the extraction of other useful products other than the intended hydrochar to improve on the efficiency of the entire biorefinery process and also influence the use to which the liquid phase can be put to after the carbonization process.

- Feedstock type

Feedstock composition is very important in determining which bio-refinery process will be good. Aside affecting the type of bio-refinery process, the composition of the feedstock also affects the composition of the final products according to [72]. Most of the feedstock used in previous hydrothermal process research has come from waste generated in advanced countries where the research has been prevalent. With the strong belief that any plant will have to deal with real biomass, a lot of research must be conducted into the use of several biomass types under different hydrothermal conditions to produce bio-oils, char, and methane gas.

- Pilot-scale plant

Laboratory-scale experiments have been good and provided some level of information contributing to a large extent to the level of understanding achieved so far. However, to move from laboratory scale to full-scale operation more data is required from pilot-scale systems to inform design, optimizing, and modelling of the real systems. As pointed out by Jin [73] and Hrncic et al. [100], a pressing need is to develop and deploy many pilot-scale plants. Pilot-scale plants will provide the necessary information to better understand the process on a real basis and be able to properly model the entire process.

- Parametric studies

Process conditions have been shown earlier to be important. However, several studies reviewed considered only temperature and reaction time [101,102]. Other very important process parameters such as heating rate have received very little attention Wang et al. [79], Further, other process parameters of interest aside heating rate to provide a better understanding of the entire carbonization process could be biomass packing ratio, total solid concentration, and catalyst to biomass ratio.

2.4.3 Biological treatment

Biological treatment of waste to produce liquid and gaseous fuels is one smart way of using natural organisms and processes to produce fuel. Several studies have been conducted to investigate the potential of fermenting waste to produce fuels. Two production pathways are readily accessible – Anaerobic digestion and aerobic fermentation

2.4.3.1 Anaerobic digestion

Anaerobic involves the use of special bacteria to break down organic matter and in the process release biogas (CH_4 and CO_2). The process involves a series of complex organic reactions that have been studied extensively. The anaerobic digestion process consists of four well-documented stages; hydrolysis, acidogenesis, acetogenesis, and methanogenesis [103]. Hydrolysis involves the breaking down of the complex sugars and proteins into their basic monomers and lipids into long-chain fatty acids. This is an especially important step in the digestion process. It sets the stage for the simultaneous conversion of the simple sugars and the amino acids into either volatile fatty acid through acidogenesis reactions which are then subsequently converted to acetates and then later to methane. The hydrolysis step though important can also be detrimental to the entire process if the rate is uncontrolled. For instance, a high rate of hydrolysis can lead to process acidification due to an imbalance in the production and consumption of volatile fatty acids during the simultaneously occurring acidogenesis and acetogenesis phases [104]. The cumulative effect of a high rate of the rapid production of volatile fatty acids is reduced pH which provides a hostile environment for the methanogenic bacteria to function as reported by [105].

In terms of net energy recovery from the waste, anaerobic digestion may not be the best way of treating the waste because the net energy produced is a fraction of the net energy of the waste product. However, the versatility of the biogas/methane produced through the anaerobic digestion process in terms of its multiple uses makes it a better fuel than the raw biomass. Additionally, the clean combustion of the biogas makes it a much better environmentally friendly fuel. Some have even argued that the biological treatment of waste should be considered more as a waste treatment technology than an energy recovery process. The anaerobic digestion process requires large reaction vessels because of the longer retention times or duration of the process. Most anaerobic fermentation processes require between 20 – 60 days retention time and that affects the design of the reaction vessels. Anaerobic fermentation's inability to handle lignin-rich substrate leading to lower gas output has been widely reported [106]. Hydrolysis of the residue during anaerobic

fermentation is a potential limiting step due to the complex lignocellulosic structure of the substrate.
With regards to bio-methane production, there is little information on the Biomethane Potential (BMP) of most of Ghana's main agricultural residues. BMP test has not been conducted on cocoa pods and husk, cashew nuts, cassava peels, corn husk, maize stovers, fish waste among other things according to [107]. Most of the literature cited used empirical formulae to estimate the biogas potential. For instance, Thomsen et al. [34] used the Buswell formula and Chemical Oxygen Demand to determine the biogas potential of selected agricultural residue. Similarly, Kemausuor [17], using a more expanded feedstock, also used mainly empirical equations to determine the biogas yield of some selected feedstock in Ghana. As good as they are, there is a vast difference between results from empirical equations and laboratory BMP determination, the latter giving more accurate results [108,109]. Also, during digestion, the possibility of the formation of inhibitors is not taken care of by these two equations. For instance, uncontrolled ammonia formation during the fermentation process could be a major inhibitor to the digestion process leading to less gas formation [110]. In addition, polysaccharides are a major constituent of cocoa pods, and as has been pointed out earlier, the presence of lignin in the polysaccharides makes it difficult for biomethane bacteria to fully digest the substrate leading to lower methane yield. Thus, some form of pretreatment may be required.

Pretreatment can be classified as biological, chemical, physical, or thermochemical depending on the catalyst and or process used, Physical pretreatment involves primarily size reduction (cutting and milling) and mechanical phase separation. While size reduction in general increases the surface area of the substrate it makes it more accessible to enzymatic attack, milling also reduces the crystallinity of the cellulose by breaking the intermolecular hydrogen bonds [111]. Mechanical phase separation is also a form of pretreatment which separates the hydrolysates that may contain most of the digestible sugars from the fibers.

Chemical pretreatment involves the use of an alkaline or an acid as a catalyst to aid the removal of or degradation of lignin to free-up the intrinsically bound hemicellulose and cellulose for digestion. Alkaline pretreatment is preferred over acid pretreatment due in part to environmental concerns of using H_2SO_4 which has been widely used and investigated [112]. Additionally, the corrosive effect of strong acid and the need to recover the acid after the pretreatment process puts acid hydrolysis in a disadvantageous position as compared with alkaline hydrolysis. Alkaline pretreatment is reported to lead to the removal of lignin through saponification and cleavage of the linkage between lignin and carbohydrates [113,114]. Consequently, this leads to the swelling of the biomass, decreased crystallinity of the cellulose, and structural changes to the lignin [112]. Chufo et al. [115], studied the effect of alkaline pretreatment on biomethane production of teff straw by using different alkaline to substrate concentration. Alkaline concentration considered were 1%, 2%, 4% and 6%. Optimum pretreatment time of 3 days was determined by soaking the substrate in the different concentrations of NaOH and measuring the pH until there was no recognized difference between the subsequently recorded pH values. They reported that using 4% NaOH in 80 g/l substrate resulted in a 40% increase in biogas yield and 48.1% biomethane content. The ability of alkaline pretreatment to solubilize lignocellulose biomass is further confirmed by Janke et al. [116] who studied the effect of alkaline pretreatment on biogas yield of vinasse and sugarcane bagasse in a batch and semi-continuous reactor. Alkaline concentration of 1.5, 3, and 6 g NaOH/100 g(substrate) was used for the batch anaerobic test and 6 gNaOH/100 g(substrate) for the semi-continuous test. The highest NaOH concentration of 6 g/100 g(substrate) resulted in higher solubilization of around 17% and higher methane yield of 22.4%. Subsequently, Ward-Doria et al. [54], investigated the effect of alkaline and acid (H_2SO_4) pretreatment on the biogas yield of cocoa pods. They reported the effectiveness of alkaline pretreatment in reducing the lignin content by 43.78% and subsequently increasing the cumulative biogas yield from 538.34 ml (untreated cocoa pods) to 687.51 ml at a substrate to inoculum (S/I) ratio of 0.3. Even though alkaline pretreatment is effective in removing lignin, one major drawback is the presence of residual alkaline in the substrate requiring the need for neutralization reaction after the pretreatment [117].

In recent times pretreatment of lignocellulose biomass using advanced methods like hydrothermal pretreatment has engaged the attention of several researchers [111,118,119]. This is driven by the relatively short processing time as compared to the traditional acid and alkaline pretreatment and the biological pretreatment time, scalability of process, and effectiveness in terms of improving the biogas yield of the pretreated substrate [112]. Hydrothermal pretreatment results in the hydrolysis of cellulose and hemicellulose fraction at subcritical conditions and lignin near or above critical conditions. Of particular interest is the combined effect of process temperature and the reaction time during hydrothermal pretreatment. Even though an increase in process temperature has been associated with higher solubilization, its effect on the subsequent hydrolysis has not been particularly positive resulting in serious process inhibition. Wang et al. [120] investigated the biogas yield of hydrothermally pretreated rice straw at different process temperatures and reported a decrease in biogas yield at higher process temperature (210 ºC) for 15 min. They recommended lower process temperature due to the possibility of the formation of inhibitory compounds. Subsequently, Ran et al. [121], reported a maximum yield when washed vinegar waste was hydrothermally pretreated at 160 ºC for 30 minutes. Costa et al. [118] opted for shorter reaction time and obtained maximum biogas yield at 200 ºC for 10 minutes and achieved a 27.4% increase in biogas yield which was higher compared to biogas yield of NaOH alkaline pretreated sugarcane bagasse. Similarly, Girolamo et al. [119], reported a 23% increase in biogas yield when they studied the effect of hydrothermal pretreatment of Giant reed on methane yield at 180 ºC and 10 minutes. The above results notwithstanding, Mustafa et al. [122] compared hydrothermal pretreatment of sugarcane bagasse at different process temperature and reaction time of 20 minutes and reported lower biogas yield for all process temperatures (160, 180, 200 and 220 ºC) investigated in comparison with the untreated sugarcane bagasse.

It is thus obvious, that some form of optimization is required in hydrothermal pretreatment to achieve the best results. Given the fact that the process requires a lot of energy in heating up to the desired temperature, optimizing the process temperature and reaction time is thus necessary for both economic reasons and to avoid inhibiting the digestion process through the production of inhibitory compounds.

2.4.3.2 Fermentation

Fermentation of organic matter to produce ethanol has dominated research for some time especially due to the unique characteristics of blended anhydrous ethanol with petrol as a good substitute for petrol/gasoline in cars. Initial research using in general food crops such as maize, cassava, sugar cane, among others were shot down vigorously because of the perceived potential food – energy war. This ushered in second-generation bioethanol which could be produced from agricultural residues. Second-generation bioethanol is considered to hold a great promise due to the relative abundance of agricultural waste resources and its non-competition with food crops in general. The fermentation process just like the anaerobic fermentation process involves the use of microorganisms to convert monomeric sugars into alcohol [68] and acids [123]. The process unlike anaerobic digestion which is also a fermentation process, proceeds well in an oxygen-rich environment, even though oxygen places no essential role in the chemical conversion process.

The process of producing ethanol from biomass involves 3 steps – hydrolysis of the complex carbohydrates into monomeric sugars, fermentation of the monomeric carbohydrates into with help of an appropriate enzyme into ethanol and the last step is the distillation of the alcohol [124].

Despite this promise, major challenges have been encountered in the full utilization of the feedstock to produce ethanol and methanol. One of the key challenges is the successful hydrolysis of polysaccharides (complex sugars) contained in lignocellulosic biomass into simple basic sugars for fermentation. This challenge has elicited several pretreatment techniques to enhance the hydrolysis process. The challenge has been getting around the complex cellulosic organic structure which is bound together by lignin – a recalcitrant compound that does not yield easily to biological treatment. To overcome this challenge, several pretreatment methods have been proposed to break down the cellulosic walls to rapidly release the simple sugars for fermentation. Kucharska et al. [125], carried out a detailed review of lignocellulose biomass pretreatment pathways which include physical, acid, alkaline, enzymatic, and thermal hydrolysis.

Ethanol production from cocoa pods from Ghana until recently was not of interest to researchers. However, Thomsen et al. [126], used the compositional analysis of cocoa pods to estimate the ethanol yield. The authors reported ethanol of 0.28 l/kgTS. This was lower than cassava peels (0.53 l/kgTS), yam peels (0.6 l/kgTS) and, maize cobs (0.52 l/kgTS) all of which are common tropical agricultural residues. However, the ethanol yield was comparable to plantain peels and plantain leaves. Further detailed experimental studies to investigate the bioethanol potential of 11 common agricultural residues including cocoa pods were carried later out by Thomsen et al. [32]. The result of the study concluded that cocoa pods were not ideal for cellulosic ethanol production due to the low yield of g xylan converted per 100 gTS (< 5 g/100 gTS).

On the contrary, most of the literature on the energetic valorisation of the cashew peduncles is in the area of ethanol production and recently on oxalic acid production. Betiku et al. [123] successfully produced oxalic acid by fermenting cashew peduncle residues. They reported a yield of 128.68 g/l and concluded that cashew peduncle residues should be considered as one of the main feedstocks for oxalic acid production. Deenanath et al. [124], investigated the possibility of producing ethanol from cashew peduncle juice using two yeast strains - Saccharomyces cerevisiae Y2084 and Vin13 and reported a maximum ethanol yield of 68 g/l and subsequently recommended both yeast strains as suitable for converting cashew peduncle juice into ethanol. Aside from the juice, other researchers have also considered the cashew bagasse as a possible substrate for ethanol production. For instance, Shenoy et al. [127] evaluated the potential of producing ethanol from dry cashew bagasse and report similar bioethanol yield (0.46 g/l) when the authors compared the results to bioethanol yield from wet cashew bagasse (0.5 g/l) and wet coffee pulp (0.46 g/l). Similarly, Rocha et al. [128], evaluated the effect of dilute acid pretreatment on cashew peduncles for bioethanol production and reported an ethanol concentration of 10 g./l after 4 hours of fermentation.

2.5 Resource estimation

Cultivation of crops is known to generate a significant amount of residues that could be used as feedstock for bioenergy production. Several studies have identified the potential of crop residues for bioenergy generation using different methodologies; residue to Crop Ratio (RCR), Geographical Information System (GIS), and organic carbon content in soil [129–131]. The most popular and simplest methodology is the RCR approach. Even though the RCR methodology is rigorous and quite useful, it is dependent on several factors such as soil conditions, crop yield, and climatic conditions which are very specific to a country [132]. As a result, variable RPR values of the same crop have been reported in the literature [130]. The organic soil carbon content methodology, is much more rigorous than the RCR methodology, as it takes into account the quantities of residues that can be removed from the field without adversely depleting the soil's organic matter content [133]. It is however very challenging to use, especially in countries where availability of data is a major challenge. The RCR methodology becomes useful when the ratios are estimated using data specific to a country or region. Earlier biomass potential estimates by [134] and [17] used published RCR values from other countries. Scarlet et al. [130] and subsequently [135] have shown that the RCR is a function of crop yield and does not vary linearly but exponentially with yield. This claim is supported by Bentsen et al. [135] who developed a logarithmic relationship between crop residue and crop yield. Since crop yield varies across countries and regions [136] and as shown in Table 2,2, using average RCR values from published data might lead to an over or underestimation of the resource potential.

Table 2.2: Cocoa and cashew yield in some West African countries.

Country	Cocoa yield (kg/hectare)	Cashew nut yield (kg/hectare)	References
Ghana	400[1]	566[2]	[137][1] [138][2]
Cote d'Ivoire	500 – 600[3]	403[2]	[139][3] [138][2]
Nigeria	400[3]	344[4]	[139][3] [22][4]
Cameroun	300 – 400[3]	A non-cashew growing country	[139][3]

3. Materials and methods

3.1 Resource potential estimation

3.1.1 Source of data

Cocoa beans production and processing data were sourced from the Ghana Cocoa Marketing Board. The Ministry of Food and Agriculture provided data on cashew nut production and processing in Ghana. Other sources of data included, the Food and Agriculture Organization, Cocoa and cashew nut processing companies, and the Gesellschaft für Internationale Zusammenarbeit **(**GIZ) under the Competitive Cashew (COMCashew) Initiatives.

3.1.2 Assessment of the theoretical residue generation

Residue generation in the cocoa and cashew industry were estimated from data provided by the Cocoa Research Institute of Ghana (CRIG), a national research body in charge of improving yield and utilization of residues in the cocoa, cashew and shea nut industry and field visit to selected farms across the country. RCR values were estimated from visiting 20 selected cocoa and cashew farms in Ghana and taking the weight of the residues as a fraction of the main crop as shown in Equation 3.1.

$$\mathrm{RCR} = \frac{\mathrm{MR}}{\mathrm{MC}} \tag{3.1}$$

Where MR = mass of residue; MC = mass of crop

Residue generation quantities were calculated backward using the RCR values and the annual average production data of the cocoa beans and cashew nuts as shown in Equation 3.2 [140].

$$\mathrm{R} = \mathrm{RCR} \times \mathrm{CP} \tag{3.2}$$

Where R = annual quantity of residues; CP = annual crop production.

Data on alternative uses of the residue products were obtained following the methodology outlined in Anabire et al. [141] by using data from CRIG, visiting twenty (20) cocoa and cashew farms, and 10 cocoa and cashew nut and peduncles processing firms in Ghana. The actual potential of the residues was estimated based on the percentage of the cocoa beans and cashew nuts and peduncles processed annually.

3.1.3 Assessment of the technical potential of residue generation

The technical potential of residue generation was determined by subtracting the amount of residues utilized for other purposes and the fraction of residues than cannot be recovered from the theoretical potential (see Equation 3). Data on alternative uses of the residue products were obtained following the methodology outlined in Anabire et al. [141]. It is understood that the fraction of residues that can be recovered is dependent on the type of residues and at what point in the value chain of the crop the residue is generated. For instance, Smeet et al. [142], reported various recoverable residue fraction for different crop residues. Residues generated at the processing unit were deemed to be 100% recoverable, while farm-based residues ranged between 25% and 75%. In order not to overestimate the resource potential, a recoverable fraction of 50% was used in this thesis. This is consistent with other studies [133,143,144].

$$\mathrm{TP} = \mathrm{P_{th}} - \mathrm{U} - \mathrm{R} \tag{3.3}$$

Where TP = Technical Potential; P_{th} = Theoretical Potential; U = Amount of residues utilized for other purposes and R = Fraction of the residues that cannot be recovered.

3.1.4 Greenhouse gas emissions

Greenhouse gas emissions from cocoa pods disposal were determined using Equation 3.4 based on the 2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventory [145]. The cocoa pod was considered as solid waste material and its disposal was modeled as an uncontrolled anaerobic digestion process with a depth of less than 5 meters [146]. This was selected because residues are usually left on the farm in heaps, with a depth of less than 5 m. Even though some residues are openly burnt on the farms, the percentage of cocoa pods combusted annually was assumed to be insignificant. Therefore, Equation 3.4 was used to determine the methane emissions with the basic assumption that none of the residues are combusted. Carbon dioxide (CO_2) equivalence emissions were determined by using the conversion factor, 1 gCH_4 = 25 gCO_2 based on the IPCC atmospheric impact of greenhouse gases on a 100 year time horizon [147].

$$\mathrm{CH_4Emissions} = \mathrm{M_r} \text{ x } (\mathrm{DOC}) \text{ x } (\mathrm{DOC})_\mathrm{f} \text{ x } \mathrm{MCF} \text{ x } \mathrm{F} \text{ x } {}^{16}/_{12} \tag{3.4}$$

Where M_r = mass of agricultural residues deposited in a particular year, Gg; DOC = Degradable Organic Carbon content of the residues; DOC_f = Fraction of Degradable Organic Carbon content of the residues; MCF = Methane Conversion Factor; F = fraction of methane in the biogas. The default values used in the calculations are presented in Table 3.1

Table 3.1: IPCC default values used to estimate the greenhouse gas emissions from cocoa and cashew residues.

Parameter	Unit	Value	Reference
MCF for shallow pits		0.4	[148]
DOC for cocoa pods	mg/g	0.41	[21]
DOC for cashew peduncles	mg/g	0.41	
DOC_f	%	0.5	[146,148]
F	%	0.5	[146]

3.1.5 Physical and chemical characterization

3.1.5.1 Sampling

The cocoa pods and cashew bagasse samples used in all the experiments were obtained from Ghana. The cocoa pods were obtained from State Experimental Farms located at the Cocoa Research Institute of Ghana in Tafo. The cashew peduncle and cashew bagasse samples were obtained directly from farms located in Wenchi, Ghana, and Mim Cashew Processing Firm Ghana Limited respectively. All the samples were initially frozen in their raw/unprocessed state in chest freezers at -20 ºC in Ghana and then transported overnight to Germany within 24 hrs in plastic containers. Once in Germany, the samples were transferred into deep chest freezers at -20 ºC for storage until needed.

3.1.5.2 Sample preparation

The particle size of the residues except the cashew bagasse needed to be reduced to render them usable in the subsequent experiment due to their initial particle size. The frozen residues were allowed to thaw naturally over a 24 hr period in the refrigerator compartment at 0 ºC. The particle sizes of the residues were first reduced with a titanium knife by manually cutting the residues into irregular pieces. After cutting, the residues were individually mixed thoroughly to achieve homogeneity after which about 300 g of each sample in triplicates was taken for further analysis. The particle size of the remaining samples was further reduced to about 300 µm with a laboratory-scale blender, Retsch GM 300, Germany. The blender was operated on program 1 at 2000 rpm for 10 s. The milled samples were then homogenized and packed into smaller containers and stored at -20 ºC in a refrigerator to reduce microbial activity. Fractions of the substrates (cocoa pods, cashew peduncle, and cashew bagasse residues) needed for experiments were subsequently thawed naturally in the refrigerator compartment at 0 ºC.

3.1.5.3 Proximate and ultimate analysis

Proximate analysis of the samples comprising the moisture content was determined following the specification EN 14744-1[149]. About 100 g of each sample in triplicates was dried in an oven at 60 ºC for 48 hrs in a temperature-controlled drying chamber. The weight difference before and after drying was used to determine the moisture and dry matter content on a wet basis (Moisture content, total solids in %OS). After drying, the particle size of the dried matter was further reduced with a Retsch ZM 200 ultra-centrifugal milling device, Germany to about 40 µm. The volatile organic compounds and ash content were determined by following, the loss of ignition procedures outlined in EN 15148 [150]. To do that, about 20 g of the dried samples in triplicates were placed in a muffle furnace and ignited to 550 ºC. The difference in weight before and after combustion was used to determine the volatile solids as a percentage of the dry matter content. Samples of the dried matter were then used to determine the elemental composition using an organic elemental analyzer, Pelken Elmer 7600 by following EN ISO 16948 [151] in an external laboratory. The fuel grade ash content of each of the samples was determined in triplicates by placing 20 g of each sample in crucibles and ignited at 815 ºC. The difference in weight of the crucibles before ignition and after ignition as a percentage of the input dry matter content of each residue was determined as the fuel grade ash content. Parr Instrument 6400 was used to determine the higher HHV of the samples as described in EN 14918 [152].

3.1.5.4 Fiber analysis

Fiber analysis of the residues was carried out by determining the acid detergent fibers (ADF), neutral detergent fibers (NDF), and the acid detergent lignin (ADL) through methods described in Liebetrau [153] which references the German Standard VDLUFA. The cellulose and hemicellulose fractions were calculated by using methods described in Van Soest et al. [154].

3.1.5.5 Mineral content analysis

Major and minor mineral content analyses were determined in an external laboratory in Germany by following methods described in EN ISO 16967 [155] and EN ISO 15297 [156] respectively.

3.2 Anaerobic digestion studies

3.2.1 Theoretical Biomethane Potential

The theoretical biogas and methane potential at standard condition (0 ºC, 1 atm) were determined using the Buswell equation as shown in Equations 3.5 and 3.6 using the results of the elemental analysis of the residues and their physical characteristics [157–159].

$$\mathrm{C_cH_hO_oN_n} + \left(\mathrm{c} - \frac{\mathrm{h}}{4} - \frac{0}{2}\right) \mathrm{H_2O} \rightarrow \left(\frac{\mathrm{c}}{2} + \frac{\mathrm{h}}{8} - \frac{\mathrm{o}}{4}\right) \mathrm{CH_4} + \left(\frac{\mathrm{c}}{2} - \frac{\mathrm{h}}{8} + \frac{\mathrm{o}}{4}\right) \mathrm{CO_2} \tag{3.5}$$

Where a, h, o, and n are the results of the elemental analysis.

$$\mathrm{Bu}\left(\frac{\mathrm{L(CH4)}}{\mathrm{KgVS}}\right) = 22.4 \left[\frac{\frac{4\mathrm{c}+\mathrm{h}-2\mathrm{o}-3\mathrm{n}}{8}}{12\mathrm{a}+\mathrm{b}+16\mathrm{c}+14\mathrm{d}}\right] \tag{3.6}$$

Where Bu is the maximum methane potential of the substrate.
The biodegradability index (BD) was determined using Equation 3.7 as reported by Girolamo et al. [119]. The BD was calculated by diving the cumulative methane yield by the theoretical methane yield.

$$\mathrm{BD} = \frac{\mathrm{BMP_{actual}}}{\mathrm{BMP_{theoretical}}} \tag{3.7}$$

3.2.2 Biogas potential, bench-scale assay

The experiment to determine the biogas potential in 500 ml Ankom bottles followed the German standard Verein Deutscher Ingenieure (VDI) [160]. The inoculum used was obtained from an active anaerobic digester operating on cow dung and maize silage and degassed in a temperature-controlled room at 38 ºC for a week before utilization. Based on the physical and chemical properties of the inoculum as shown in Table 4.1, appropriate quantities of substrate and inoculum were weighed into each bottle maintaining a ratio of 1:3 respectively based on volatile solids present. The bottles were filled to about 300 ml leaving a headspace of about 200 ml as shown in Figure 3.1. The experiments were carried out in triplicate and benchmarked with pure cellulose and a blank containing only the inoculum. The bottles were covered with a specially designed cap equipped with a pressure sensor and pressure release valve. The pressure sensor measured the relative pressure of the accumulated gas in the headspace and the atmospheric pressure. A wireless sensor was used to transfer the result of the pressure measurement in real-time to a computer every 20 seconds. Results of the pressure measurement were used to estimate the biogas yield using an ideal gas equation. The pressure release valve was set to trip at 50 mPa to control the accumulation of gas in the headspace. All the bottles were placed in a temperature-controlled water bath at 38 ºC to maintain uniform temperature around the bottles. The experiments were halted after 28 days when the daily gas production was less than 2% of the previous amount.

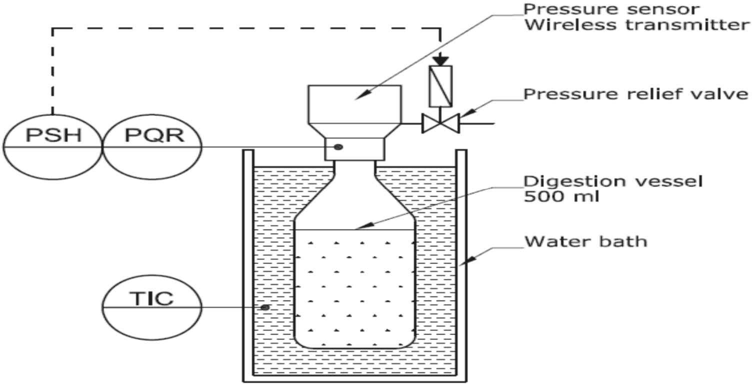


Figure 3.1: 500 ml bench-scale Ankom anaerobic digestion bottle.

3.2.3 Biomethane potential in a 30 l reactor

The large-scale BMP assay was carried out in a 30 l batch reactor. Each vessel was filled with inoculum and substrate in the ratio of 3:1 based on the volatile solids of the residues and the inoculum. Gasholder bags were attached to each vessel to collect the gas from the headspace. The vessels were placed upside down to enhance mixing which was done once a day for 10 minutes with a magnetic stirrer. The complete setup was placed in a temperature-controlled room maintained at 38 ºC for 36 days. Gas production and its composition were monitored daily by removing the gas holder bags to measure the volume of gas collected and as well as its composition. The daily gas production was accumulated to determine the specific gas production. The volume of gas was measured with a Ritter drum-type gas meter, Germany, after 5 l of biogas had accumulated in the gasholder. This was the minimum volume of gas required to turn the gas drum through one complete revolution for accurate measurement.

3.2.4 Kinetic study

The modified Gompertz model [158,161] was used to model the kinetics of anaerobic digestion. The experimented data was fitted to the Gompertz model (Equation 3.8). Using Microsoft Excel

2013 solver function, the kinetic constants P, R_m, and Ø were determined by minimizing the squared errors between the experimental values and the predicted values using non-linear methods as described by Pozdniakova et al. [162].

$$M(t) = P\exp\left[-\exp\left(\frac{R_m x e}{P}\right)(\emptyset - t) + 1\right] \tag{3.8}$$

Where M(t) is the cumulative biogas production (l/kgVS) at a given time, P is the specific maximum biogas potential (l/kgVS), R_m is the maximum specific biogas production rate (l/kgVS-day), Ø is the lag phase of the anaerobic digestion process (day) and t is the reaction/retention time (day).

The maximum time to achieve the highest volume of biogas generated was calculated using Equation 3.9 as reported by Ran et al. [121].

$$t_{max} = \emptyset + \frac{P}{R_m e} \tag{3.9}$$

Cocoa and cashew residues are known to contain fermentable sugars which are likely to degrade faster than the lignocellulose fibers which will take a longer time to degrade. As a result, a second kinetic model (Equation 3.10) developed by Brulé et al. [163], which models the anaerobic digestion as a dual-pool 2-step process was also used to fit the kinetic data.

$$M_l = S \times \left[\alpha \times \left(1 + \frac{K_f \times e^{-K_{vfa}t} - K_{vfa} \times e^{-K_f t}}{K_{vfa} - K_f}\right) + (1 - \alpha) \times \left(1 + \frac{K_l \times e^{-K_{vfa}t} - K_{vfa} \times e^{-K_l t}}{K_{vfa} - K_l}\right)\right] \tag{3.10}$$

Where M_l is the cumulative gas potential (l(N)/kgVS); S is the Substrate amount (l(N)/kgVS), α is the ratio of the fast degradable fraction to slow degradable fraction; K_f is the rate constant for the fast degradable fraction (day^{-1}); K_l is the rate constant for the slowly degradable fraction (day^{-1}) and K_{vfa} is the rate constant for the formation of volatile fatty acids (VFA) (day^{-1}). The five constants were determined using the solver function in Microsoft Excel 2013 by minimizing the squared errors between the model and the kinetic data.

3.2.5 Hydrothermal pretreatment

3.2.5.1 Experimental setup

The hydrothermal pretreatment experiments were carried out in a Parr Instrument hydrothermal process unit 4520. The unit comprised a 1 l reaction vessel with a pressure gasket designed to withstand a maximum pressure of 150 bar, a heating jacket equipped with a 2000 W heating coil, a 550 (maximum) rpm stirrer with an attached motor and a temperature and a pressure sensor. To enable the study of the combined effect of process temperature and reaction time on the biogas yield, all other process parameters except the two were kept constant. Mass concentration for all the experiments was maintained at 5% dry matter content. The mass of the empty reactor was first weighed after which the specified mass of residues was weighed directly into the reactor. Deionized water was used to top up the mass of the content of the reactor to 700 ml leaving a headspace of 300 ml to allow for the expansion of the vapor during the process. Once the reactor was fixed in its place and the heating mantle was attached, heating was carried at a constant rate of 2 K/min until the reaction setpoint temperature was attained. The 2 K/min heating rate was maintained for all process temperatures. Once the reaction temperature was achieved, the inbuilt controller maintained the reaction temperature for the specified reaction time. The heater was immediately switched off after the reaction to allow the reactor to cool down by natural convection since there are no cooling devices attached. The content of the reactor was separated with a Buchner funnel attached to a vacuum pump into the hydrolysate and the solid fraction. The pH of the hydrolysate was then measured with an electrode pH meter. The solid fraction was split into two equal fractions. One of the fractions was immediately dried in an oven at 105 ºC for 24 hrs, while the other fraction was stored in a chest freezer at -20 ºC for further analysis.

3.2.5.2 Experimental design

The pretreatment experiment was designed with a central composite response surface methodology with 5 central points using Design Expert 11. Two independent process variables; temperature and reaction time were varied between 150 – 220 ºC and 5 – 15 minutes respectively (See Appendix A-1). All other process parameters such as heating rate, the rate of stirring, and the mass concentration were kept constant for each experiment. This resulted in 13 experimental runs. Two independent response variables; lignin content and biogas potential were used to evaluate the effect of the process parameters on the hydrothermal pretreatment process. The severity of the pretreatment which is a function of temperature (T) and reaction time (t) was calculated using Equation (3.11) [164].

$$\log \mathrm{S} = \log\left[\mathrm{t} * \exp\frac{(\mathrm{T}-100)}{14.75}\right] \tag{3.11}$$

Where S is the severity of the hydrothermal treatment, t is the reaction time (s) and T is the reaction temperature (ºC).

The lignin content and the biogas potential experiment of the pretreated samples were used to fit the linear and quadratic equations generated by Design Expert 11 (Equation 3.12 and 3.13).

$$\mathrm{y} = \beta_o + \beta_i X_i + \beta_j X_j \tag{3.12}$$

$$\mathrm{Y} = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i<} \sum_{j=2}^{k} \beta_{ij} X_i X_j \tag{3.13}$$

Where y and Y represent the response variable for lignin content and biogas yield respectively; β_o is the intercept; β_i and β_j are first-order coefficients and β_{ii}, β_{iij}, β_{jj} and β_{jji} are the quadratic coefficients.

3.2.6 Semi-continuous mono digestion of cocoa pods, cashew peduncle, and cashew bagasse

The limiting effect of organic loading rate (OLR) on the biogas yield and process stability of the anaerobic digestion process was studied for all the residues (cocoa pods, cashew peduncles, and cashew bagasse) under mesophilic conditions in continuously stirred tank reactors (CSTR). Eight (8) reactors, each with a working volume of 5 l were used for the experiments. To allow for the duplication of the experiment, each substrate was run on two reactors operating in parallel mode, making a total of six reactors. The last 2 digesters were set up as a control experiment and fed with only maize silage. The inoculum used was obtained from a municipal waste treatment plant anaerobic digester and incubated for one week at mesophilic conditions to get rid of all residual methane before using it for the study. Individual substrates were initiated at a low OLR of 2.5 kgVS/m^3.day to avoid startup challenges. Feeding was done in equal fractions twice in a day and only on weekdays. The digester was constantly stirred automatically with a motor drive except during feeding and sampling when the stirrer is switched off.

3.2.7 Co-digestion in a continuous reactor

Co-digestion of cocoa pods, cashew peduncle, and cashew bagasse with maize silage was carried out in a 5 l continuous stirred reactor (CSTR). The same reactor configuration running under mesophilic conditions was used as described under section 3.2.6. To determine the effect of co-digestion of the cashew peduncle with maize silage, on the biogas potential and the process stability, initial feeding was prepared in a ratio of 50:50 to the cashew peduncle/bagasse: maize silage respectively based on VS at an OLR of 2.5 kgVS/m^3.day. The composition of the feed was varied by increasing the share of cocoa pods, cashew peduncles, and cashew bagasse monotonically by 10% every 4 weeks while tailoring down the fraction of maize silage by the same percentage but maintaining the same OLR (2.5 kgVS/m^3.day). Feed composition changes were carried out until mono digestion was achieved for both cashew peduncle and cashew bagasse.

3.2.8 Synergetic index (SI)

The synergetic index was determined by comparing the experimental methane yield of the co-digested substrate to the weighted averages of the methane yield of mono digested substrates [165] as shown in Equation 3.14. Synergetic effect was assigned to a ratio greater than 1, while the antagonistic effect was assigned to a ratio of less than 1 [166].

$$\mathrm{SI} = \frac{\mathrm{SB_{exp}}}{\sum_{i=1}^{n} \mathrm{SB_i X_i}} \tag{3.14}$$

Where SB is the specific biogas yield of the co-digested substrate, i is the substrate, n is the nth substrate, and X is the fraction of substrate in the feed composition in terms of volatile solids.

3.2.9 Analytical methods

The volume and composition of the biogas were measured daily with a Ritter drum-type gas meter and VISITEhiem 02 gas analyzer respectively. Samples of the digestate were taken from each reactor once a week and tested for the pH and total alkalinity (TAC), volatile organic acids (FOS), and speciation of the volatile acids. The TAC and FOS concentration were determined by titrimetric methods. The Chemical oxygen demand (COD) was determined following ASTM D-1252 using standard photometric test kits (Hach Lange, Düsseldorf, Germany). The measurement for each sample was carried out in triplicates and the average was used for the analysis.

3.3 Hydrothermal carbonization

3.3.1 Experimental Setup

The hydrothermal carbonization process was carried out in a 1 liter Parr Instrument reactor. A fixed mass of the fresh cocoa pods (350 g) and cashew peduncles (366 g) was used for each of the experiments. To maintain a 10% total solid concentration, 350 g and 334 g of deionized water respectfully for cocoa pods and cashew peduncle substrate was added to bring the total mass to 700 g, leaving a headspace of about 300 ml. The pH of the sample was measured before and after the carbonization process. After each carbonization process, before the reactor was opened, the gas in the headspace was evacuated into a gas bag. After opening the reactor, the carbonized sample was separated into solid hydrochar and the hydrolysate with a Buchner funnel attached to a vacuum pump. The wet hydrochar was then dried in an oven at 105 ºC. Samples of the dried hydrochar was used to determine the calorific value, ash content, and volatile solids. The hydrolysate was stored at 4 ºC until needed for further experiments.

3.3.2 Experimental design

The effect of process reaction temperature, heating rate, and reaction time on the fuel properties of the hydrochar was studied. Each process parameter was varied at three different levels (see Table 3.2). The reaction temperature was varied between 180 – 240 ºC (Appendix B-2). The heating rate which is measured as the time taken for the reactor to reach the reaction temperature was varied between 2 and 10 K/min. Meanwhile, the reaction time was measured from the time the reactor reached about 95% of the setpoint until the end of the reaction and was thus varied between 1 – 8 hrs. A Box-Behnken response surface model with 3 central location allowing for flexibility of rotation was used to design the experiment. This resulted in 15 runs (Appendix B-1). The severity of treatment was determined using Equation 3.11 as described by several authors [77,167,168].

Table 3.2: Hydrothermal pretreatment experimental design.

	Parameter	Unit	Lower Level	Intermediate level	High level
A	Temperature	ºC	180.0	210.0	240.0
B	Heating rate	K/min	2.0	6.0	10.0
C	Reaction time	Hr	1.0	4.5	8.0

3.3.3 Yield of Hydrochar

The yield of the hydrochar was determined gravimetrically. The mass of the oven-dried hydrochar after the carbonization process was divided by the original mass of the substrate used in terms of the total solids as described in Equation 3.15.

$$\mathrm{Yield(Y)} = \frac{\mathrm{m}}{\mathrm{MxTS}} \mathrm{x}\ 100\% \tag{3.15}$$

Where m is the mass of the oven-dried hydrochar (g), M is the mass of cocoa pods substrate taken for the carbonization process (g), and TS is the fraction of total solids contained in the substrate.

3.3.4 Energy Content

The energy content of hydrochar was determined by multiplying the yield of the hydrochar with the higher heating value of the hydrochar as described in Equation 3.16.

$$\mathrm{E(Energy\ Content)} = \mathrm{Y\ x\ C} \tag{3.16}$$

Where Y is the yield and C is the higher heating value of the hydrochar at the specific treatment condition

4. Results

4.1 Resource potential estimation

4.1.1 Cocoa beans production and processing

Ghana has been a leading producer and exporter of cocoa beans since 1948 when the crop was officially identified as a potential cash crop. Since then, cocoa has maintained its lead as Ghana's main agricultural produce foreign exchange earner. Ghana has consistently maintained its position as the second leading producer of cocoa beans in the world for the last two (2) decades. Over the last decade, production of beans has averaged about 0.78×10^6 t annually. Cocoa beans procured from the farmers are either sold to local processing companies that mainly process into cocoa butter and press cake for export or exported as raw beans to processing companies outside the shores of Ghana. Primary processing of cocoa beans into value-added products is a multi-billion-dollar industry that involves dehusking, milling, and extraction of the butter. As of 2015, Ghana had an installed cocoa milling capacity of about 0.53×10^6 t/a with the completion of the Touton Cocoa Processing Company in 2017. Despite the seemingly impressive installed milling capacity, less than 10% of the beans are processed locally [169]. The bulk (over 90%) of the beans are exported mainly to Europe and Japan.

4.1.2 Cashew nut production and processing

Cashew is fast establishing itself as an important cash crop globally. According to Rabany et al. [22], cashew nut overtook palm oil, rubber, banana, and cotton in 2014 and was only second to cocoa in terms of export value in West Africa. Unlike cocoa beans, cashew nut was not considered an important economic crop in Ghana until 2002 when after a comprehensive study by the Ministry of Agriculture, cashew was identified as one of the key non-traditional economic crops for the country. An initial assessment identified the three Northern Region: Northern, Upper East, and Upper West and the Brong Ahafo regions as suitable areas for large scale cultivation of cashew nut. The result of this study was the launching of the cashew initiative which saw the production of cashew increasing from an average of 5×10^3 t/a in 1980-2000 to about 45×10^3 t/a in 2014 [170]. Ghana's share of world cashew nut production has seen a marginal increase from about 1% in 2011 [171] to 2.6% in 2015 [22]. As shown in Figure 4.1, there is a wide variation between raw cashew nuts (RCN) produced in Ghana and the total number of nuts traded. The wide difference could be due to smuggling activities on the Ghana - Cote d'Ivoire and Ghana – Burkina Faso borders, with the former accounting for the greater majority. According to Rabany et al. [22], the annual production of cashew nuts in Ghana is expected to increase by 14×10^3 t/a 2016 - 2020.

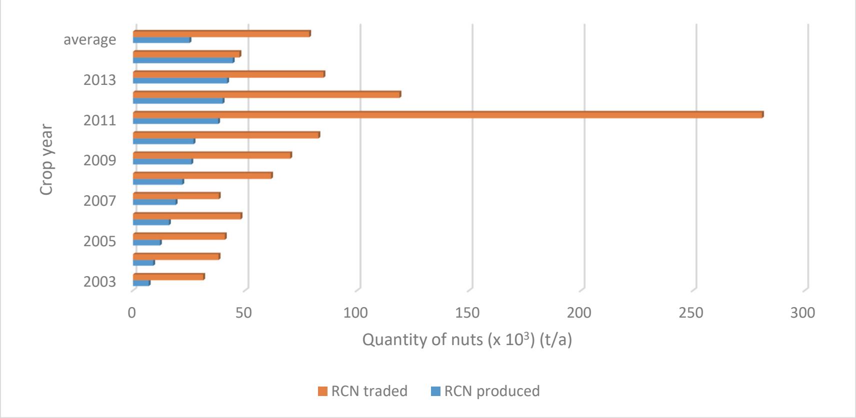


Figure 4.1: Cashew nuts produced and exported annually between 2003 and 2013 [170].

4.1.3 Residue to crop ratio (RCR) estimation

The main residues from the two crops are cocoa pods and shells and cashew peduncles, bagasse, shells, testa, and cashew nutshell liquid oil. The residues are generated at various stages of the processing chain. The pods and cashew peduncles are generated during the harvesting of the nuts, while the cashew bagasse is generated during processing. The cocoa fruit which comprises the pods and the beans is oval-shaped and comes in various sizes. On the average, cocoa fruit weighs 451 g. An average of 9.6 cocoa fruits yields 1 kg of wet beans, while 27 fruits yields 1 kg of dry beans respectively [172]. Since national cocoa beans production figures are reported on dry basis of the beans, the yield of cocoa beans on dry basis was used to estimate the RCR. In effect, about the weight of 27 fresh cocoa fruits will amount to about 12,285 g. However, the fresh beans contained in the 27 pods will amount to 2,812 g. Therefore, applying Equation 3.1 will result in an RCR of 9.3.

Just like cocoa, cashew peduncles vary in sizes, thus the weight depends on the type. Red cashew apples are usually smaller than yellow apples which are also usually smaller than orange apples according to [23]. The mass of cashew apples and nuts in Ghana are presented in Table 4.1. Yields of cashew in Ghana are reportedly quite low, even though a substantive increase from 400 – 800 kg/ha have been recorded over the last ten years [173]. RCR of cashew peduncles was estimated to be about 6.4 on a wet basis.

Table 4.1: Average mass of cashew peduncles and nuts in Ghana based on field investigations from 20 farms in Ghana in 2017.

Type of cashew nut	Average mass of fresh fruits (g)	Average mass of fresh cashew nut (g)
New breed from Brazil	105	14
Local breed	52	12
Average	78.5	13

4.1.4 Resource potential of residues

Results of the theoretical resource potential of cocoa and cashew residues using the estimated RCRs are presented in Table 4.2. Cocoa pods are by far the largest residues in terms of quantities. Using the average crop production over the last ten years, about 7.2×10^6 t of cocoa pods is generated annually. If the government can achieve the 1 million tons of cocoa beans target, which might be only possible after about 3 years, then a corresponding 9.34×10^6 t of cocoa pods will be generated annually. Similarly, current cashew peduncles resource potential based on the average annual nut production of 0.035×10^6 t/a was estimated to be about 0.226×10^6 t/a. Apart from cashew bagasse, the potential and actual residue generation were similar for cocoa pods and cashew peduncle. The difference in potential and actual residue generation for cashew bagasse arises from the current situation where only utilization of cashew peduncles in Ghana is only 10%. In the event that all the cashew peduncle residues are processed into either juice or alcohol, the remaining residues will constitute the potential residue generation.

.

Table 4.2: Cocoa and cashew nut residue potential in Ghana based on average production levels from 2003 – 2015.

Crop type	Average production, $\times 10^6$ t/a	Residue type	RCR	Potential residue generation, $\times 10^6$ t/a	Actual residue generation, $\times 10^6$ t/a
Cocoa beans	0.778	Cocoa pods	9.3 (wet basis)	7.2	7.2
		Cocoa pods	2.5 (air dry basis)	1.945	1.945
Cashew nut	0.035	Cashew peduncles	6.04 (wet basis)	0.226	0. 226
		Cashew peduncle	2 (air-dry basis)	0.075	0.075
		Cashew bagasse	4.8 (wet basis)	0.1808	0.0018
			1.5 (air-dry basis)	0.0525	0.00525

4.1.5 Current residue utilization

Cocoa and cashew nut crop residues have various uses in the local industry. Cocoa pod, for instance, is known for its high potash content [49,50]. The ash obtained after combusting the dried pod is rich in potassium carbonate and thus a good source of cheap alkali for soap production. Due to the unregulated nature of traditional soap manufacturing in Ghana, it was difficult to estimate the quantities of cocoa pods used for soap making. When ripe, the cashew peduncles turn bright red, yellow, or orange, delicious and can be eaten raw without processing. It is mainly fleshy and could contain between 10 – 29.9 ml of juice [56]. The peduncle, even though delicious, is not eaten in Ghana. An old myth that the juice becomes toxic when mixed with milk and could lead to instant death is to blame for the misconception. As a result, the peduncle is left on the farms to decay after harvesting the nuts. Processing of the peduncles is made much complex by the short shelve life of the peduncle. According to Das and Arora [23], the reactivity of the apples doubles for every 10 °C rise in temperature. Harvested peduncles must, therefore, be processed as quickly as possible or risk going bad. Further, fallen ripe peduncles are a delicacy of bats and other birds. The risk of salmonella contamination of ripe fallen peduncles from Bats is thus high. Currently, Mim Cashew Limited and Pinora Ltd are the only companies commercially processing the peduncle. Mim Cashew processes peduncles from its 60 hectares farm into gin leaving behind the fibrous material (bagasse) as waste. The capacity of the plant is however small, 6 – 7 t/day of fresh peduncles. Pinora exports the pressed juice from the apples from its 4,500 t/a processing plant. In total, current utilization of cashew peduncle residues is about 3%. However, in order not to overestimate the resource potential, a 10% utilization for other purposes is used in this thesis. The result of the technical potential of the residues after taking out the current residue utilization and the unrecoverable from the theoretical residue potential are presented in Table 4.3.

Table 4.3: Technical potential estimation for cocoa and cashew nut residues in Ghana.

Residue type	Actual Potential, $\times 10^6$ t/a	Use in Ghana	Utilization	Recoverable, %	Technical potential, $\times 10^6$ t/a
Fresh cocoa pods	7.2	Soap making	<1%	50%	3.564
Cashew peduncles	0.226	Alcoholic beverage, juice	<10%	50%	0.1017
Cashew bagasse	0.00181	Animal feed	20%	100%	0.00036

4.1.6 Regional distribution of residues

Ghana is not known for having large agricultural plantations as pertains to other countries. The cultivation of cocoa is dominated by peasant farmers who form the bulk (88%) of the over 800,000 households involved in cocoa farming. The average farm size of each household is about 2 acres culminating in a total of 1.6 million acres of cultivated land. As shown in Figure 4.2, the cultivation of cocoa is spread across six out of the ten regions of Ghana. While production from the Ashanti Region has been relatively stagnant in the last two decades, the Western region has seen a significant increase in production level since 1984/85 crop season, surpassing the Ashanti Region as the leading producer of cocoa beans in Ghana as shown in Figure 4.3 Harvesting of the crop takes place twice in the Calendar year. The major crop season is from September – March, while minor crop season is from May-August. Due to the weight of the crop, and the fact that cultivation of the crop is manually driven, the harvested cocoa fruits are cut open on the farms. Though not a recommended farm practice, the pod residues are left on the farm in a pile after the beans have been removed.

Apart from the Olam Cocoa Processing Company, which is located in Kumasi and WAMCO in Takoradi, all the remaining active cocoa milling facilities are situated in the free zone enclave of Ghana near the Tema harbor.

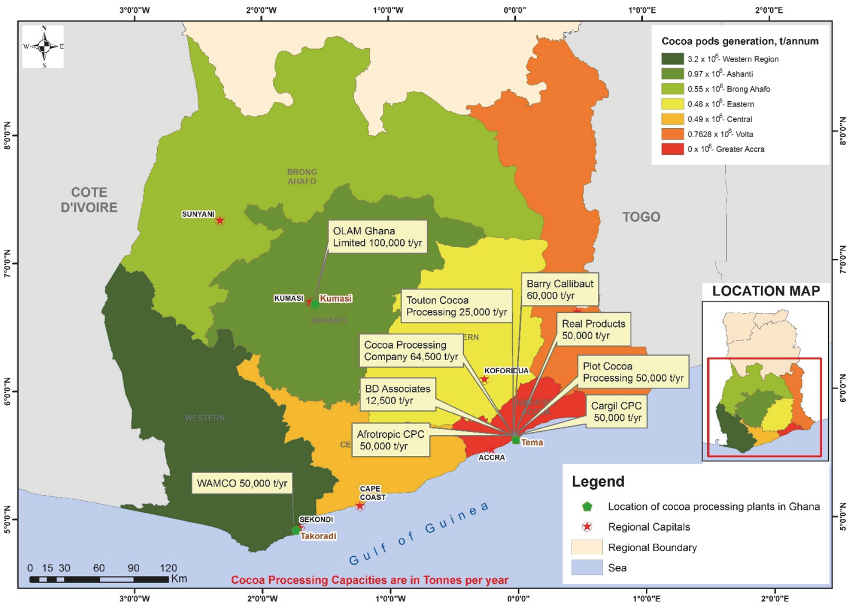


Figure 4.2: Regional distribution of cocoa-growing areas in Ghana and their respective residue generation potential computed with data from Ghana Cocoa Board.

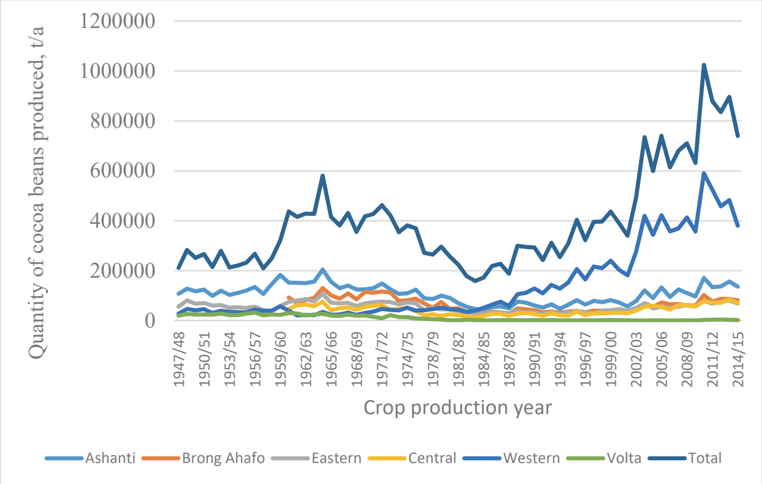


Figure 4.3: Regional distribution of cocoa beans production in Ghana [174].

Cashew production takes place in about four regions in Ghana as shown in Figure 4.4. However, the bulk of cashew nuts are produced in the Brong Ahafo and Northern regions. Sampa is the epicenter of cashew nut production in Ghana. The cultivated area has increased steadily from 35 000 hectares in 2003 to about 89 000 hectares in 2014. Cashew nut cultivation is not very much different from cocoa beans production. Several households are involved in the cultivation of cashew nuts in Ghana. According to the African Cashew Initiative [170], over 400,000 households are involved in the cultivation of cashew in Ghana with farm sizes ranging between 2 and 15 hectares. A recent survey carried out by the Ministry of Agriculture established that cashew could grow very well in non-cocoa growing areas in Ghana. This implies, the whole of Northern region, part of Central, Greater Accra, Eastern and Volta Regions were cocoa is not cultivated could be used to cultivated cashew.

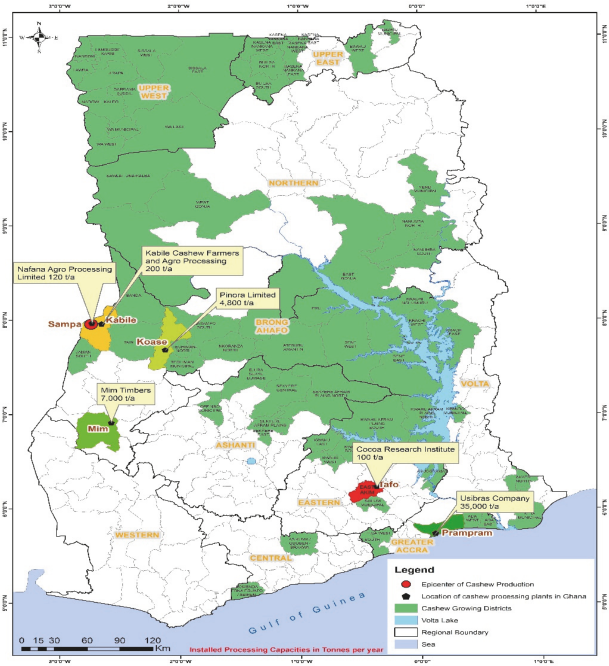


Figure 4.4: Current Cashew growing areas and location of major processing facilities in Ghana drawn with data from the Crop Services Directorate of the Ministry of Food and Agriculture.

4.1.7 Greenhouse gas emissions from cocoa pods and cashew peduncles.

Untreated agricultural residues have the potential to contribute significantly to the emission of greenhouse gases. Cocoa pods and cashew peduncles are often left on the farm in heaps to decay naturally in an uncontrolled way. Using the IPCC methodology to model the greenhouse gas emissions, the uncontrolled disposal of cocoa pods and cashew peduncles in Ghana resulted in an average greenhouse emission of 10.37 and 0.21 MtCO$_{2eq}$/annum respectively over the last 10 years as shown in Figure 4.5. Cumulatively, about 137.4 MtCO$_{2eq}$ emissions have been released from the non-treatment or uncontrolled disposal of these two residues from 2003 to 2015. A second-order polynomial growth model was developed based on the assumption that Ghana will continue to grow the same cocoa and cashew breed with similar yield characteristics as compared to current ones and the area of cultivation might increase only marginally. Using this model as shown in Equations 4.1, 4.2, and 4.3, it is estimated that, the cumulative emissions from the uncontrolled disposal of cocoa pods and cashew peduncles could reach about 210 and 375 MtCO$_{2eq}$ by 2020 and 2030 respectively as shown in Figure 4.6.

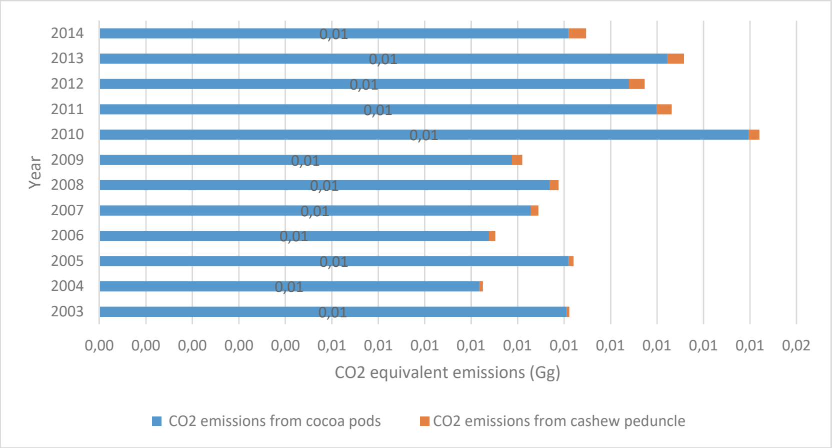


Figure 4.5: Annual greenhouse gas emissions from cocoa pods and cashew peduncles.

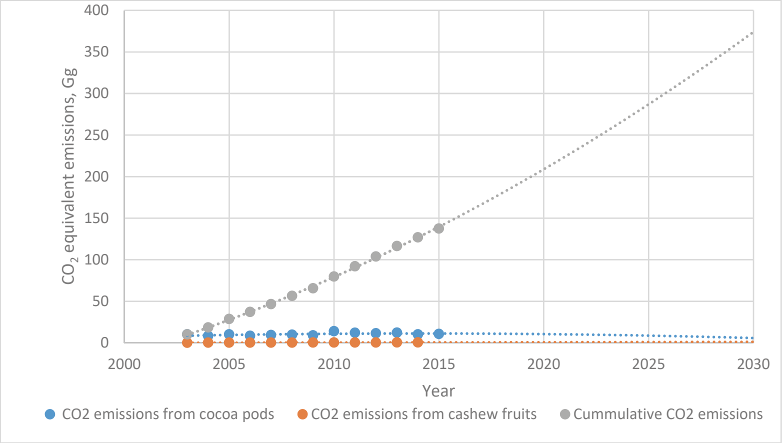


Figure 4.6: Greenhouse gas emissions from cocoa pods and cashew peduncle residues using a second-order polynomial forecast model.

$$\text{Cumulative Emission (E)} = 0.1779\,(\text{Y} - 2003)^2 - 704.05(\text{Y} - 2003) + 0.6964 \text{ x}10^6;\quad \text{R}^2 = 0.9989 \qquad (4.1)$$

$$\text{Cocoa pods Emissions (E)} = -0.0217(Y - 2003)^2 + 87.352\,(Y - 2003) - 87957;$$
$R^2 = 0.2972$ (4.2)

$$\text{Cashew peduncles Emissions (E)} = 0.0005(Y - 2003)^2 - 1.8991(Y - 2003) - 1876.4;$$
$R^2 = 0.9821$ (4.3)

4.1.8 Physical and chemical characteristics of the residues.

Result of the physical and chemical characteristics are presented in Table 4.4. The moisture content and volatile organic solids of cocoa pods and cashew peduncles were similar. Cashew bagasse and cashew peduncles, on the other hand, contained lower lignin and cellulose fractions. However, the hemicellulose fraction in cashew bagasse was quite high representing about 20.13% of the structural carbohydrates. This could be as a result of the extraction of the juice leaving behind the fibrous material. The carbon:nitrogen ratio (C/N) for both the cashew peduncles and cashew bagasse is 27 and 22 respectively. The HHV of the residues were similar and fell in the range of 16.71 – 18.60 MJ/kg on a dry basis. Cocoa pods had the highest fraction of lignin and cellulose in the structural carbohydrates among the residues. Comparatively, the elemental carbon content was highest in the cashew peduncles than in cocoa pods and in cashew bagasse. The carbon:oxygen ratio (C/O) were similar for all the three residues. Also similar was the oxygen:hydrogen ratio (O/H)s for all the residues.

Table 4.4: Physical and Chemical properties of the cocoa and cashew residues after thawing and the inoculum.

Parameter	Unit	Cashew bagasse	Cocoa pods	Cashew peduncles
Proximate analysis				
Moisture content	%OS	67.20	79.70	80.90
Total solids	%OS	32.80	20.30	19.10
Volatile solids	%TS	98.50	92.60	97.99
Crude Ash (550 °C)	%TS	1.52	7.39	2.10
Ash (815 °C)	%TS	0.015	0.064	0.021
HHV	MJ/kg	18.60	17.73	16.71
Ultimate analysis				
N	%OS	1.53	1.42	2.03
C	%OS	42.25	44.60	45.99
S	%OS	0.06	0.08	0.37
O	%OS	44.50	43.00	49.10
H	%OS	6.30	6.00	6.70
C/N		27.64	31.34	22.69
H/C		0.15	0.13	0.15
O/C		1.05	0.96	1.07
Fiber analysis				
Lignin	%TS	11.01	21.29	7.24
Cellulose	%TS	12.19	26.10	8.81
Hemi-Cellulose	%TS	20.13	4.82	9.36

NB: TS = Total Solids; OS = Original Sample

4.1.9 Major and minor mineral content

The result of the mineral content analysis is shown in Table 4.5. Minor elements content was higher in the cashew peduncles than in cashew bagasse. This is expected since some of the minerals would be in the liquid phase and as a result will be lost during the mechanical extraction process of the hydrolysates. Similarly, the mechanical process of hydrolysate separation could be the reason for the high major element content of the cashew bagasse than the cashew peduncles due to the possibility of wearing of the metal surfaces in the crushers into the bagasse. Comparatively, results for the cocoa pods were consistently higher than both cashew peduncles and cashew bagasse. The effect of the soil characteristics where the cocoa pods and cashew peduncle and cashew bagasse were obtained cannot be overlooked. The soil characteristics could have affected the mineral concentration, thus the result must be put into perspective and applied as such.

Table 4.5: Minor and major minerals content of the cocoa and cashew residues.

Parameter	**Unit**	**Cashew bagasse**	**Cocoa pods**	**Cashew peduncles**
Phosphorus	%TS	0.14	0.39	0.15
Potassium	%TS	0.61	3.22	0.95
Sodium	%TS	0.08	0.45	0.10
Magnesium	%TS	0.01	0.00	0.02
Calcium	%TS	0.05	0.30	0.02
Copper	%TS	13.34	29.09	6.28
Nickel	%TS	1.18	8.66	0.90
Zinc	%TS	10.84	56.23	12.27
Iron	%TS	65.89	351.24	24.64
Boron	%TS	14.74	54.92	6.46
Cobalt	%TS	0.05	0.83	0.03
Magnesium	%TS	14.39	50.10	8.33
Molybdenum	%TS	0.16	0.38	0.10
Selenium	%TS	0.24	0.19	0.12
Aluminum	%TS	14.46	318.59	6.61

TS = Total Solids; OS = Original Sample

4.2 Biomethane potential

4.2.1 Theoretical biomethane potential

Using the Buswell equations (3.1) and equation (3.2), the theoretical biogas and biomethane potential (BMP) were determined (Figure 4.7). Cocoa pods had the highest biogas potential of about 922 l/kgVS with a biomethane content of about 51%. The BMP of cocoa pods was followed closely by cashew bagasse and cashew peduncles, both with a biogas potential of about 871 l/kgVS but with a similar methane content of 51% just as cocoa pods. The theoretical biomethane potential of cocoa pods, cashew peduncle and cashew bagasse were compared to potential biomass feedstock compiled by Allen et al. [9]. The BMP of the residues were found to be comparable to the theoretical biomethane potential of maize silage (898 l(N)/kgVS), brown algae (Laminaria digitata) (939 l(N)/kgVS), Seaweed (Alaria esculenta) (929 l(N)/kgVS), and seaweed (Ulva lactuca) (970 l(N)/kgVS)), domestic food waste (923 l(N)/kgVS) and green city park waste (925 l(N)/kgVS).

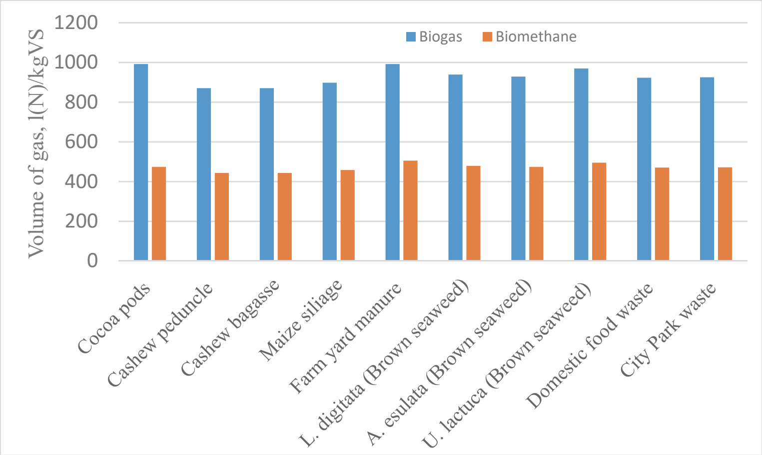


Figure 4.7: Calculated theoretical biogas and biomethane yield of cocoa pods and cashew residues compared with other residues biomass feedstock compiled by Allen et al. [8].

4.2.2 Batch test biomethane potential (BMP)

Result of the BMP carried out in the batch 500 ml bottles of the residues are shown in Table 4.6. The result shows that the cumulative daily biogas potential of cocoa pods and cashew peduncles are similar. After 28 days of retention, the cumulative biogas potential of cocoa pods was about 374.5 l/kgVS with a corresponding methane fraction of 51% representing about 40% of the theoretical BMP estimation. The low biodegradability index of cocoa pods could be due to the high lignin and hemicellulose content. Cashew bagasse recorded the lowest biogas potential of 288 l/kgVS. This represents about 33% of the theoretical potential and 77% of the BMP of cashew peduncles and cocoa pods. The relatively low biodegradability index of the residues is a confirmation of the recalcitrance of lignocellulosic residues to anaerobic digestion.

Table 4.6: Biogas yield of residues from the bench-scale experiment.

Substrate	S/I (kg_{vs}/kg_{vs})	Specific biogas yield l(N)/kgVS	Biodegradability Index
Cashew peduncles	0.30	357	0.41
Cashew bagasse	0.30	288	0.33
Cocoa pods	0.30	357	0.41
Pure cellulose	0.30	703	0.83

s/l = substrate to inoculum ratio

4.2.3 Kinetic study

The data fitting exercise generated the kinetic constants in Table 4.7 which were used to model the kinetics of the reactions using the modified Gompertz and the 2 pool 2 step models (equations 5.4 and 5.5) as shown in Figure 4.8. The R^2 of the Gompertz model for the 3 residues was between the range of 0.90 – 0.96 with cashew bagasse recording the highest of 0.96. A zero-lag phase was obtained for all the residues. This is an indication of the presence of readily digestible sugars which could lead to the instantaneous production of methane. The result showed that the maximum specific biogas production rate could be reached in approximately 1.55, 2.0, and 1.67 days respectively for cashew peduncles, cashew bagasse, and cocoa pods. Further, for purposes of engineering design t_{80}, the time taken to reach 80% of the cumulative biogas potential was calculated. Anaerobic digestion of cocoa pods, cashew peduncles, and cashew bagasse without pretreatment can reach 80% of their maximum biogas potential in 4.2. 4.0 and 5.0 days respectively.

Table 4.7: Modified Gompertz model and dual-pool 2-step model constants used to model the kinetics of the anaerobic digestion process.

	Dual-pool 2-step model						Modified Gompertz model				
Constants	K_l	α	K_f	K_{vfa}	S	R^2	P	R_m	Ø	t_{max}	R^2
Units	day^{-1}	-	day^{-1}	day^{-1}	l(N)/kgVS		l/kgVS	l/kgVS-day	day	Day	
Cashew peduncles	0.09	0.6	0.75	11964	370.0	0.998	332.5	78.95	0	1.5	0.903
Cashew bagasse	10.7	0.9	0.25	15.75	300.0	0.992	274	50.33	0	2.0	0.963
Cocoa pods	0.08	0.7	11.0	0.42	408.7	0.998	345.6	76.31	0	1.7	0.918
Cellulose (Standard)	0.17	0.8	0.16	27858	724.7	0.959	680.9	119.3	1.6	3.7	0.993

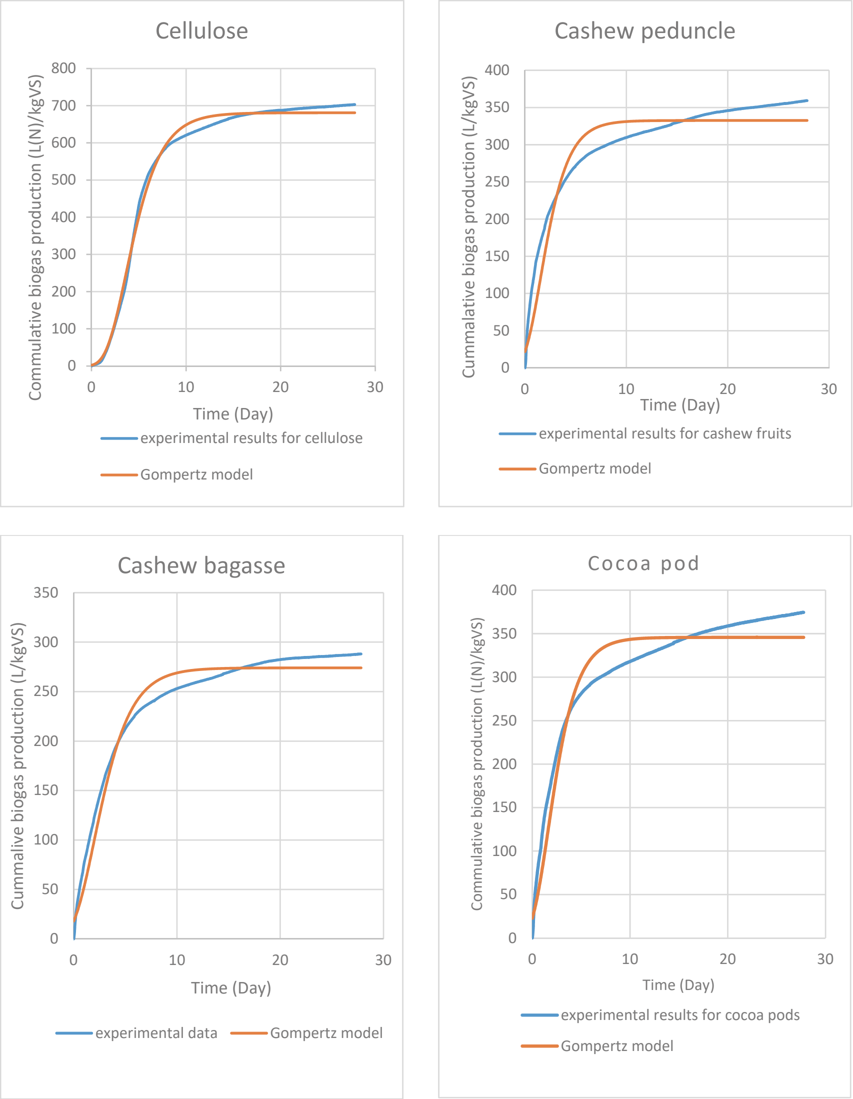


Figure 4.8: Comparison between experimental data and modified Gompertz model fitted to the kinetic data

The result of the dual-pool 2-step model is shown in Figure 4.9. The dual-pool 2-step model fitted the kinetic data better than the Gompertz model with R^2 in the range of 0.9927 – 0.9988. According to Table 6, the ratio of the fast degrading fraction to the slow degrading fraction of cashew peduncles (0.6) was similar to cocoa pods (0.7) but different for cashew bagasse (0.9). While the fast degrading fractions of cashew peduncles and cocoa pods reach their maximum potential and saturates after 7 and 10 days respectfully, the slow degradation fractions show a potential of continuous degradation beyond the retention time (28 days) for especially cocoa pods.

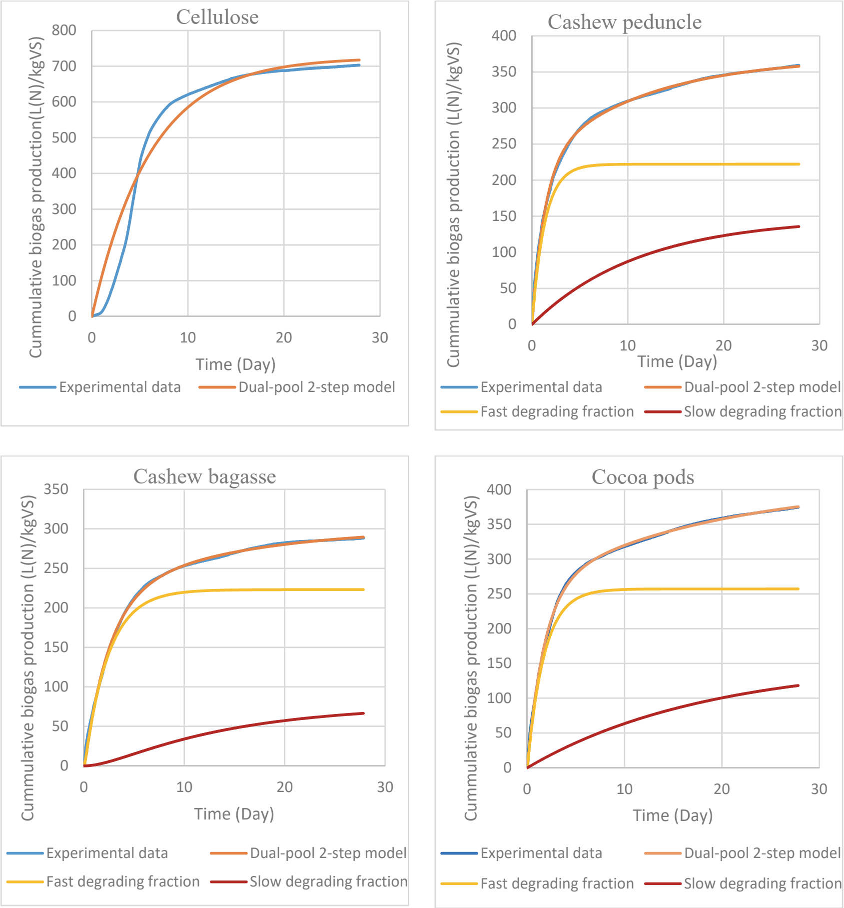


Figure 4.9: Comparison between the experimental dual-pool 2-step kinetic model fitted to the kinetic data.

4.2.4 Thirty (30) l batch anaerobic digestion (AD) reactor test

Much as result from small-batch reactors (500 ml) is quite useful in predicting the actual methane potential, results from large-sized reactors tend to mimic real plants better and are thus needed to inform the correct engineering design of biogas digesters. The result of the large-scale experiments (30 l reactors) is presented in Table 4.8.

Table 4.8: Specific biogas and biomethane yields of the residues (30 l batch).

	Units	Cashew peduncles	Cashew bagasse	Cocoa pods	Cellulose
S/I	kg_{tm}/kg_{tm}	0.33	0.42	0.29	0.42
Specific biogas yield	l(N)/kgVS	543	457	432	712
Specific methane yield	l(N)/kgVS	286	250	237	337
Methane fraction		52.67	54.70	54.86	47.33
Biodegradability index		0.62	0.52	0.47	0.84

S/I = Substrate to inoculum ratio

In comparison with the bench-scale experiments, the specific biogas yield was consistent for cellulose but wide deviations for all three residues were observed. All three residues reported higher biogas yield when compared to result with the 500 ml reactors. Cashew peduncles recorded the highest specific biogas yield of 543.2 l(N)/kgVS representing 62% of the theoretical yield as shown in Figure 4.5. The specific biogas potential of the cashew bagasse also improved from 288 to 457 l(N)/kgVS. This resulted in the biodegradable index of cashew bagasse also improving from 0.33 to 0.52. The result for cocoa pods shows a marginal increase in the biodegradability index from 0.41 to 0.47 which is still below 50% of the theoretical available biogas potential. This could be due to the longer retention time of 36 days rather than the 28 days used for the bench-scale reactor test which could have allowed for the degradation of a fraction of the hemicellulose fraction of the residues. Further, this could also be attributed to better adaptation of the methanogenic bacteria leading to partial but significant hydrolysis of the hemicellulose.

4.2.5 Kinetics of the reaction

The kinetic 2-step dual-pool model was fitted to the result of the pilot study using the constant obtained from the bench-scale batch BMP test (Figure 4.10). While the model accurately predicted the cumulative biogas production of cocoa pods, it failed to correctly predict the biogas yield of cashew peduncles and cashew bagasse. The model deviated from the experimental results, reaching a difference of about 200 ml/kgVS between the experimental value and the model by the end of the experiment for both cashew bagasse and cashew peduncles. This was quite an anomaly especially given the quantum of the deviation for both the cashew peduncle and the cashew bagasse. This was due to the significantly higher observed biomethane potential for both substrates as compared to the bench-scale BMP test. Unlike the BMP of cocoa pods, the higher BMP of cashew peduncle and cashew bagasse could not be explained by the longer retention time. Rather, a more possible explanation could be the inoculum used. No inhibition, as a result of rapid hydrolysis, was observed.

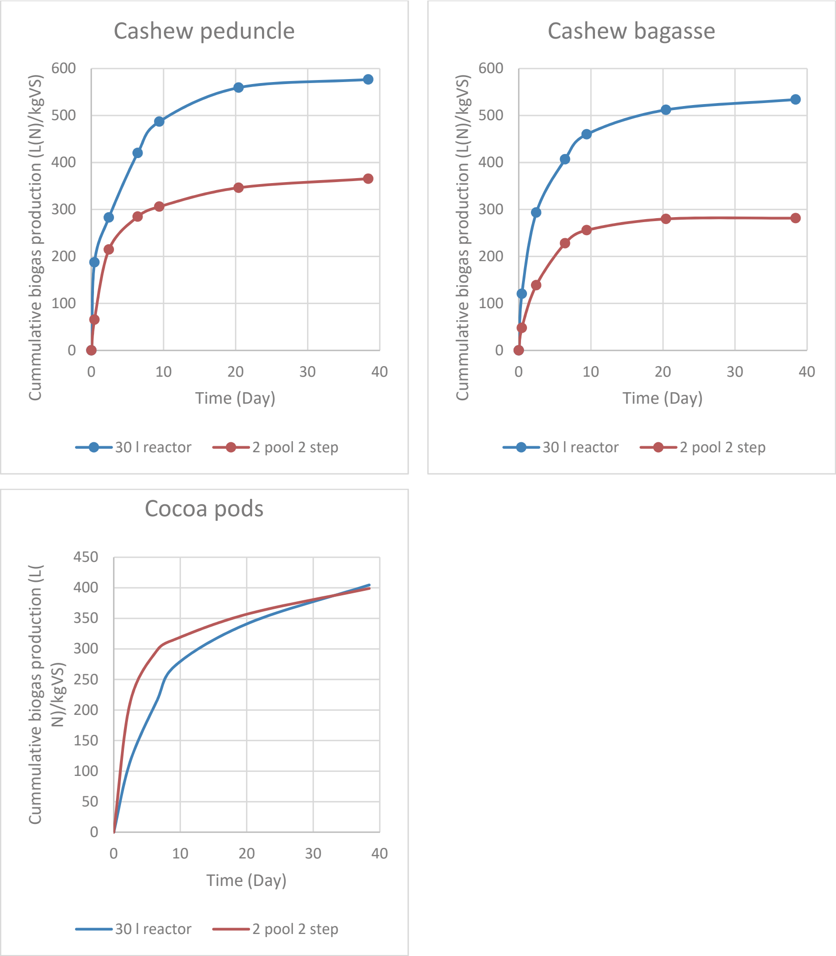


Figure 4.10: Comparison between experimental data and the dual-pool 2-step kinetic model using previously determined kinetic constants.

4.2.6 Effect of hydrothermal pretreatment on cocoa pods

4.2.6.1 Effect of hydrothermal pretreatment on fiber analysis of cocoa pods

Hydrothermal pretreatment is mainly employed to increase the hydrolysis rate by hydrolyzing fractions of the structural carbohydrates. This was largely found to be true. The composition of the structured carbohydrates was found to be changing in response to increasing the hydrothermal pretreatment process severity (Figure 4.11). The fraction of hemicellulose in the pretreated samples was found to decrease with increasing severity of treatment. For instance, the hemicellulose content in the pretreated cocoa pods fibers reduced from 5.2% at a severity 2.0 to 2.3% at a severity of 4.9. Despite the observed decrease in the hemicellulose content in the pretreated cocoa pods fibers with increasing process severity, the linear correlation between hemicellulose fraction and process severity was found to be weak with an R^2 of 0.3691.

Similarly, a negative correlation was observed between the cellulose fraction of the structural carbohydrates and the process severity. A marginal reduction in the cellulose fraction of the pretreated cocoa pods fibers from 36.1% at 2.0 severity to 32.9% at a severity of 4.9 was observed. Contrary to the observed decrease in hemicellulose and cellulose fractions in the pretreated cocoa pods samples, the process severity correlated positively with the lignin content. An increase in lignin content was observed with increasing process severity. The increase in the percentage of lignin after pretreatment showed that, while the hydrothermal process was able to solubilize the cellulose and hemicellulose into simple carbohydrates, its ability to deconstruct the lignin and make it more accessible to digestion was limited. As a result, while the cellulose and hemicellulose fractions decreased, the lignin content rather increased from 29.7% to 35.0%, at process severities of 2.0 and 4.9 respectively for cocoa pods. It was further observed that process severity and lignin content of the pretreated samples correlated better with the coefficient of linear correlation R^2 of 0.7176.

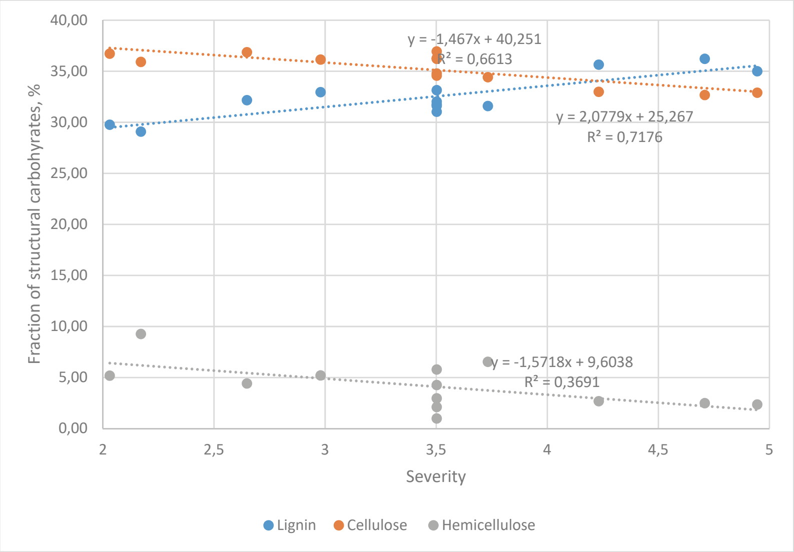


Figure 4.11: Effect of severity of hydrothermal pretreatment on the structural carbohydrates of three residues [175].

4.2.6.2 Effect of hydrothermal pretreatment on biogas yield

No clear trend was observed between the biogas yield of the pretreated cocoa pod and the process severity. While biogas yield increased in some cases, severe process inhibition leading to reduced biogas yield or complete process failure was also observed. Generally, lower than 3 process severity resulted in higher biogas yield than higher severities (above 3) which resulted in lower biogas yield than the untreated sample even though there was an exception. For instance, at process severity 2.03, the specific biogas yield (606 l(N)/kgVS) was the highest (Figure 4.12). This represented an increase of 70% above the actual biogas potential (See Table 4.9). An increase in process severity to 2.17 however, resulted in a marginal increase (1%) in biogas yield. This notwithstanding, a further increase in process severity to 2.6 and 2.9 resulted in identical biogas yield of about 556.6 and 559.5 l(N)/kgVS respectively representing about 57% increase in yield above the specific biogas yield of the untreated sample. This was also an anomaly since it was expected that more toxins would have been produced during the extended reaction time leading to the cessation of biogas production.

The result further pointed to serious process inhibition above process severity of 3.0 in most cases. The biogas yield for instance of the pretreated cocoa pods samples at process severities of 3.5, 3.7, and 4.9 resulted in complete process failure. The biogas yield was lower than the blank, an indication that the process was seriously inhibited. This was however not the case at process severity of 4.2. Instead of complete failure of the digestion process, lower specific biogas yield representing 25% of the specific biogas yield of the untreated cocoa pods was observed. An anomaly was observed at the process severity of 4.7. A 10% increase in the specific biogas yield (393.57 l(N)/kgVS) over the untreated cocoa pods sample was observed. This was largely unexpected and did not follow the earlier trend of reduced specific biogas yield at severities above 3.

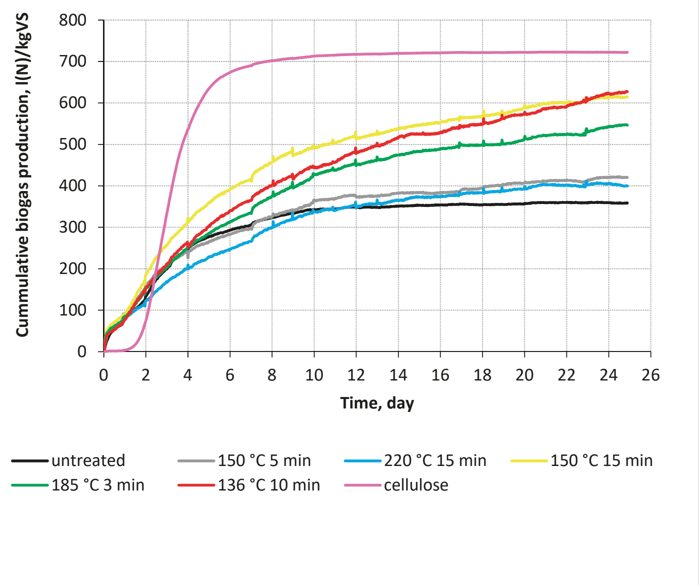


Figure 4.12: Cumulative biogas production from pretreated and untreated cocoa pod samples [175].

Table 4.9: Summary of results of fiber analytics before and after hydrothermal pretreatment [175].

Test conditions	Severity	Lignin (ADL)	Cellulose	Hemi-cellulose	Biogas yield	Increase in yield
	-	%	%	%	L(N)/kgVS	
Untreated	0.00	21.60	26.10	4.82	357.00	1.00
135 ºC_10 min	2.03	29.75	36.13	5.20	606.77	1.70
150ºC_5 min	2.17	29.07	35.91	9.26	369.37	1.03
150 ºC_15 min	2.65	32.16	36.85	4.41	556.60	1.56
185 ºC_3 min	2.98	32.94	36.13	5.20	559.52	1.57
185 ºC_10 min	3.50	33.14	35.72	3.22	failed	-
185 ºC_17 min	3.73	31.59	34.41	6.53	failed	-
220 ºC_5 min	4.23	35.64	32.98	2.68	88.49	0.25
220 ºC_15 min	4.71	36.21	32.67	2.48	393.57	1.10
234 ºC_10 min	4.94	34.99	32.90	2.35	failed	-

4.2.6.3 Response surface methodology (RSM) analysis

The result of the fiber analysis and the specific biogas yield were fitted to two separate models. This was done by minimizing the sum of least squares using Design Expert 12 to determine the constants in Equations 6.2 and 6.3. The curve fitting resulted in Equations (4.4) and (4.5). The lignin response model was significant with an F-value of 15.25 and a 0.09% chance that such an F-value could occur due to noise. Similarly, the biogas yield response factor was significant with an F-value of 75.06 and a P-value of 0.001. Additionally, the lignin response model was insignificant with respect to the lack of fit. The lack of fit F-value was 3.02 with a P-value of 0.152. The adequate ratios for both signals were above 4. Results of the analysis of variance and the significance of the models are summarized in Table 4.10.

$$\text{Lignin content} = 20.11144 + 0.064358 * \text{T} + 0.04365 * \text{t} \tag{4.4}$$

$$\text{Gas output} = -12999 + 147.48 * \text{T} + 2036.26 * \text{t} - 21.58 * \text{T} * \text{t} - 0.39 * \text{T}^2 - 15.69 * \text{t}^2 + 0.05 * \text{T}^2 * \text{t} + 0.12 * \text{T} * \text{t}^2 \tag{4.5}$$

Where T is the process temperature (ºC) and t is the reaction time (min)

Both models have an acceptable coefficient of linear correlation R^2 of 0.75 and 0.99 for the lignin and gas yield response factors, respectively. This implies the models can be used to predict the lignin content and the specific gas yield of subcritical hydrothermally pre-treated cocoa pods residues. The result further showed no interaction between the process parameters investigated in the case of the lignin response factor. The 3-D surface response plots of the two response factors and the plot of actual and predicted response are shown in Figure 4.13. The perturbation plot (Appendix C-1) shows that temperature was the dominant factor in comparison with reaction time for the lignin content response factors. This can be seen from the steepness of the temperature curve as compared to the near horizontal curve of the reaction time. Further, the interaction curves showed that no combined interaction effect was observed for the lignin response factor (see Appendix C-2). The perturbation curves for the specific biogas yield response factor showed the negative correlation between temperature and reaction time with the specific biogas yield factor (Appendix C-3). No clear difference could be elicited from the two curves as both were similar thus indication none was dominant over the other. Further analysis of the interaction plot showed significant multiple interactions between the two process parameters (Appendix C-4).

Table 4.10: Summary of analysis of variance for the two response factors - lignin content and biogas yield.

Lignin content response						Gas yield response				
	df	SS	MS	F-value	P-value	df	SS	MS	F-value	P-value
Model	2	40.97	20.49	15.25	0.0009	7	7.73E5	1.10E5	75.60	0.0001
Residual	10	13.43	1.34			5	7304.78	1460.96		
Lack of fit	6	11.00	1.83	3.02	0.1520	1	7304.78	7304.78		
Pure error	4	2.43	0.61			4	0.00	0.00		
R^2		0.7531				0.9906				
Adequate precision		11.43				21.24				

df = degree of freedom; SS = Sum of Squares; MS = Mean Square

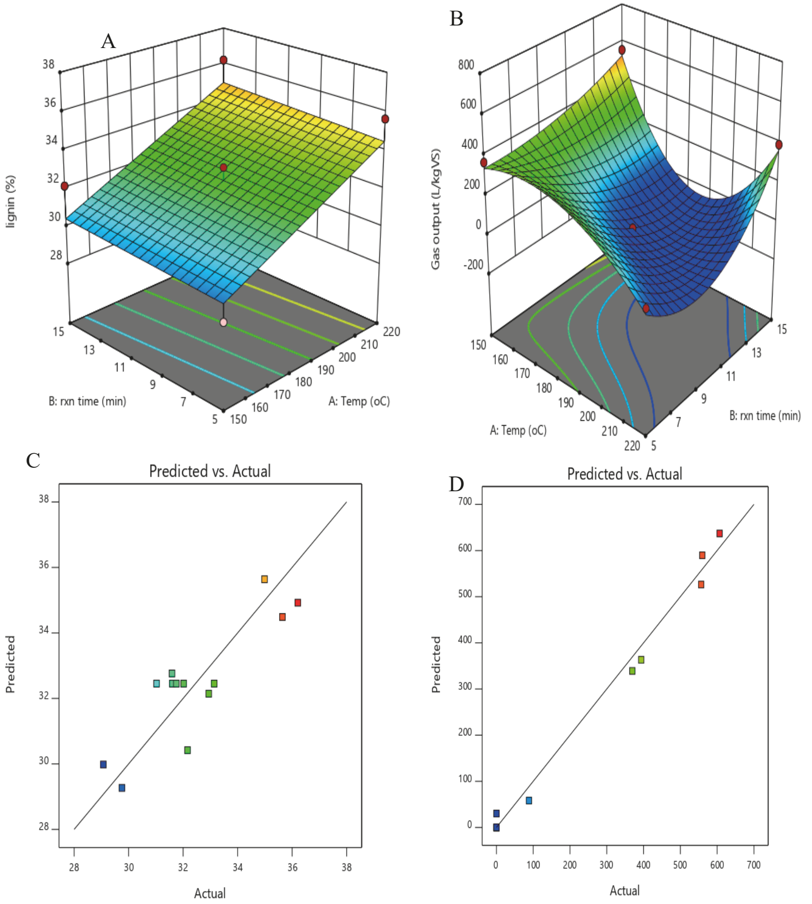


Figure 4.13: Surface Response model plot of the lignin content in the pretreated samples (A), Surface response model for biogas yield (B), Actual lignin content vrs the predicted lignin content (C) and Actual gas yield vs the predicted gas yield (D).

4.2.3.4 Process optimization

The regression equations (Equations 4.14 and 4.15) were used to optimize the hydrothermal process conditions for optimum specific biogas yield. To obtain the optimum specific biogas yield, the process temperature was minimized, while the reaction time and lignin content were fixed in range. The result of the optimization was a specific biogas yield of 526 l(N)/kgVS obtained at a temperature of 150 ºC and 15 minutes reaction time.

4.2.7 Semi-continuous anaerobic digestion study

4.2.7.1 Semi-continuous co-digestion of cocoa pods, cashew peduncle and cashew bagasse with maize silage

Further, the specific biogas production was determined to be 633 l(N)/kgVS-added, 521 l(N)/kgVS-added and 516 l(N)/kgVS-added (Figure 4.14) respectively for cashew peduncle-maize silage, cashew bagasse-maize silage, and cocoa pods maize silage with the following corresponding biomethane fraction of 51.7%, 52.5% and 51.16% (Figure 4.15). Biogas production rate from the control experiment which was feed with only maize silage averaged 639 l(N)/kgVS-added with a biomethane fraction of 52%. When the feed ratio was increased to 60:40, a marginal decrease in specific biogas yield was observed in all cases. Specific biogas yield for cashew peduncle-maize silage feed composition decreased from 631 to 621 l/kgVS-added. The cumulative biogas yield reduced further to 521 l/kgVS-added and then to about 463 l/kgVS-added when the composition of the co-substrate (cashew peduncle) was increased. This trend in a marginal decrease in specific biogas yield as a result of increasing the percentage of the co-substrate in the feed composition continued for feed ratios of 70:30 and 80:20 except for 90:10 where there was a marginal increase as shown in Figure 4.14. At a feed composition of 90:10 and 100:0, the cumulative biogas yield reduced from 546 to 442 l/kgVS-added respectively. A similar trend of reducing cumulative biogas yield was observed for cashew bagasse-maize silage feed composition. As the percentage of cashew bagasse increased in the feed composition from 50% to 90%, the specific biogas yield decreased from 521 to 394 l(N)/kgVS-added. Likewise, the specific biogas yield of cocoa pods:maize silage feed composition also decreased linearly from 516 to 292 l(N)/kgVS-added when the fraction of cocoa pods was increased from 50% to 100%. The daily biogas and biomethane yields are summarized in Appendix E-1.

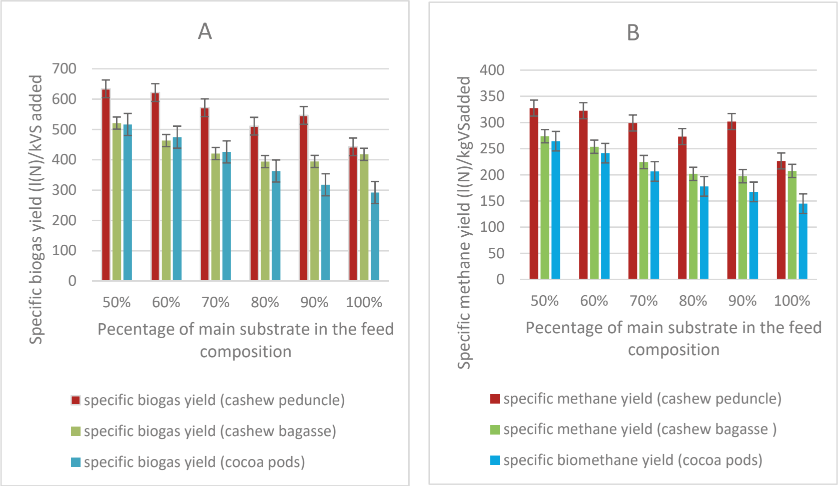


Figure 4.14: Specific biogas (A) and biomethane (B) yield with standard error bars from co-digested cashew peduncle/bagasse with maize silage at various feed composition.

4.2.7.2 Synergetic index

The synergetic effect is one of the main advantages of co-digestion. This could be as a result of improved carbon:nitrogen ratio, trace metal in one of the substrates and or rapid hydrolysis of either the main or co-substrate. The synergetic index was determined by comparing the specific biogas yields of the co-digested substrates to the weighted averages of the specific biogas yields of the mono digested substrates. The result points to a positive synergetic effect at all feed ratios for cashew peduncle: maize silage feed composition (Figure 4.15A). For instance, mono digested maize silage produced a specific biogas yield of 606 l(N)/kgVS-added (Figure 4.16D), and mono digested cashew peduncle also produced about 440 l(N)/kgVS-added. However, the combined specific biogas yield from the 50:50 co-digested substrate (633.75 l(N)/kgVS-added) exceeded the summation of fractions of the individual specific biogas yield of each substrate (550.5 l(N)/kgVS-added) by about 83 l(N)/kgVS-added. Two sample t-test analysis showed however that the synergetic effect depended on the feed composition. For instance at 50:50 and 30:70 cashew peduncle:maize silage feed composition, the difference in gas production was significant with a p-value of 0.0181 and 0.037 respectively. Similarly, the result for 90:10 feed composition was also significant with a p-value of 0.033. However, at feed composition of 60:40 and 80:20 cashew peduncle:maize silage, the t-test analysis showed that the increase in gas production was not significant.

In the case of the co-digested cashew bagasse and maize silage substrate, an antagonistic effect was rather observed (Figure 4.15B). There was a marginal decrease in biogas yield at all feed composition considered in this study. The biogas yield from the co-digested substrates was observed to be lower than the calculated yield from the individual substrate. Despite the antagonistic effect observed, the difference in gas production was insignificant.

Similarly, a marginal difference in biogas yield was observed for cocoa pods-maize silage feed composition (Figure 4.15C). For every percentage increase in the amount of cocoa pods in the feed composition, the specific biogas yield declined by 4.7 l(N)/kgVS-added. The methane content of the biogas did not change much with increasing cocoa pods in the feed composition. It averaged about 50%. The decrease in specific biogas yield was expected, given that in the control experiment which was fed with only maize silage, the specific biogas yield was 606 l(N)//kgVS-added which was twice as much as the specific biogas yield of 100% cocoa pods feed composition (298 l(N)/kgVS-added). This notwithstanding, when the actual biogas yield was compared to the predicted biogas yield a trend of higher biogas yield was observed for 50:50, 60:40, and 70:30 cocoa pods-maize silage feed composition. However, there an extent to which the promotional effect was possible. At 80:20 difference in actual and predicted specific biogas yield was marginal. At 90:10 antagonistic effect was observed leading to a lower specific gas production than the predicted specific biogas yield. However, the difference between the actual yield and the predicted yield was not significant with p values of 0.06, 0.10, 0.16, 0.06, and 0.31 respectfully for 50%, 60%, 70%, 80%, and 90% cocoa pods in the feed composition.

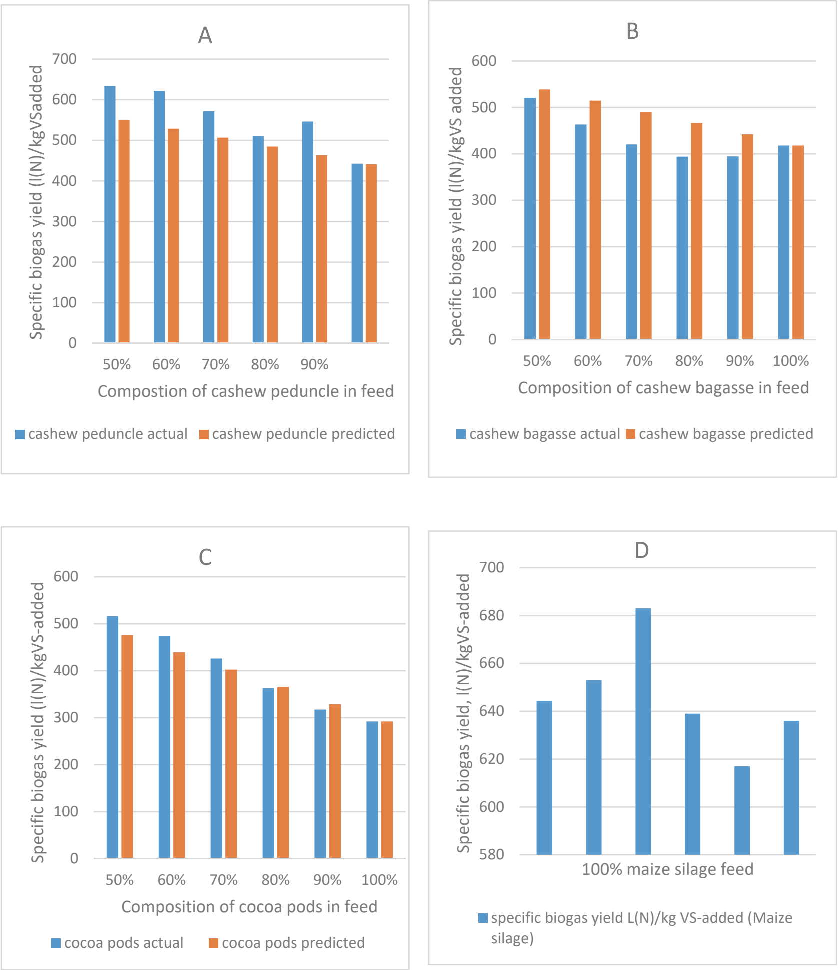


Figure 4.15: Synergetic effect of co-digestion of cashew peduncle (A), cashew bagasse (B) and cocoa pods (C) with maize silage and mono digested maize silage (D).

4.2.7.3 Mono digestion and the effect of increasing organic loading rate (OLR) on biogas biomethane yield of cashew peduncle, cashew bagasse, and cocoa pods

The result of the specific biogas yield from the semi-continuous digestion of cocoa pods, cashew peduncle and cashew bagasse are shown in Table 4.11, while the biomethane yield are shown Table 4.12. The results show that at OLR of 2.5 kgVS/m^3.day and 3.0 kgVS/m^3.day mono digestion of cashew peduncle had the highest biogas yield, whereas cocoa pods had the lowest. Mono digestion of cashew peduncle was possible until OLR of 3.0 kgVS/m^3.day. At OLR of 3.5 kgVS/m^3.day, the mono digestion of cashew peduncle experienced some process inhibition (See Figure 4.16 A). This resulted in declining specific biogas yield until the process completely failed leading to zero specific biogas being recorded. On the contrary, the mono digestion of cashew bagasse proceeded smoothly without any process inhibition at OLR of 3.5 kgVS/m^3.day and 4.0 kgVS/m^3.day (Figure 4.16B). The digestion of cocoa pods residues on the hand did not experience any process inhibition up to OLR of 5.0 kgVS/m^3.day (Figure 4.16C).

Table 4.11: Specific biogas yield of mono digested cashew peduncle, cashew bagasse and cocoa pods.

OLR (kgVS/m^3.day)	Specific biogas yield (l(N)/kgVS-added)		
	Cashew peduncle	Cashew bagasse	Cocoa pods
2.5	437.70 ± 3.25	392.75 ± 16.11	286.25 ± 5.40
3.0	398.25 ± 19.14	371.67 ± 3.21	265.00 ± 16.18
3.5	214.65 ± 93.23	413.75 ± 11.77	273.25 ± 5.02
4.0	0	402.00 ± 1.44	246.67 ± 10.37
4.5	-	-	234.75 ± 9.08
5.0	-	-	239.00 ± 8.89

Table 4.12: Specific biomethane yield of mono digested cashew peduncle, cashew bagasse and cocoa pods.

OLR (kgVS/m^3.day)	Specific methane yield (l(N)/kgVS-added)		
	Cashew peduncle	Cashew bagasse	Cocoa pods
2.5	226.75 ± 3.01	194.00 ± 8.53	142.50 ± 2.32
3.0	205.25 ± 14.17	183.00 ± 3.97	132.25 ± 7.19
3.5	98.05 ± 48.71	204.00 ± 8.46	135.75 ± 2.72
4.0		200.50 ± 1.78	130.00 ± 4.58
4.5			117.25 ± 3.22
5.0			125.00 ± 9.19

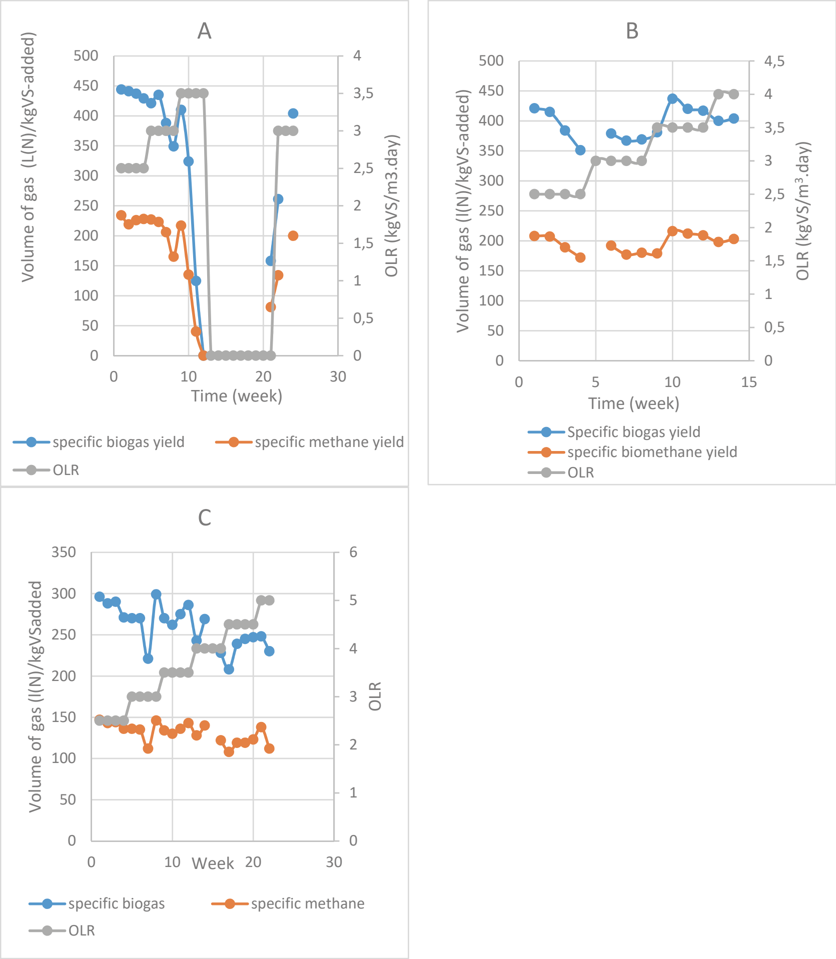
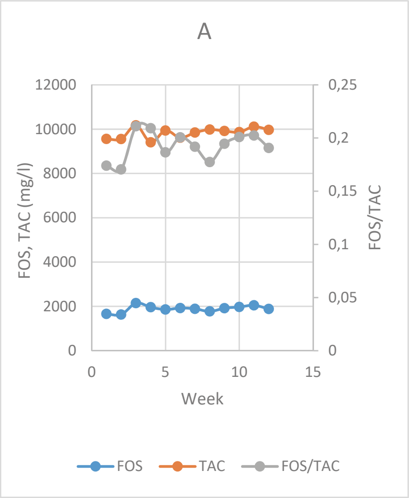


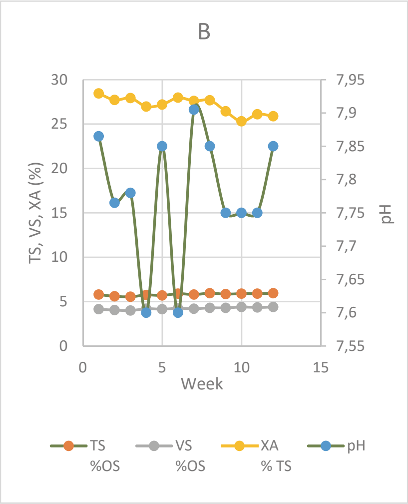
Figure 4.16: Specific biogas and biomethane production from mono digested cashew peduncle (A), cashew bagasse (B) and cocoa pods (C) at different OLR.

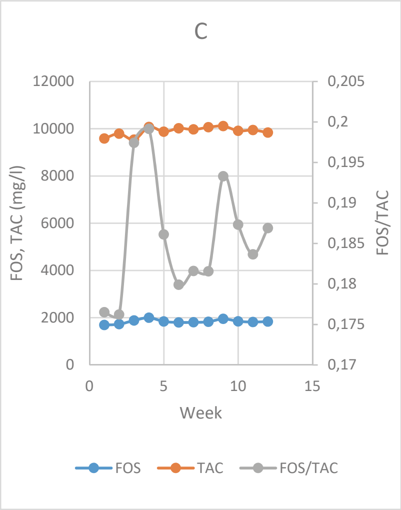
4.2.8 Process stability

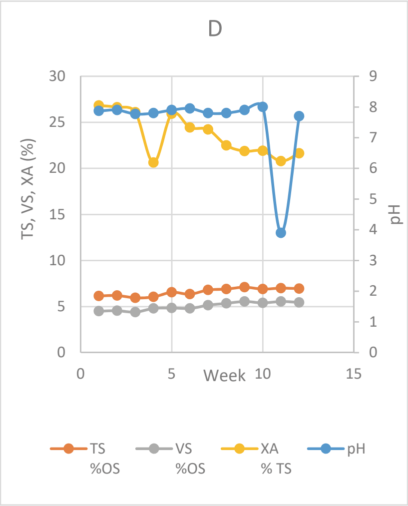
4.2.8.1 Effect of co-digestion on process stability

Using the FOS and TAC matrix which is widely reported in the literature, the process stability of the anaerobic digestion was determined. Co-digestion of the three residues (cashew peduncle, cashew bagasse, and cocoa pods) with maize silage did not experience any process instability as shown in Figure 4.17 (A-F). During the entire co-digestion process of cashew peduncle and maize silage, FOS/TAC matrix was about 0.2 (See Figure 4.17 A, C, and E). This was below the threshold of 0.3 which is mostly considered as the distress level above which the digestion process becomes unstable. In the first week of digestion, the FOS concentration measured was 1590 mg/l. As the ratio of the main substrate was increased to 60%, a marginal increase in volatile organic acid concentration was observed. However, there was a corresponding increase in the buffer capacity to ensure that the ratio of organic acid concentration to the buffer capacity was below the 0.3 thresholds. The buffer capacity of the digestion process ranged between 9,400 and 10,111 mg/l. for the cashew peduncles. The pH which is another measure of process stability was monitored throughout the experiment. A higher/rapid rate of hydrolysis without a corresponding buffer capacity could lead to process acidification which will result in lower pH below 7 and eventually inhibit the digestion process. The pH was fairly stable and only varied between 7.3 and 7.8 which is ideal for anaerobic digestion. No accumulation of total solids or volatile solids was observed. Rather the total solids and volatile solids concentration in the digester were relatively stable and ranged between 5.0% - 7.9 %OS and 4.05 – 4.3 %OS respectively. Co-digestion of the cashew bagasse and maize silage followed a similar trend as cashew peduncle and maize silage. As shown in Figure 4.17 (B and C) the ratio of organic carbons to inorganic carbons was also below the 0.3 thresholds even though some noticeable fluctuations were observed. This was mainly due to fluctuations in the buffer capacity and organic acid concentration. In the case of co-digestion of cocoa pods and maize silage, no accumulation of volatile organic acids (FOS), resulting in increased concentration, was observed (see Figure 4.17E and 4.17F). This means the balance in the rate of production of volatile organic acids (acidogenic reaction) and consumption of volatile fatty acids (acetogenic) reactions was maintained throughout the study period under different feed compositions. The balance in production and consumption in volatile organic acids is reflected in the pH, which falls within the permissible range ideal for the anaerobic digestion (7-8). Further, the total alkalinity (TAC), which is a measure of the buffer capacity of the reaction medium was also relatively stable at about 10,000 mg/l. This resulted in a FOS/TAC matrix lower than 0.3, an indication of the process stability. There was a marginal decline in the VS removal rate (XA) from 28% to about 25% as the percentage of cocoa pods (Figure 4.17F) and cashew peduncle (Figure 4.17B) increased in the feed composition. This did not however affect the total solids accumulation (TS) in both cases (Figures 4.17 B and F). Given that feeding was initiated at a low OLR to avoid start-up challenges and process instability, it remains to be seen if the process will continue to be stable at higher OLR because of the high fiber content of cocoa pods (52.25%).


A
FOS, TAC (mg/l)
12000
10000
8000
6000
4000
2000
0
FOS/TAC
0,25
0,2
0,15
0,1
0,05
0
0
5
10
15
Week
FOS
TAC
FOS/TAC


B
TS, VS, XA (%)
30
25
20
15
10
5
0
pH
7,95
7,9
7,85
7,8
7,75
7,7
7,65
7,6
7,55
0
5
10
15
Week
TS %OS
VS %OS
XA % TS
pH


C
FOS, TAC (mg/l)
12000
10000
8000
6000
4000
2000
0
FOS/TAC
0,205
0,2
0,195
0,19
0,185
0,18
0,175
0,17
0
5
10
15
Week
FOS
TAC
FOS/TAC


D
TS, VS, XA (%)
30
25
20
15
10
5
0
pH
9
8
7
6
5
4
3
2
1
0
0
5
Week
10
15
TS %OS
VS %OS
XA % TS
pH

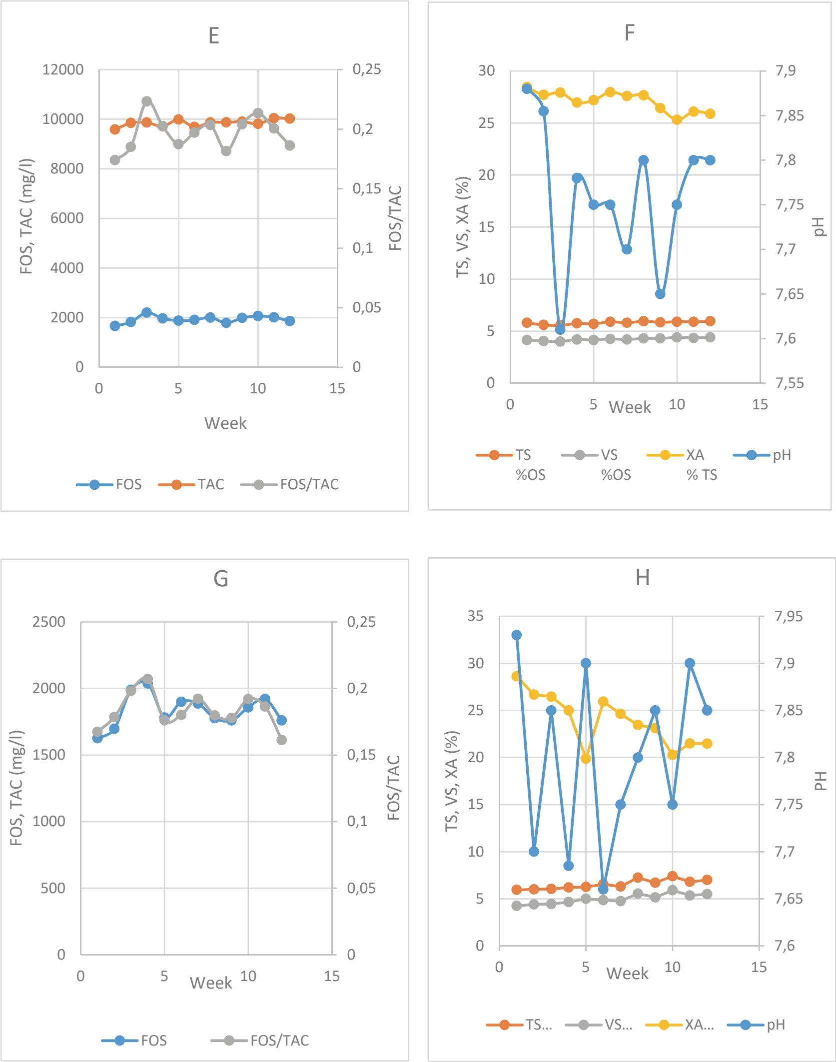


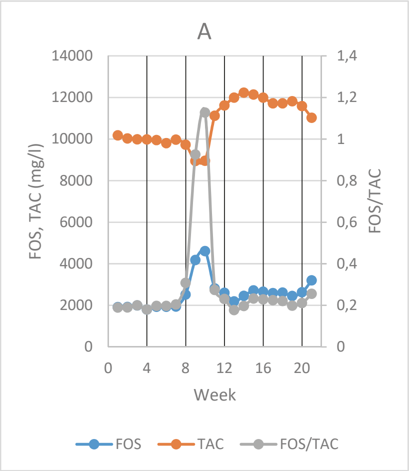
Figure 4.17: Process stability for co-digested cashew peduncle, cashew bagasse and cocoa pods: Cashew peduncle (A and B), cashew bagasse (C and D), cocoa pods (E and F) and maize silage (G and H)

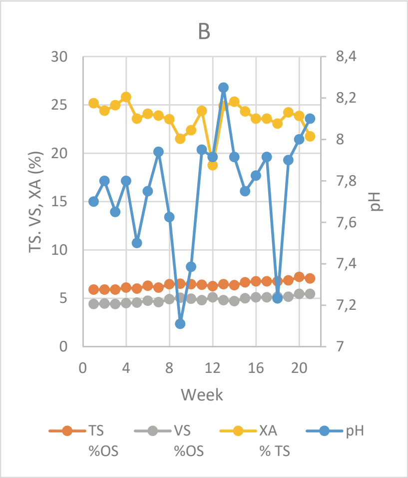
4.2.8.2 Effect of increasing organic loading rate (OLR) on process stability of mono digested cocoa pods, cashew peduncle and cashew bagasse

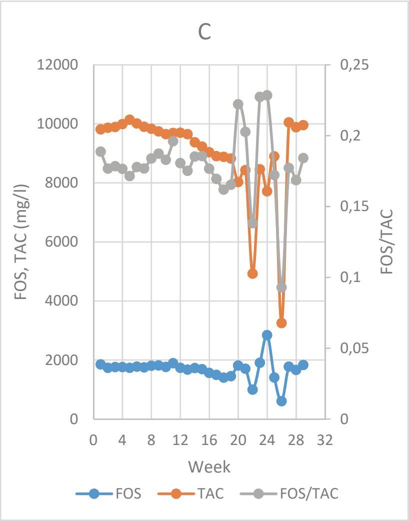
During the mono digestion stage of the cashew peduncle, the buffer capacity and the volatile organic acid concentration remained relatively constant at OLR of 2.5 kgVS/m^3.day as shown in Figure 4.18 (A and B). The FOS was about 2,000 mg/l, while the buffer capacity was about 10,000 mg/l. This resulted in a stable pH ranging between 7.75 and 7.80. Meanwhile, the total solids and volatile solids also remained constant ranging between 5.9 and 5.95. However, a gradual increase in VS content was observed during this period. The VS content increased from 4.3 to 4.45. When the ORL was increased to 3.0 kgVS/m^3.day, the process was stable with a buffer capacity still about 10,000 mg/l, while the volatile organic carbon acid concentration was also about 2,000 mg/l. The process began experiencing unstable conditions when the OLR was increased to 3.5 kgVS/m^3.day. An increase in organic acid concentration without a corresponding increase in the buffer capacity was observed. Rather than increase, a decrease in buffer capacity was observed. Meanwhile, the VS content began to show signs of increasing 4.45 to about 4.75%. By the third week of digestion, the organic acid concentration had doubled to about 4,000 mg/l, while the buffer had decreased to about 9,000 mg/l. The inability of the buffer capacity to neutralize the increase in fatty acid concentration resulted in the process failure.

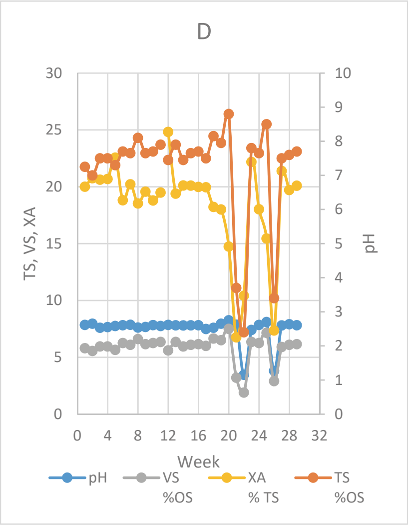
The digestion process was relatively stable for the cashew bagasse substrate as shown in Figure 4.18 (C and D). Even though there was a general decrease in buffer capacity when the OLR was increased to 3.0 kgVS/m^3.day, no increase in the volatile acid concentration was observed. Rather, a corresponding decrease in volatile acid concentration was observed. This resulted in stable pH and generally acceptable FOS/TAC ratio of less than 0.3. The trend of decreasing buffer capacity continued when the OLR was increased to 3.5 kgVS/m^3.day. This notwithstanding, a marginal decrease in volatile organic acid concentration was observed resulting in the reduction of FOS/TAC ratio from 0.18 to 0.15. At OLR of 4.0 kgVS/m^3.day, fluctuations in the buffer capacity and volatile acid concentration were observed. For instance, an initial decrease in buffer capacity during the first and second weeks from about 8,000 to 5,000 mg/l was observed. However, by the third week, buffer capacity had increased to about 9,000 mg/l. The FOS/TAC matrix was largely below 3.0, an indication of stability and the ability of the process to take on additional organic matter. The pH reduced to about 4 during the second week. This was largely due to the massive reduction in buffer capacity however, process inhibition was not immediately observed. The sudden decrease in buffer capacity was an anomaly that could not be readily explained. The subsequent increase in buffer capacity during the third week ensured that the pH increased to the desirable range of 7 – 8.

In the case of cocoa pods, the FOS/TAC matrix was below the 0.3 threshold for the entire duration of the study despite an increase in the OLR (Figure 4.18E). The pH fluctuated between a high of 8.2 and a low of 7.45 (Figure 4.18F). No clear trend was observed for the VS removal. The positive linear correlation was observed between the total solids and the OLR which was similar to that of VS and OLR.


A
FOS, TAC (mg/l)
14000
12000
10000
8000
6000
4000
2000
0
FOS/TAC
1,4
1,2
1
0,8
0,6
0,4
0,2
0
0
4
8
12
16
20
Week
FOS
TAC
FOS/TAC


B
TS. VS, XA (%)
30
25
20
15
10
5
0
pH
8,4
8,2
8
7,8
7,6
7,4
7,2
7
0
4
8
12
16
20
Week
TS %OS
VS %OS
XA % TS
pH


C
FOS, TAC (mg/l)
12000
10000
8000
6000
4000
2000
0
FOS/TAC
0,25
0,2
0,15
0,1
0,05
0
0
4
8
12
16
20
24
28
32
Week
FOS
TAC
FOS/TAC


D
TS, VS, XA
30
25
20
15
10
5
0
pH
10
9
8
7
6
5
4
3
2
1
0
0
4
8
12
16
20
24
28
32
Week
pH
VS %OS
XA % TS
TS %OS

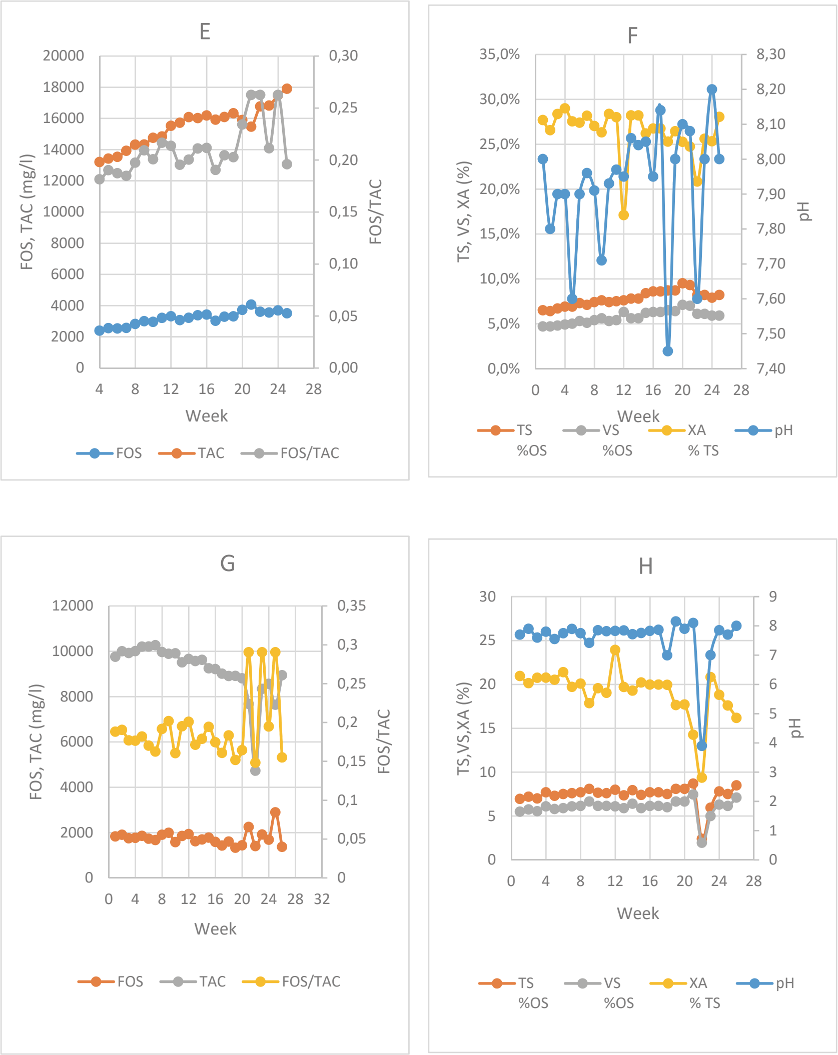


Figure 4.18: Process stability during mono digestion studies: Cashew peduncle (A and B), cashew bagasse (C and D), cocoa pods (E and F) and maize silage (G and H).

4.3 Hydrothermal carbonization

4.3.1 Yield of hydrochar

4.3.1.1 Yield of hydrochar as a function of process severity

The yield of hydrochar was found to depend on the severity of the carbonization process as shown in Figure 4.19. A generally weak inverse correlation ($R^2 = 0.3474$) can be observed for cocoa pods hydrochar yield and the process severity. Similarly, in the case of the cashew peduncle, the correlation between the hydrochar yield and the process severity could best be described by a weak 2nd order polynomial with an $R^2 = 0.4794$. This notwithstanding, the yield was found to be generally higher at low process severity and lower at higher process severity with respect to cocoa pods. In the case of cashew peduncle residues, the yield was found to increase with increasing process severity until a maxima is achieved and then decreased marginally as the process severity was increased further.

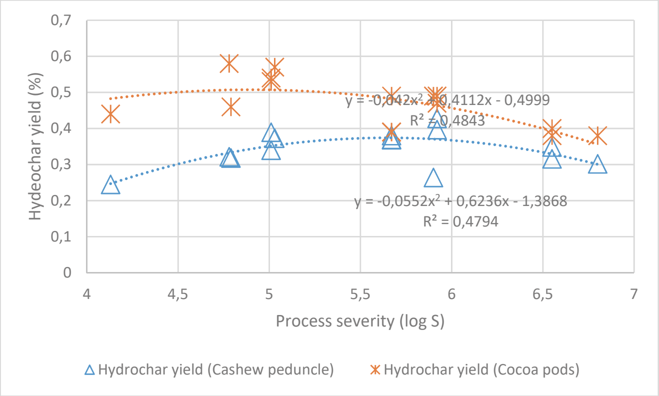


Figure 4.19: Correlation between hydrochar yield from cocoa pods and cashew peduncle and process severity.

4.3.1.2 Response surface models

The dependence of the hydrochar yield (Y) from cocoa pods and cashew peduncle carbonization on the process parameters investigated were found to be different. The hydrochar yield from cocoa pods was found to depend on just the process temperature and the reaction time and not the heating rate (Equation 4.6) with a low R^2 of 0.5323. However, the yield of hydrochar from cashew peduncle was found to be dependent on all three process parameters investigated (Equation 4.7) with an R^2 of 0.9855.

$$Y_{\text{cacoa pods}} = 29.11 + 0.09 * T + 11.67 * t - 0.057 * T * t \tag{4.6}$$

$$Y_{\text{cashew peduncle}} = -4.37 + 0.04 * T + 0.09 * r + 0.30 * t - 0.0006 * T * r - 0.003 * T * t - 0.0001 * T^2 - 0.007 * r^2 + 0.000006 * T^2 * t + 0.00004 * T * r^2 \tag{4.7}$$

Both models were found to be significant with an F-value of 4.17 and 37.69 respectfully for cocoa pods and cashew peduncle residues. The possibility that these F-values occurred due to noise were both less than 5%. Additionally, both models had an insignificant lack of fit F-value relative to the pure error. The lack of fit F-values were 0.81 and 5.39 respectfully for cocoa pods and cashew peduncle, with corresponding probabilities of 66.20 and 16.40 that such lack of fit F-values could occur due to noise. Furthermore, in both cases, the differences between the adjusted and predicted R^2 values were less than 0.2.

The 2D, 3D, and cube surface models of the yield of hydrochar from the cashew peduncle are shown in Figure 4.20. The 3D surface models of response factor point to an optimum yield between a heating rate of 2 – 4 k/min, reaction time range of 7 – 8 hrs and temperature, and a reaction temperature range of 195 – 220 ºC. From the 2D (Appendix D-1) models, the highest yield could occur at a temperature of 215 ºC, a reaction time of 8 hrs, and a heating rate of 2 k/min.

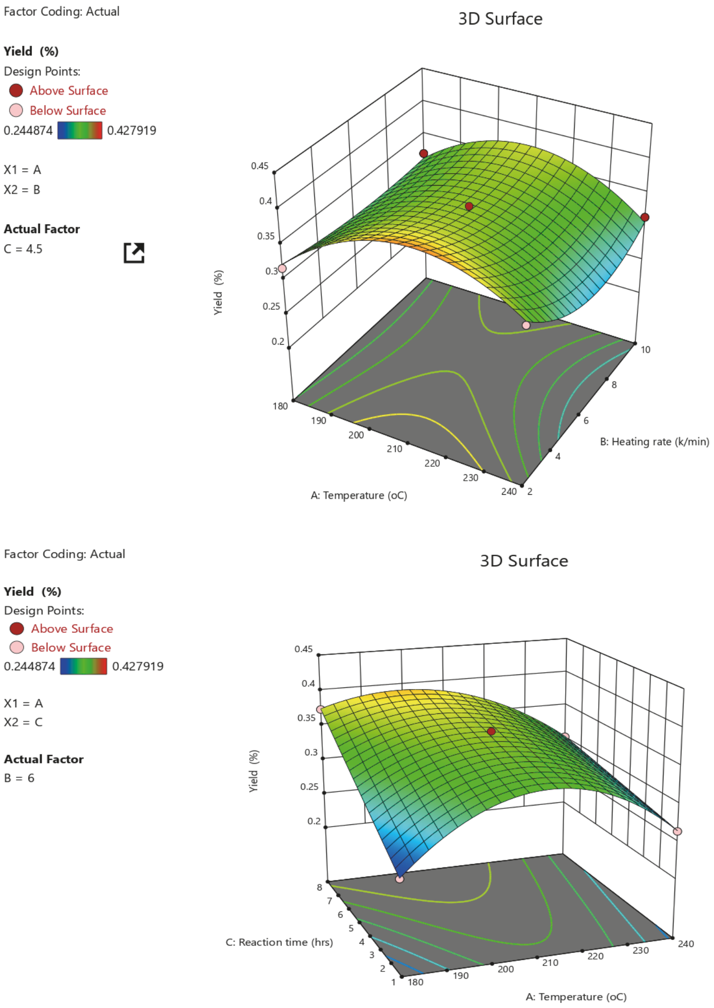


Figure 4.20: 3-D Response surface models for the yield of hydrochar from cashew peduncle residues.

In the case of the cocoa pods, the 3-D model of all the independent parameters pointed to an inverse linear relationship between the yield of hydrochar and the process temperature (Figure 4.21). Lower temperature and longer reaction time resulted in a higher yield of the hydrochar, while higher temperatures and longer reaction time resulted in lower yields of hydrochar. From the 2D plot (Appendix D-2), the highest yield of hydrochar occurred between a temperature range of 180 – 190 ºC and a reaction time of 7 – 8 hrs.

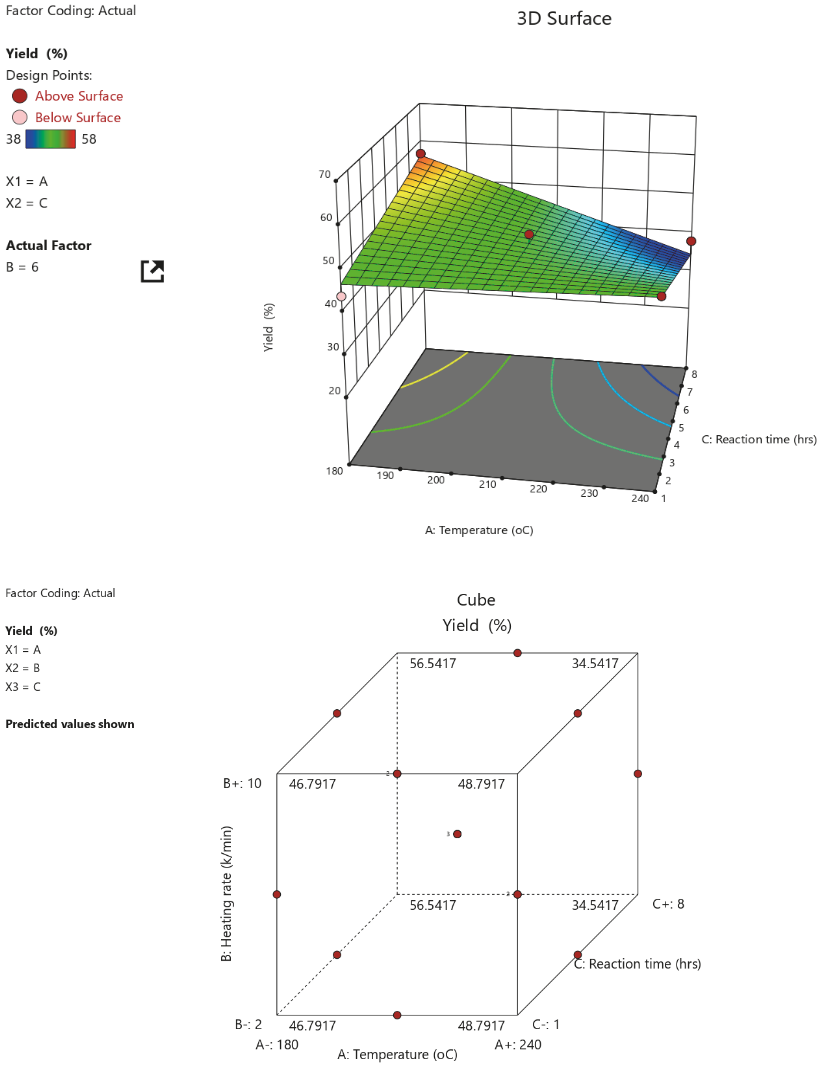


Figure 4.21: 3-D Response surface model for hydrochar yield from cocoa pods residues.

4.3.1.3 Factor interaction

The extent to which the independent factors interacted was of interest. In the case of cocoa pods, temperature, and reaction time were determined to affect the process yield, while the heating rate had no significant effect (Appendix D-4). The perturbation curve shows a strong dependence of the process yield on the temperature than reaction time. Strong factor interaction was observed between the two process parameters (temperature and reaction time) such that the predictions were not significantly different (Figure 4.22). The perturbation plot (Appendix D-3) for the cashew peduncle shows the effect of each process parameter on the yield of the hydrochar from the cashew peduncle. All three process parameters affected the yield of the hydrochar from the cashew peduncle albeit differently. Aside from the individual effect, several multiple factor interactions were observed (See Figure 4.23). Strong factor interactions were observed between temperature and heating rate on one side and temperature and reaction time on the other side. The overlapping of the least significant difference I-beams lines around the temperature and process heating rate predictions suggest a not significantly different prediction. However, in the case of process temperature and reaction time, the non-overlapping I-beam lines suggest a significantly different prediction for both factors

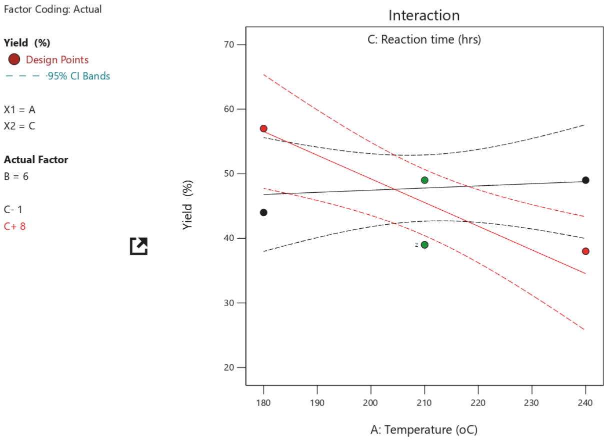


Figure 4.22: Factor interaction plot for the yield of cocoa pods hydrochars.

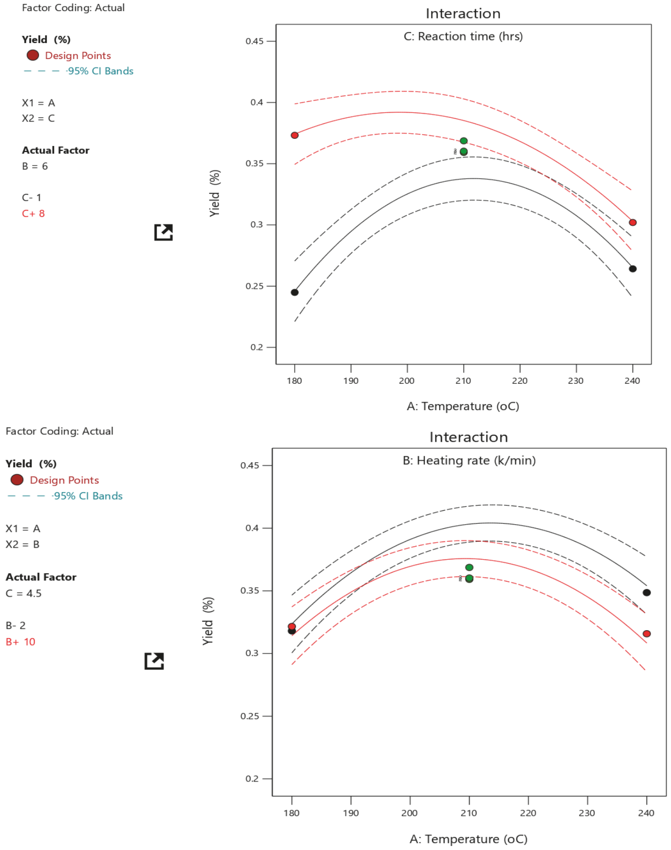


Figure 4.23: Factor interaction plot for the yield of cashew peduncle hydrochars.

4.3.2 Higher heating value

4.3.2.1 Higher heating value and severity of treatment

The HHV (28.18 MJ/kg) which represents an energy intensification of 1.59 over the untreated cocoa pods was achieved at the severity of 6.8 which corresponds to a reaction time of 8 hrs and process temperature of 240 °C. Conversely, the lowest heating value (18.75) which corresponds to an energy intensification of 1.06 was obtained at a process severity of 4.13. It was generally observed that the higher heating value correlated positively ($R^2 = 0.856$) with increasing severity as shown in Figure 4.24. A similar trend was observed for the HHV of cashew peduncle hydrochar.

The highest HHV (26.86 MJ/kg) was also obtained at a severity of 6.8 with the lowest HHV (occurring at process severity of 4.13 corresponding to a temperature of 180 °C and reaction time of 1 hr. Further, a strong linear correlation was observed between the higher heating value of cashew peduncle hydrochar and the process (R^2 = 0.8686). Generally, the HHV of cashew peduncle hydrochar was observed to be higher than the higher heating value of cocoa pods hydrochar. However, the difference in HHV values tapered down as the process severity was increased until they were almost similar at Process severity of 6.8.

Notwithstanding, no correlation was observed between the energy yield of cocoa pods hydrochar and the process severity, while the second-order polynomial correlation found between cashew peduncle hydrochar and the process severity was found to be very weak (R^2 = 0.5583).

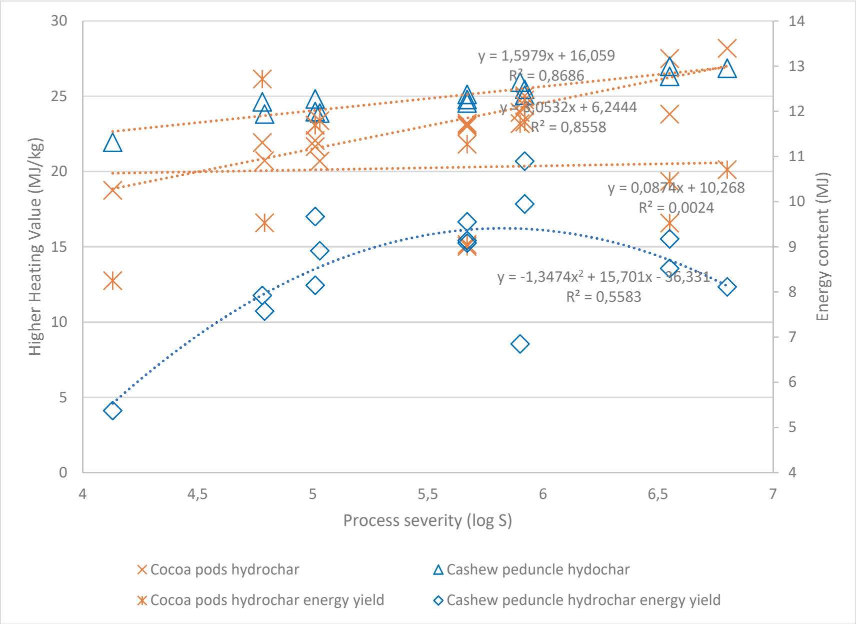


Figure 4.24: Effect of process severity on the heating value of hydrochar.

4.3.2.2 Response surface models

The higher heating value of cashew peduncle hydrochar was found to be dependent on the reaction temperature (T), and reaction time (t) and not so much on the heating rate (r) as shown in the model equations in Equation 4.8. However, the heating value of the cocoa pods hydrochar was found to be dependent on all three process parameters investigated as shown in Equation 4.9. Both models were quadratic.

$$\mathrm{HHV}_{\mathrm{cashew\ peduncle}} = 22.69 - 0.47 * \mathrm{T} + 0.47 * \mathrm{t} + 0.00213 * \mathrm{T}^2 - 0.034 * \mathrm{t}^2 \tag{4.8}$$

$$\mathrm{HHV}_{\mathrm{cocoa\ pods}} = -51.93 + 0.73 * \mathrm{T} + 6.23 * \mathrm{r} * - 0.72 * \mathrm{t} - 0.092 * \mathrm{T} * \mathrm{r} + 0.006 * \mathrm{T} * \mathrm{r} - 0.003\mathrm{T}^2 * \mathrm{r} - 0.002 * \mathrm{T} * \mathrm{r}^2 \tag{4.9}$$

In both cases, the models were significant with F-values of 19.41 and 376.28 for cashew peduncle and cocoa pods respectively. The corresponding P-values 0.0001 and < 0.0001 for cashew peduncle and cocoa pods respectively, had only a 0.01% and < 0.01% chance respectively for the cashew peduncle and cocoa pods hydrochar heating values that, an F-value this large could be due to noise. Additionally, both models were found to have a not significant lack of fit F-values. Not significant lack of fit F-values is an indication of the goodness of fit of the model to the actual experimental values. Thus, a not significant lack of fit value is generally good. In both cases, the F-values were 3.96 and 3.23 with corresponding P-values of 0.222 and 0.2451. Thus, a possibility that lack of fit F-values this large could be due to noise was not significant in both cases. Further, the R^2 of both models was acceptable (0.8859 and 0.9985 respectively for cashew peduncle and cocoa pods), while the differences between the adjusted and predicted R^2 values were found to be less than 0.2 in both models.

The model graphs for cashew peduncle and cocoa pods as shown in Figures 4.25 and 4.26 respectively point to increased higher heating value with respect to increasing process temperature and process reaction time. Generally, lower process temperature and reaction time resulted in lower heating value as shown in the 2D and 3D surface models, respectively. In the case of cashew peduncle residues, the 2D (Appendix D-5 and D-7) and 3D models showed the invariability of the heating rate to the higher heating value. However, in the case of cocoa pods, the optimum heating rate was in the range of 6 – 10 K/min.

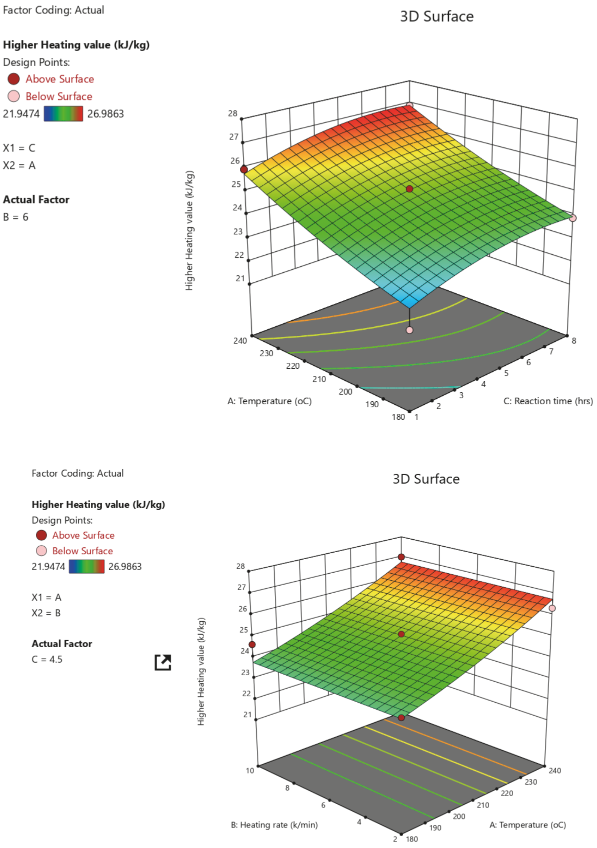


Figure 4.25: Surface response models for higher heating value response factor for hydrochar from cashew peduncle residues.

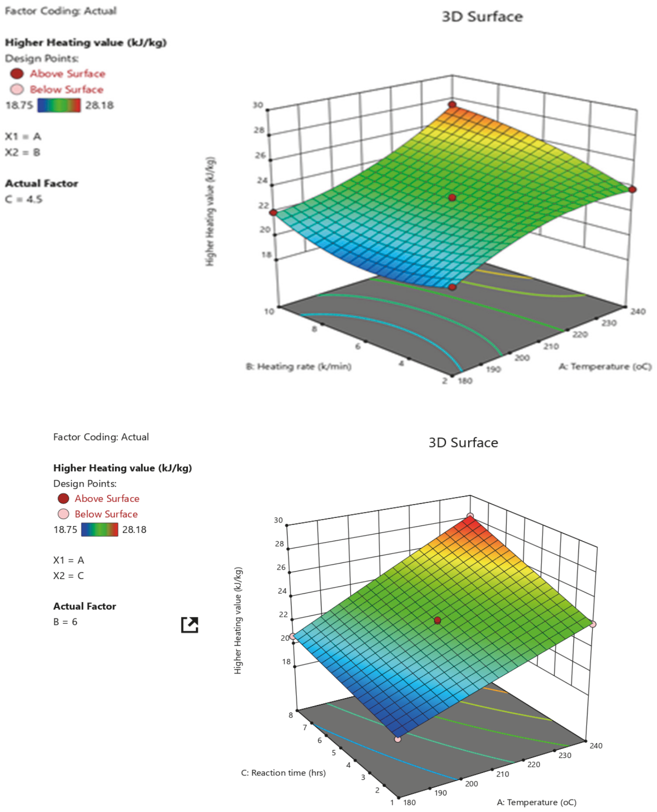


Figure 4.26: Surface response models for the higher heating value of hydrochar from cocoa pods residues.

4.3.2.3 Factor interaction

In terms of the higher heating value of the hydrochars produced from cashew peduncle residues, no interactions were found between the independent process factors (reaction temperature, heating rate and reaction time) as shown in Figure 4.27 and in Appendix D-7. Further, the perturbation chart points to a strong dependency of the higher heating value on the process temperature as compared to the reaction time. Even though the reaction time influenced the higher heating value content of the hydrochar, its effect was marginal when compared to the effect of the process temperature. No combined effect of process temperature and heating rate was observed as shown in the interaction plot. However, since the I-beam least significant difference plots overlap, the difference between process temperature and reaction time predictions is significant. Similarly, the perturbation plot of the independent factors for the heating value of cocoa pods hydrochar showed that even though the heating value was affected by all the three process parameters, the effect of process temperature was dominant with a steeper slope than the effect of reaction time. On the contrary, the effect of reaction time was marginal with a gentle slope. Process temperature was involved in multiple interactions with heating rate and reaction time. While the interaction between the heating rate and process temperature was not significant, the interaction between temperature and reaction time was significant (Figure 4.28 and Appendix D-10).

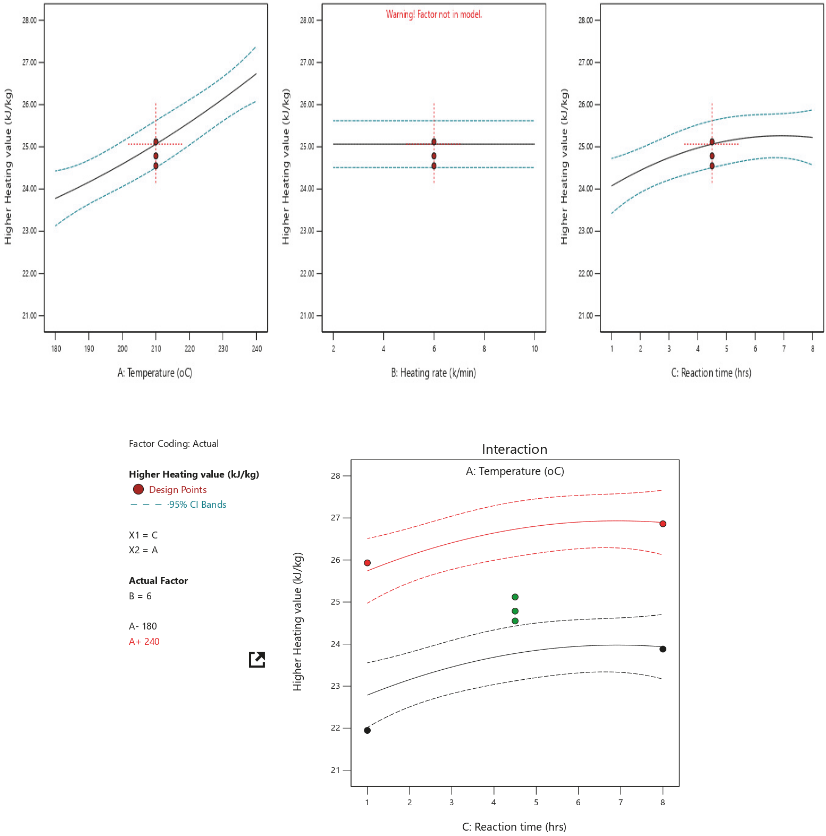


Figure 4.27: Factor interaction for higher heating value response factor for cashew peduncle hydrochar.

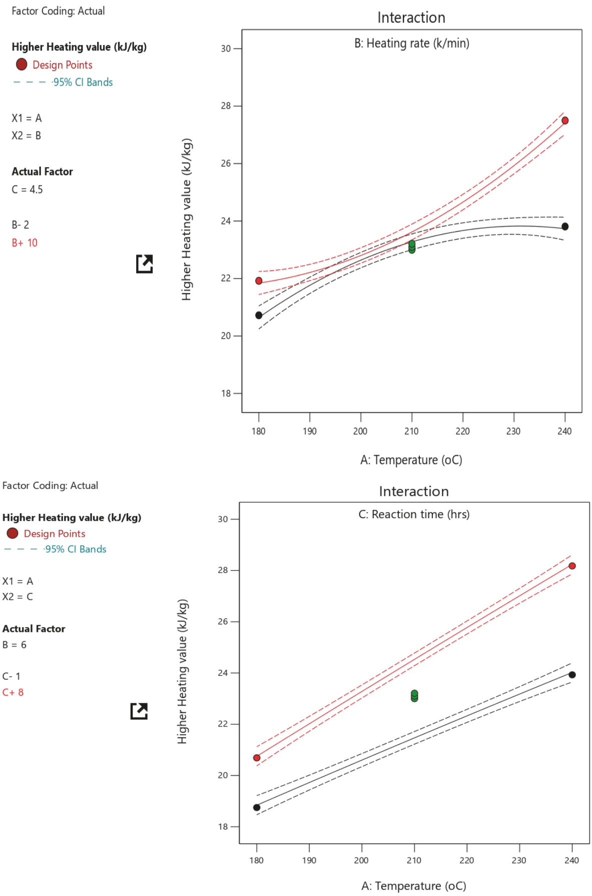


Figure 4.28: Factor interaction for higher heating value response factor for cocoa pods hydrochar.

4.3.4 Ash content

4.3.4.1 Ash content as a function of process severity

The ash content of the hydrochars from cashew peduncle and cocoa pods were found to be generally decreasing with increasing process severity. However, no clear trend was established even though the decrease in ash content with increasing process severity was observed. As shown in Figure 4.29, the linear correlation between ash content and process severity was very weak with an R^2 of 0.5739 and 0.4983 respectively for cashew peduncle and cocoa pods hydrochars. Both R^2 values fell below the acceptable limit of 0.8 for a good linear correlation.

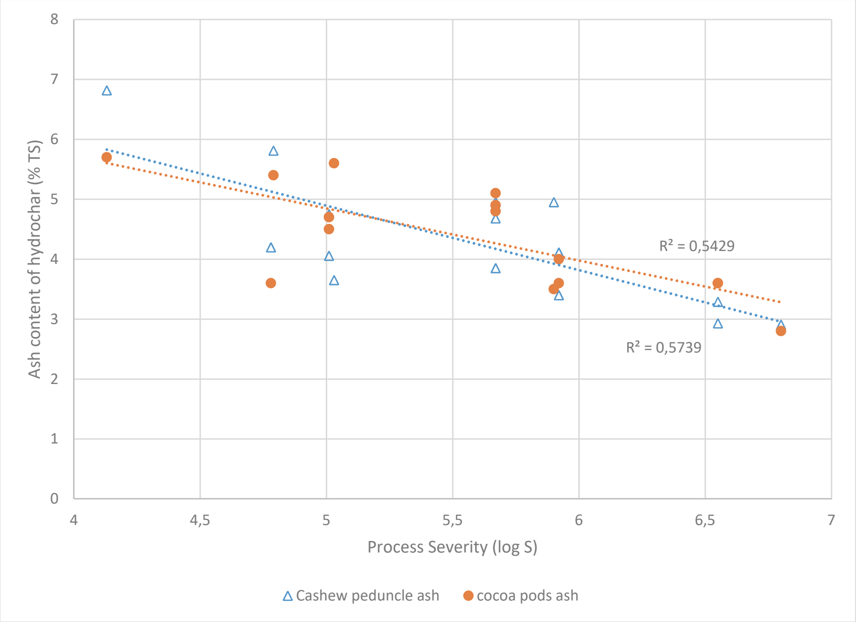


Figure 4.29: Effect of process severity on the ash content of the hydrochar from cocoa pods and cashew peduncle residues.

4.3.4.2 Response surface models

The ash content response factor was found to be dependent on the reaction temperature and the process reaction time. The model Equations (4.10 and 4.11) for both ash content from cashew peduncle hydrochars after loss of ignition test and cocoa pods hydrochars were found to be significant with F-values of 10.81 and 20.5 respectively. The corresponding P-values of 0.0021 and 0.0056 respectively for cashew peduncle and cocoa pods imply the probability of such high F-values being due to noise was only 21% and 56% respectively. Similarly, the lack of fit F-values was found to be not significant relative to the pure errors for both residues which is an indication of goodness of fit of the models to the respective experimental values. The lack of fit F-value of the cashew peduncle was found to be 1.56 with a corresponding P-value of 0.4534. The lack of fit F-value and its corresponding P-value of the ash content response factors for cocoa pods was 2.0 and 0.5678 respectively. This indicates that the chances that the lack of fit F-values could be due to noise for cashew peduncle and cocoa pods were 45.34% and 56.78% respectively. Both models had characteristically low R^2 values even though the adjusted and predicted R^2 were in reasonable agreement (< 0.2 difference). Both models were linear.

$$\text{Ash content}_{\text{cashew peduncle}} = 10.94 - 0.0267 * \mathrm{T} - 0.232 * \mathrm{t} \tag{4.10}$$

$$\text{Ash content}_{\text{cocoa pods}} = 10.70 - 0.03 * \mathrm{T} - 0.086 * \mathrm{t} \tag{4.11}$$

Both 3-D surface response models for the ash content of cashew peduncle (Figures 4.30) show decreasing ash content with increasing temperature and reaction time. Similarly, the 3-D surface response models (Figure 4.31) show decreasing ash content with increasing temperature and reaction time. The 2-D models are shown in Appendix D-11 and D-12.

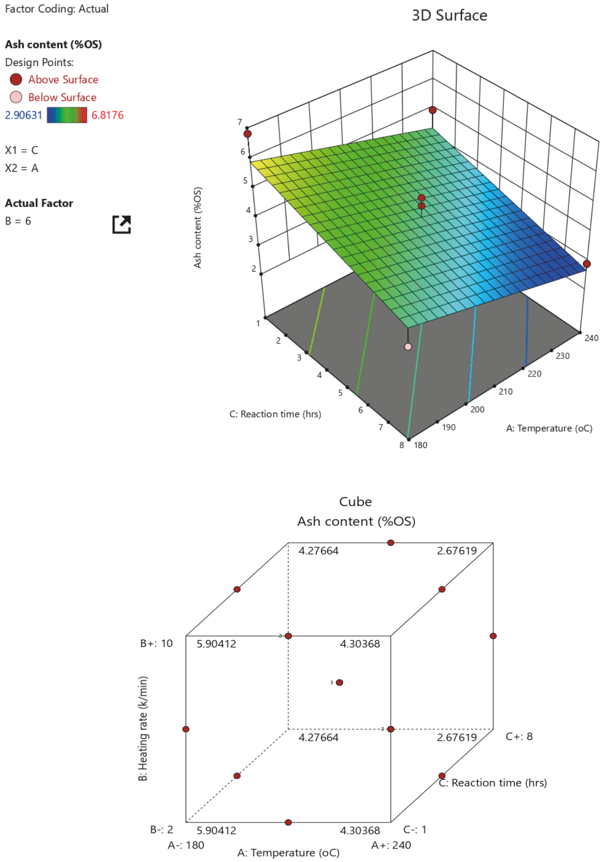


Figure 4.30: Surface response models for ash content of hydrochar from cashew peduncle residues.

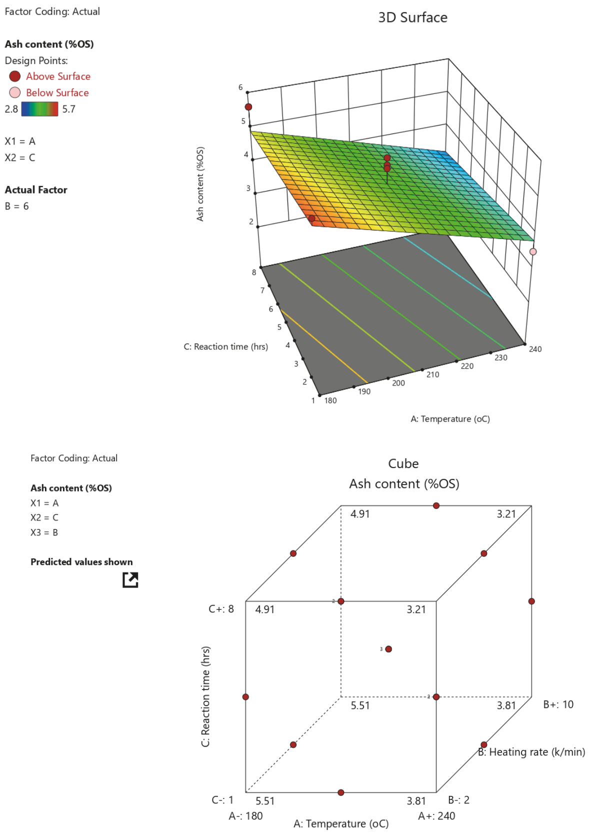


Figure 4.31: Surface response models for ash content of hydrochar from cocoa pods residues.

4.3.4.3 Factor interaction

The perturbation plot in Figure 4.32 and Appendix D-13 showed that the effect of temperature and residence time on the ash content of the cashew peduncle were the same. In the case of cocoa pods, the process temperature had a much greater influence on the ash content than reaction time since the slope of the temperature line was steeper than the slope of the reaction time (Figure 4.33 and Appendix D-14). In both cases, no factor interaction was observed between the process temperature and the reaction time. However, the overlapping least significant difference I-beams lines around the predictions shows that in both cases, the dependence of the ash content on the process temperature and process reaction time were not significantly different for cocoa pods hydrochar and cashew peduncle hydrochar.

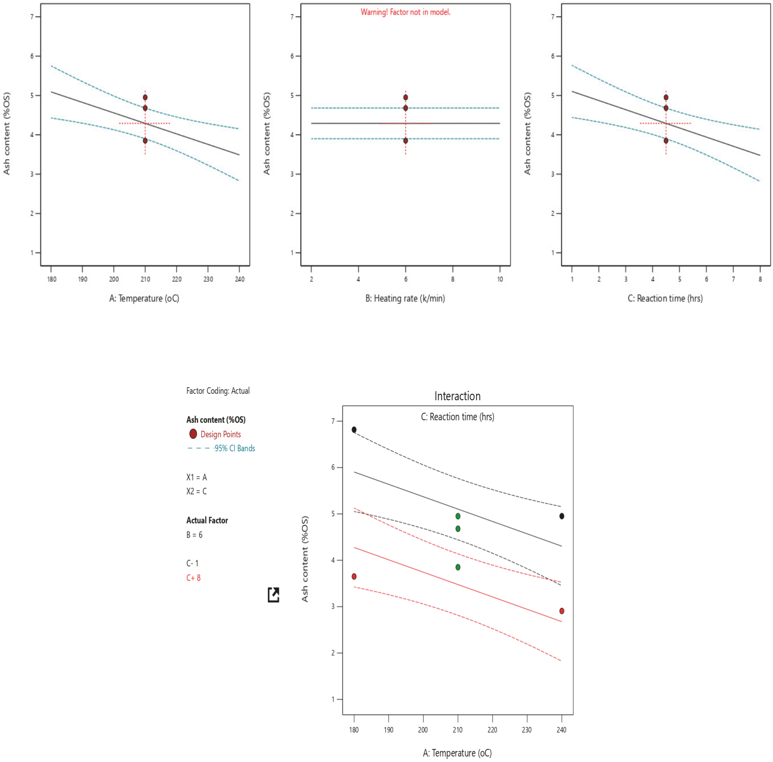


Figure 4.32: Factor interaction for ash content response factor for cashew peduncle residues.

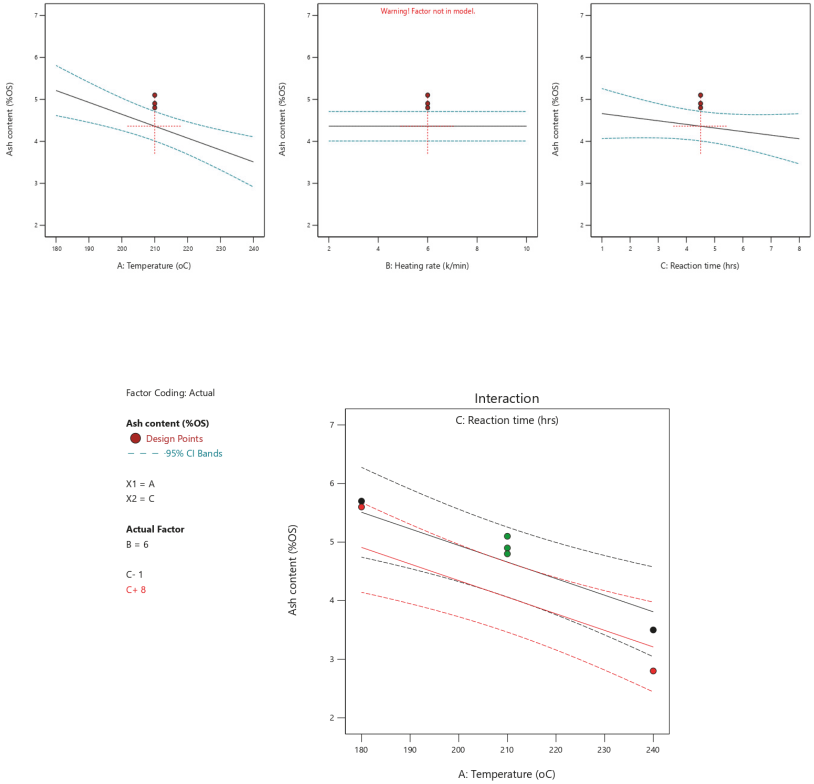


Figure 4.33: Factor interaction for ash content response factor for cocoa pods hydrochar.

4.4.4 Analysis of the hydrolysate

4.4.4.1 Effect of process severity on the chemical oxygen demand (COD) of the hydrolysate

No clear trend was observed between the COD of the hydrolysate after the carbonization process and the process severity for cashew peduncle residues (Figure 4.34). Even though the COD of the hydrolysate from cocoa pods carbonization correlated positively with the process severity, the correlation can be termed as generally weak (R^2 = 0.2687). Similarly, the linear correlation between process severity and COD of the cashew peduncle hydrolysate was found to be generally weak (R^2 = 0.5464) even though a negative correlation can be observed.

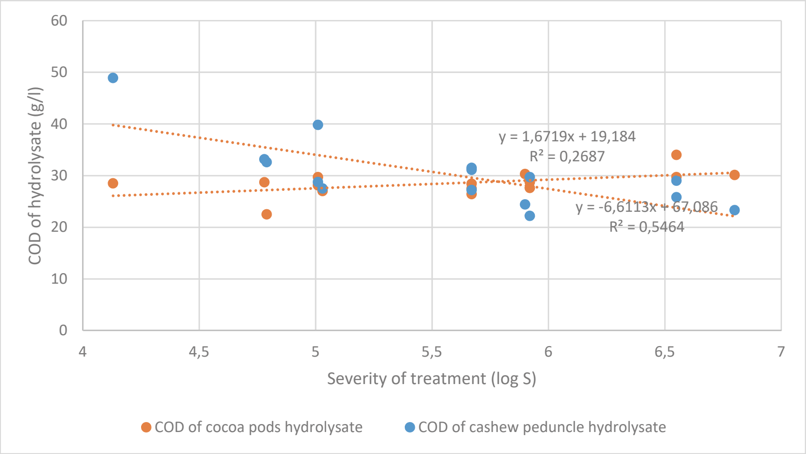


Figure 4.34: Effect of process severity on the COD of the hydrolysate from cocoa pods and cashew peduncle carbonization.

4.4.4.2 Response surface models

The model equation (Equation 4.12) showed that the COD response factor of the hydrolysate from cashew peduncle carbonization was dependent on the reaction temperature and reaction time and not so much on the heating rate. On the other hand, the COD response factor of the hydrolysate from cocoa pods carbonization was dependent on all three process parameters investigated.

$$\mathrm{COD}_{\text{cashew peduncle hydrolysate}} = 116.98 - 0.38 * \mathrm{T} - 11.55 * \mathrm{t} + 0.0483 * \mathrm{T} * \mathrm{t} \qquad (4.12)$$

$$\mathrm{COD}_{\text{cocoa pods hydrolysate}} = 5.75 - 0.091 * \mathrm{T} + 14.4 * \mathrm{r} - 0.61 * \mathrm{t} - 0.069 * \mathrm{T} * \mathrm{r} + 0.001 * \mathrm{T}^2 - 0.805 * \mathrm{r}^2 + 0.055 * \mathrm{t}^2 + 0.004 * \mathrm{T} * \mathrm{r}^2 \qquad (4.13)$$

The model equation for the cashew peduncle was significant with an F-value 11.8 and only 0.9% chance that this F-value occurred due to noise. Similarly, the lack of fit F-value of 2.77 and a 29.31% chance that such large F-value occurred due to noise meant the model equation was not significant with respect to the lack of fit. Further, the model has an R^2 value of 0.7635 with a reasonable agreement between the adjusted R^2 value and the predicted R^2 value of a difference of less than 0.2.

Regarding the COD of the hydrolysate from cocoa pods carbonization, the model equation (Equation 4.13) was also significant with an F-value of 23.60 and a 0.5% chance that such an F-value could occur due to noise. The model equation was not significant with respect to the lack of fit F-value. The F-value was 0.14 with a 95% chance that this F-value could occur due to noise.

Meanwhile, the R^2 of the model was determined to be 0.9692 and a reasonable agreement between the predicted and adjusted R^2 values with a difference < 0.2.

The 2D and 3D model graphs for cashew peduncle are presented in Figure 4.35 and Appendix D-15. While the 2D and 3D graphs point to a higher COD at relatively low process temperature and reaction time and tapering down with an increase in process temperature and reaction time, the 2D and 3D graphs for cocoa pods depicts the opposite (Figure 4.36 and Appendix D-16). The COD is least at relatively low temperature and low heating rate but highest at high temperature but low heating rate.

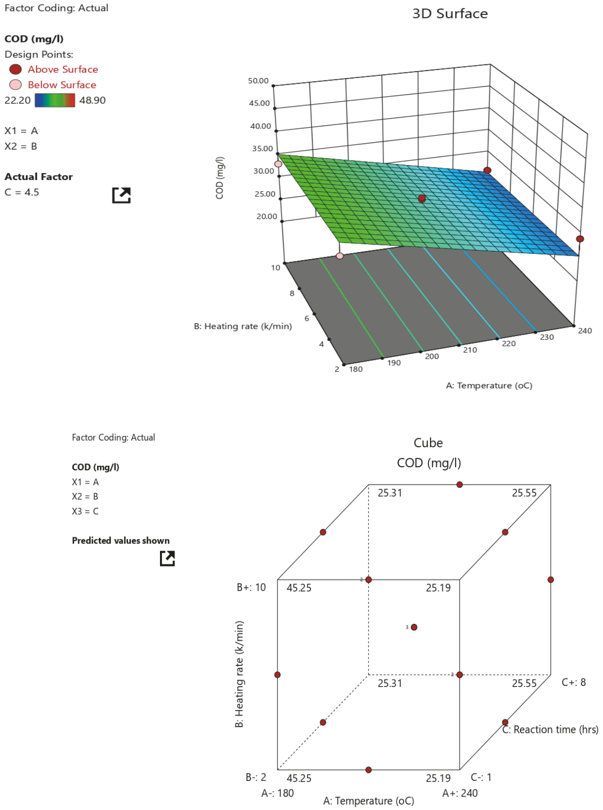


Figure 4.35: Surface response models of the COD of the hydrolysate from cashew peduncle carbonization.

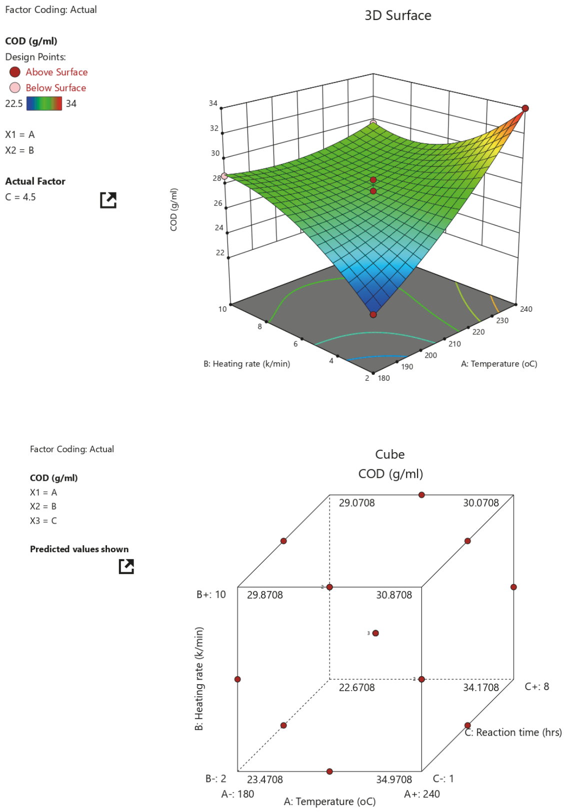
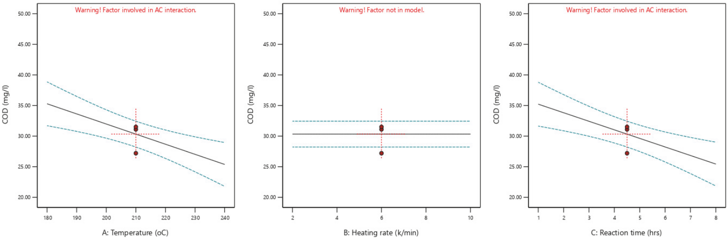


Figure 4.36: Surface response models of COD content of the hydrolysate from cocoa pods carbonization.

4.4.4.3 Factor interaction

The perturbation plot showed that both process temperature and reaction time had similar effect on the response factor (Figure 4.37 and Appendix D-17). Both correlated negatively with the COD response factor. On the contrary, the heating rate had little or no effect on the COD response factor. Factor interaction between the process temperature and reaction time was observed with overlapping least significant difference I-beam lines. This shows that the predictions are not significantly different. On the other hand, the perturbation plot for each of the factors for cocoa pods (Figure 4.38 and Appendix D-18) shows the dependence of the response factor on the process parameters under investigation. The effect of temperature and reaction time were almost identical except that, while the slope of process temperature was positive, that of reaction time was negative. Strong interaction was observed between process temperature and heating rate. Similarly, the overlapping least significant difference I-beam lines point to significantly different predictions



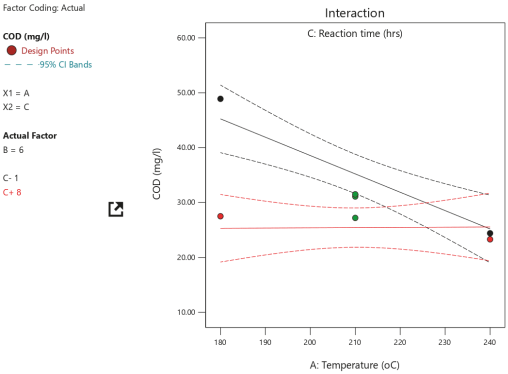


Figure 4.37: Factor interaction for COD response factor for cashew peduncle carbonization.

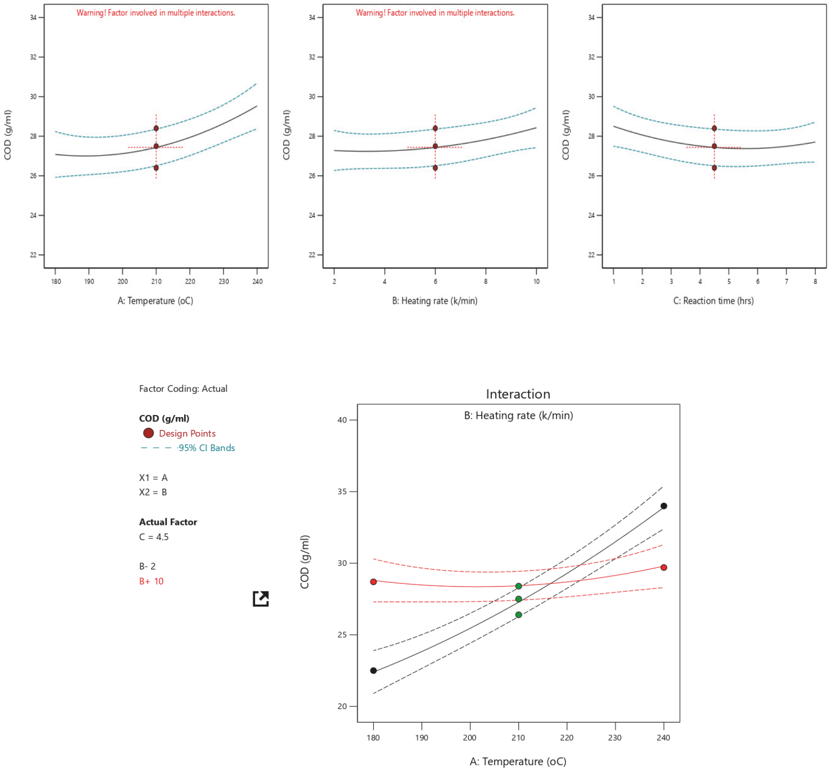


Figure 4.38: Factor interaction for the COD of the hydrolysate response factor from cocoa pods carbonization.

4.4.5 Optimization of the models

The models developed for each of the response factors were optimized to obtain the optimum operating conditions for each of the residues using Design Expert 12 software. The goal was to maximize higher heating value response factor of the hydrochar and minimize the ash content of the hydrochar produced. The hydrochar yield and COD of the hydrolysate were kept in range. Further, all the process parameters were given equal weightage.

The results obtained showed that the optimum operating conditions were not necessarily similar to the residues investigated (cocoa pods and cashew peduncle). In the case of the cashew peduncle residues, the optimum operating conditions were; temperature = 240 ºC, heating rate = 2.26 K/min, and reaction time of 7 hrs. This resulted in a hydrochar yield of 36% (input TS), a higher heating value of 26.99 MJ/kg, and an ash content of 2.9% (output TS) (Figure 4.39) with a result desirability of 0.995.

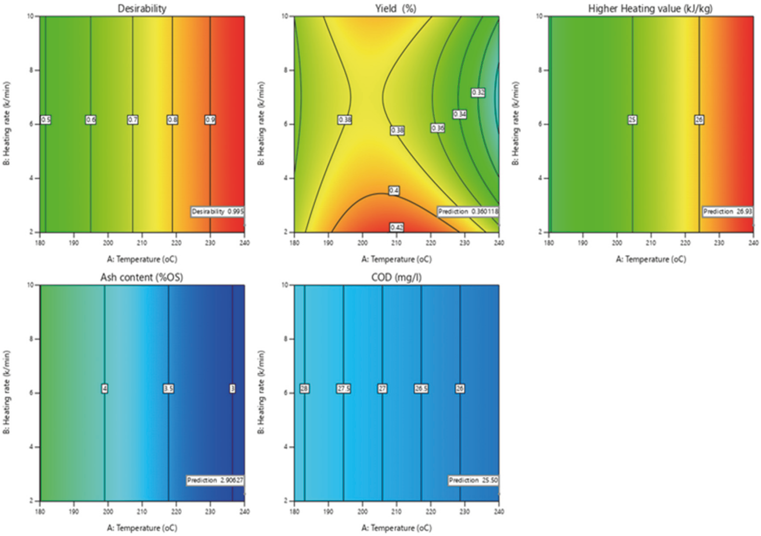


Figure 4.39: Optimization of process parameters for cashew peduncle hydrochar production.

By contrast, the optimum operating conditions for cocoa pods were. The result of the optimization showed that higher heating value of 28.3 MJ/kg, a yield of 38% (input TS), an ash content of 3.3

(output TS) and a COD content of the hydrolysate of 29.33 mg/l could be obtained under the optimized process conditions (Figure 4.40).

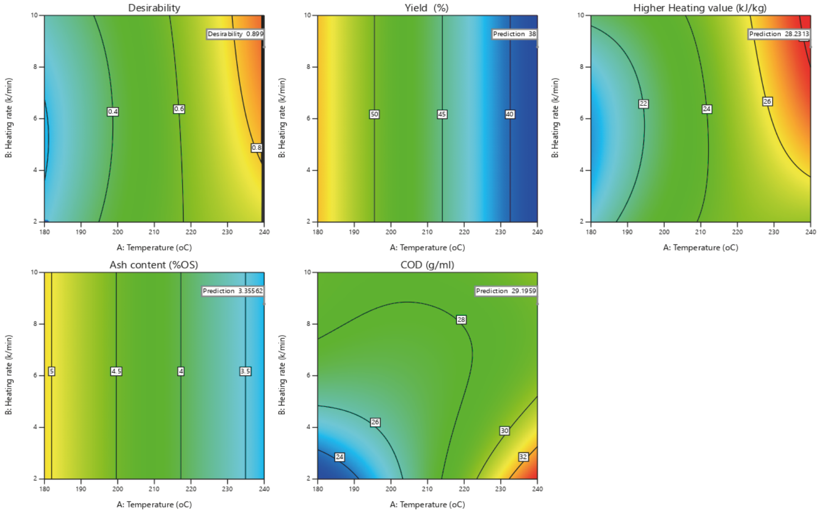


Figure 4.40: Optimization of process parameters for cocoa pods hydrochar production.

5. Discussion

5.1 Resource estimation and characterization of residues

5.1.1 Resource potential estimation

Cocoa and cashew nut cultivation will continue to play a vital role in the economy of Ghana. Ghana's dependency on cocoa and cashew to earn hard currency to support the local currency and drive economic development is expected to remain strong. In the coming years, the two crops are likely to experience higher production levels due to the commitment of government in the recent past to increase production through the distribution of new planting materials and free fertilizer in the cocoa sector and the launching of the cashew master plan. An increase in production level and processing capacities will result in a corresponding linear increase in the residues generated. However, new planting materials with better yield are expected to exponentially increase crop residue yield [135].

The re-estimated RCR value for cocoa pods was found to be higher than the RCR values for cocoa pods reported by Kemausuor et al. [17] and Duku et al. [15]. Duku et al. [15], for instance, used an RCR for cocoa pods based on an estimate reported by Eisentraut [176], which was not stated for specific countries. Therefore, one can argue that it could have been an average of several estimates even though literature searches for country specific RCR for cocoa and cashew residues did not yield much result. Additionally, the estimated RCR values reported by Eisentruat [176] were based on a 15% moisture content, which could be rightly assumed to be the equilibrium moisture content of the pods after air drying. On the other hand, Kemausuor et al. [17], used an average of two RCR which includes the Eisentruat [176] RCR value of cocoa pods (1). This suggests that the other RCR value for cocoa pods which culminated in an average RCR of 0.93 is 0.86. Comparatively, this is lower than the estimated cocoa pods RCR of 1.5 used by the FAO[1]. Thus, using the full complement of the moisture content of freshly harvested cocoa pods as was used in this thesis, the RCR is expected to significantly increase the quantity of residues generated. However, even when the RCR is estimated using a moisture content of 15%, the RCR which is obtained (2.5) is still higher than the reported RCR value used by Eisentruat [176]. The estimated RCR is also higher than the default RCR value used in the FAO residue estimation toolkit (1.5). Applying the estimated RPR resulted in a 250 % increase in cocoa pods potential in Ghana over previously estimated cocoa pods residue potential on a dry basis. Given the high quantity of cocoa beans produced annually in Ghana, the difference in RCR estimation is expected to significantly affect the estimation of the potential quantities of cocoa pods residues generated annually.

Hitherto not considered as a potential residue for bioenergy generation in Ghana, cashew peduncles residues should now be given attention as a potential resource for bioenergy production due to the high resource potential. The estimation of the RCR for cashew peduncle residues should serve as reference point for estimation of cashew peduncle residues.

Aside from the physical and chemical characteristics, the availability of the residues is critical in siting an energy exploitation facility. Widely spread residues may not help ameliorate

---

[1] FAO residue tool 1.0 xlms

environmental costs, especially when the environmental cost involved in gathering the residues is very high. This may end up outweighing any perceived environmental benefit. The wide distribution of cocoa pods and cashew peduncles is due in part to the unavailability of precise data on the exact location of farms within the country. Even though the spread of cocoa pods and cashew peduncle residues may be wide, farms may be clustered around certain towns with proximity. Precise data on farm size and location can be used to disintegrate the cocoa pods and cashew peduncle residue resource potential. Careful siting of treatment facilities in geographically proximate locations will aid the collection and processing of the residues at a lower environmental cost.

5.1.2 Physical and chemical composition analysis

5.1.2.1 Proximate analysis

The utilization of cocoa and cashew residues is strongly governed by the residues' physical and chemical characteristics. Even though some authors have prescribed wholly thermal or biological treatment methods, care must be taken in applying the results. Additionally, the high moisture content of cocoa pods makes thermal treatment expensive. A significant amount of energy must be expended first to dry the pods before any thermal treatment can be applied. Cocoa pods are known to contain high lignin content [126]. Anaerobic digestion and fermentation's inability to handle lignin-rich substrate leading to lower ethanol and gas output has been widely reported [106]. Further, the high content of theobromine which makes digestion of cocoa pod meals by ruminant a challenge according to Ofori-Boateng et al. [48] could also limit the amount of energy that can be extracted using anaerobic and aerobic fermentation methods.

The characteristically high moisture content of the cocoa pods and cashew peduncle was expected since these were obtained fresh from the field and not subjected to any form of pretreatment before their transportation to Germany. Since most of the moisture is not chemically bound to the chemical constituents of the residues, it could serve a useful purpose in the anaerobic digestion and hydrothermal carbonization process. The amount of process water needed to decrease the total solid concentration in both anaerobic digesters and hydrothermal carbonization process to obtain optimum operating conditions will be reduced substantially. Further, moisture in the lignocellulosic substrate is expected to increase the contact area between the microbes and the surface area of the substrate by increasing the area of attachment. This exposes large areas of the substrates to microbes to attach themselves leading to increased methanogenic activity. As reported by Fujishima et al. [110], decreasing the moisture content of dewatered sewage sludge had a detrimental effect on volatile solids removal efficiency, biogas production, and carbohydrate removal efficiency. This result was corroborated by Liotta et al. [177] when they investigated the effect of moisture content and particle size on the biogas yield of carrot waste under wet mesophilic anaerobic conditions. They reported a 4.3 and 40.8% decrease in final methane yield in semi-dry and dry conditions when compared to wet mesophilic anaerobic digestion conditions.

The higher heating values were similar for all three residues. The HHV of cocoa pods especially agreed with what has been reported in the literature [31,57]. The HHV of the cocoa pods, cashew peduncle, and cashew bagasse were found to be comparable to wood (18 MJ/kg) [178] but significantly higher than municipal solid waste (12 MJ/kg) [179]. Further comparison with charcoal which is carbonized wood, however, showed that the HHV of all the residues was lower than that of charcoal (30.6 MJ/kg) [180].

The results of the proximate analysis of the cocoa pods and cashew peduncle residues compared favorably with other feedstock for anaerobic digestion and hydrothermal carbonization like food waste [181] and cattle manure paunch [157]. On the contrary, the results differed significantly from the proximate analysis of some of the widely used anaerobic digestion substrates like maize silage [182] which has lower moisture content and higher dry matter content of about 33.3% and sewage sludge which has a dry matter content of about 1% [183].

5.1.2.2 Ultimate analysis

In an anaerobic digestion process, the carbon to nitrogen ratio (C/N) of the substrates is of key importance. This is because carbon serves as a source of feed for the methanogenic bacteria to convert to methane gas, a low carbon to nitrogen ratio leads to the starvation of the methanogenic bacteria. Further, the production of ammonia from the nitrogen sources serves to act as a buffer to control the process pH by neutralizing the organic acids produced. However, excess ammonia also leads to process inhibition by shifting the pH of the reaction medium into the alkaline region, which is unsuitable for the methanogenic activity. On the contrary, a high C/N ratio leads to the production of less ammonia to serve as a buffer for controlling the process pH. This leads to acidification due to the accumulation of volatile fatty acids by reducing the pH of the process. Thus, optimum C/N ratio in the range of 20 – 30 is essential for biogas production as reported by several authors [184,185]. The C/N ratio of cashew bagasse was similar to reported C/N ratio of cashew bagasse by Santos et al. [186] but differed from the reported C/N ratio by Silva et al. [187]. The C/N ratios of cashew peduncle and cashew bagasse fell within the proposed optimum C/N ratio, thus making them suitable substrate for anaerobic digestion. However, the C/N ratio of cocoa pods fell outside of the optimum C/N ratio marginally.

The Oxygen-Carbon (O/C) and Hydrogen-Carbon (H/C) ratios are used as measures to determine the level of coalification and energy densification. Reduction in the O/C ratio shows the occurrence of decarboxylation and dehydration reaction in the HTC process [188]. Further, the plot of O/C and H/C of fuels reflects the degree of carbonization [189]. The high O/C and H/C ratio of the residues is thus an indication of the uncarbonized state of the biomass. Subsequent carbonization may lead to its reduction.

5.1.2.3 Fiber analysis

The result of the fiber analysis shows the presence of lignin in the structural carbohydrates in all three residues albeit in varying quantities. The chemical structure of lignin which is made of complex irregular polyphenolic polymers renders anaerobic digestion ineffective in degrading it [190]. Thus, the presence of high content of lignin in the structural carbohydrate of all the residues especially cocoa pods that had the highest lignin content could be inhibitory to the anaerobic digestion process. The fiber analysis of cocoa pods was similar to those reported by Vriesmann and Petkowicz [191] but significantly lower than values reported by Thomsen et al. [126], who reported a lignin and hemicellulose content of about 37.2% and 9.9% respectively

A notable difference in lignin, cellulose, and hemicellulose content was observed for cashew peduncle and cashew bagasse. The difference in structural carbohydrates content of cashew peduncle and cashew bagasse could be due to the mechanical extraction process. The mechanical process of separating the hydrolysates in the cashew peduncle involves crushing and pressing. The mechanical extraction of the juice is analogous to mechanical pretreatment of milling before anaerobic digestion. Mechanical pretreatment (milling) is reported to disrupt the lignin-carbohydrate matrix leading to the accessibility of hemicellulose and cellulose thus altering the compositional fraction. Further, due to the difference in relative hardness and the anatomical and physical characteristics of starch and the structural carbohydrates, lignin could be fractionated during grinding of fresh biomass resulting in its accumulation in the smaller particle sizes [192]. Similar results of increasing hemicellulose, cellulose, and lignin content in smaller particle size as a result of different biomass has been reported [192–195]. The Hemicellulose and cellulose content of cashew bagasse compared favorably with reported values, however the lignin content differed significantly [186,187]. Comparatively, Reis et al. [196] reported a much higher cashew bagasse lignin content of 43.28% than the reported values of other authors including what was obtained in this study.

5.1.2.4 Major and minor mineral content

The presence of minor minerals in the residues could aid in the digestion process by acting as micronutrients or essential supplements for bacteria growth. However, the presence of heavy metals may rather inhibit the anaerobic digestion process by poisoning the bacteria [197,198]. This notwithstanding, the presence of major nutrients in the digestate is essential for plant growth and could, therefore, aid its application as a soil amendment when applied as compost. The major elements known to inhibit the digestion process such as mercury, cadmium, or chromium were either undetected because of their concentration or were not present. This eliminates the possibility of inhibition of the anaerobic digestion assay due to the absence of these heavy metals. On the contrary, the presence of all the other minerals could serve as important trace metal supplements for the growth of the methanogenic bacteria. This means all the residues may possess the ability to release essential trace elements automatically to enhance bacteria growth and the anaerobic digestion process.

In the hydrothermal carbonization process, the effect of the mineral content on the carbonization conversion process is not yet understood and may, therefore, be assumed to have minimal effect in the absence of any comprehensive data to the contrary. However, it can affect the fuel properties of the hydrochar especially when the minerals remain in the solid-phase or are attached to the solids instead of dissolving in the liquid state. For instance, the presence of potash in cocoa pods makes it unsuitable to extract energy through direct combustion [30,62]. The mineral component of biomass is non-combustible and as such present themselves in the form of ash after the combustion process. During combustion, some of the minerals are oxidized resulting in the formation of new compounds. For instance, potassium is oxidized to potassium carbonate (K_2CO_3) popularly referred to as potash during combustion. The conversion of the potassium in the cocoa pods to potash presents a very serious problem during combustion due to its highly corrosive nature. Thus, its ability to affect the performance and durability of the canisters/combustion chamber could be highly significant. Further, slagging and fouling are major problems in the use of solid fuels. Fuels with low slagging and fouling indices are mostly preferred to fuel with high fouling and slagging indices. Since the mineral content directly affects the fouling and slagging indices, lower mineral concentration of the substrates is mostly desired in the hydrothermal process. However, the role of minerals in catalyzing intermediate reactions and aiding product selectivity during hydrothermal carbonization is not yet understood. Thus, further research is needed to establish the effect of major and minor minerals on product selectivity and yield of the hydrochar.

5.2 Anaerobic digestion

5.2.1 Theoretical biomethane potential (BMP) and bench-scale BMP assay

Theoretical biomethane potential is a particularly useful tool to determine the biodegradation potential of the organic fraction of biomass. It also serves as the theoretical limit of biogas potential beyond which further biogas production is not possible. In comparison with other results from the literature, the result of the theoretical BMP of cocoa pods was found to be much higher by 47% than the result obtained by Thomsen et al. [126] using the Buswell equation. This could be due to the different methods used in determining the theoretical BMP of the substrates. While Thomsen et al. [126] calculated the biomethane potential based on the individual compositional constituent of starch, cellulose, hemicellulose, and protein, leaving out the lignin fraction, the approach used in this study was based on the elemental constituent of the cocoa pods. The difference in the approach lies in the avoidance or inclusion of the lignin component in the cocoa pods in estimating the theoretical BMP. Given that the lignin component accounts for 21% of the structural carbohydrates, this will inadvertently affect the results when it is either omitted or included in the theoretical BMP estimation. This could be the reason why the result obtained in this study was similar to the result obtained by the same authors when they used the Chemical Oxygen Demand (COD) equations [126]. The COD method, just like the elemental analysis, measures the total organic carbon in the biomass which includes lignin. The effect, therefore, is a higher estimation of BMP. Taking out the lignin content in the estimation of the theoretical BMP even though it may result in lower theoretical BMP estimation, it nonetheless presents an overly optimistic view about the degradability of cocoa pods unless the presence of lignin is taken into consideration in the computation of the biodegradability index of cocoa pods. In contrast, the theoretical BMP of cashew peduncle and cashew bagasse were similar despite the slight difference in lignin content observed.

Often theoretical BMP serves as a useful indicator however, the results must be confirmed through experiment. The actual BMP of cocoa pods obtained in this study (191 l(N)/kgVS) compared favorably with results obtained by Ward-Doria et al. [54], who reported a cumulative BMP of 200 ml/gVS for untreated cocoa pods but slightly higher (8%) than results obtained by Acosta et al. [190] who reported a biomethane potential of cocoa pods to be 173 l/kgVS using two different inocula. In the case of cashew peduncle and cashew bagasse, the actual BMPs were no longer similar. The significant difference in biogas potential between cashew peduncles and cashew bagasse could be due to the amount of readily digestible sugars in the cashew juice which represents about 15% of the peduncles mass. During the processing of cashew peduncles into juice or alcohol, a significant fraction of the juice that contains the sugars are squeezed out leaving the fibrous residues which constitute the bagasse. This is reflected in the fiber analysis where a large fraction (21%) of the residues constituted the hemicellulose fraction of bagasse as compared to 9.36% for the cashew peduncle. As noted by several authors, even though the hemicellulose fraction is degradable, the rate is rather slow and requires a longer residence time to degrade [199–201].

In comparison with other feedstock, the actual BMP of cocoa pods and cashew peduncle except cashew bagasse was similar to the BMP result obtained for the organic fraction of municipal solid waste [202] and chopped banana peels, rambutan and longan wastes and but significantly lower by about 40% than ground banana peels [203].

5.2.2 Kinetics of the digestion process

The kinetic parameters of the BMP assay were determined by fitting the experimental data to two popular kinetic models. The empirical modified Gompertz model which is widely used to model anaerobic fermentation reactions, and the modified first-order kinetic model which assumes the feedstock to be composed of two fractions – fast degrading fraction and slow degrading fraction and considers the digestion process from a process engineering point of view comprising of 2 instead of the widely reported 4 steps. Thus, the name of the model, dual-pool 2-step kinetic model. The choice of the second model was based on the chemical properties of the residues which showed the presence of structured carbohydrates suggested a pool of slow degrading components made of up the hemicellulose and cellulose fractions. The correlation coefficient R^2 for both models were above 0.90 for all the residues, an indication that both models could be used to predict the methane yield of the substrates. The results show that even though the modified Gompertz model fitted the data well as shown in Figure 5.5, there were wide deviations of the model from the kinetic data at two key points. At start-up when the reaction time is zero, the Gompertz model predicts a greater than zero biogas yield for all three residues. Further, the experimental data curve seems to be pointing to an increase beyond the 28 days while the kinetic model asymptotically approaches the maximum methane potential. Thus, the deviation between the Gompertz model and the experimental results for all the substrates beyond the 28 days retention time is likely to become more pronounced which will affect the respective R^2 of the residues. Therefore, the ability of the Gompertz model to predict biogas production beyond the 28 days retention time is called into serious question. Unlike the modified Gompertz model, the dual-pool 2-step model accurately predicts gas yield at start-up and shows the propensity to predict gas yield beyond the 28 days retention time. Thus, the dual-pool 2-step model could be accepted as the better model of the two to accurately predict gas production from the anaerobic digestion assay of cocoa pods, cashew peduncle, and cashew bagasse. Generally, the dual-pool 2-step model is expected to perform better in predicting the biogas yield from lignocellulosic substrates than general organic feedstock.

5.2.3 Pilot-scale experiment and the application of the kinetic model

The result of the pilot-scale BMP study pointed to an increase in biogas yield for all three substrates. This could be due to the longer hydraulic retention time when compared to the result of the 500 ml assay. The effect of retention time on biogas yield has been well documented in the literature. Longer hydraulic retention time allows the microbial community enough time to acclimatize and populate. On the contrary, shorter retention time in batch mode may leave behind undigested substrate, while in continuous or semi-continuous mode, a shorter retention time could lead to the washing out of the acetoclastic and methanogenic bacteria necessary for the conversion of organic substrates into intermediates and thereafter into biogas. Further, it has been proven that shorter hydraulic retention time could lead to the overloading and subsequently the accumulation of volatile fatty acids in the reaction medium which could lead to system instability and failure. This explanation holds, so long as the biogas yield is marginal and can be predicted using kinetic models. A substantial increase in biogas yields like what was observed for cashew peduncle and cashew bagasse assay could not, however, be due to only the increase in hydraulic retention time. Much so when the increase cannot be predicted with the kinetic parameters developed earlier. The substantial increase in biogas yield for the two substrates (cashew peduncle and cashew bagasse) could be due to the source of inoculum used. The effect of inoculum source on biogas yield has been the subject of investigations by several authors [162,204,205]. While some researchers reported no significant increase in biogas yield, others have also reported a marginal but significant increase in biogas yield which can be primarily attributed to the type of inoculum used. As pointed out by Elbeshbishy et al. [204], the source of inoculum brings with its difference in bacteria population, substrate adaptation, and residual anaerobic biodegradable substrate. Thus, the change in inoculum source during the pilot-scale study could have resulted in higher substrate adaptability and or higher methanogenic bacteria population and could be the reason for the substantial increase in biogas yield for cashew peduncle (57%) and cashew bagasse (90%). In comparison with results from the literature, Pozdniakova et al. [162], reported a significant difference in methane yield of category 2 animal by-products when they studied the effect of different inocula sources on the BMP. Similarly, Rajput and Shiekh [205] reported a significant difference in yield of biogas when they studied the effect of two inocula sources on the biogas yield of sunflower meal and wheat straw. As a result of the substantial increase in biogas yield from the two substrates (cashew peduncle and cashew bagasse), the kinetic constants obtained from the bench-scale study could not be used to predict the biogas yield accurately. Recently Santos et al. [186], reported significant difference in the biogas yield of cashew bagasse anerobic assay using two different inoculum and concluded that industrial sludge inoculum was better than sewage sludge inoculum. This corroborates findings made in this study that biomethane assay of cashew peduncle and cashew bagasse was dependent on the source of inoculum used. Unlike the cashew peduncle and cashew bagasse substrates, the source of inoculum did not have any effect on the biogas yield of cocoa pods. Thus, the increase in biogas yield could be due to only the longer hydraulic retention time used. This also explains the ability of the dual-pool 2-step kinetic model using the previously determined constants to correctly predict the final cumulative biogas yield of the cocoa pods.

5.2.4 Effect of hydrothermal pretreatment on fiber analysis of pretreated cocoa pods

Hydrolysis of the complex carbohydrates has been widely reported as the limiting step in the anaerobic digestion of lignocellulose feedstock [118,164,206]. This is mainly due to the role that lignin plays in the cell wall of most plants. Apart from giving rigidity to the cell wall it also binds the cellulose and hemicellulose through covalent linkages, thus making it very difficult for bacteria to access the hemicellulose and cellulose component. The lignin content in the cell wall can be correlated to the rigidity of the cell wall, which renders it insusceptible to anaerobic digestion. Additionally, the accessibility of the cellulose and hemicellulose by the bacteria media during the anaerobic digestion process is severely limited to the lignin content in the residues. Thus, enhanced solubilization of the cellulose and hemicellulose fractions into their basic fermentable units can only be achieved through either the removal of lignin, hydrolysis or degradation of lignin into its polyphenol components or softening of lignin to make the cellulose and hemicellulose more accessible.

Th reduction in the hemicellulose fraction of the pretreated cocoa pods was consistent with the general theory. The hydrolysis of hemicellulose into its main component xylan, galactan, and mannose of the cocoa pods which is evident from the negative correlation between the process severity and the percentage of hemicellulose in the cocoa pods fibers after pretreatment is consistent with and supports earlier findings that hemicellulose degradation is enhanced by the higher process severity. This is largely expected as the activation energy of the hemicellulose is reported by Jin [73], to be much lower than cellulose. As a result, partial thermal degradation of hemicellulose is reported to occur at temperatures below 200 ºC, while complete hydrolysis of hemicellulose could occur between 200 and 230 ºC. For instance, Costa et al. [118], reported the hydrolysis efficiency of 21% during hydrothermal pretreatment of sugarcane bagasse at 200 ºC and 10 min and postulated further that if all the sugars produced were coming from the hemicellulose fraction, then the hydrothermal pretreatment process achieved a 61% process efficiency. This is possible due to the spatial structure of hemicellulose and the low degree of polymerization which allows for its complete degradation under subcritical condition. Wang et al. [120] reported a higher degree of solubilization of hemicellulose than cellulose when they hydrothermally pretreated rice straw prior to anaerobic digestion. The solubilization of hemicellulose at higher process temperatures below 240 ºC during hydrothermal pretreatment was also reported by Sun et al. [81] when they hydrothermally pretreated Eucalyptus urophylla between 100 – 240 ºC for 30 minutes. The degree of solubilization was correlated to the degree of crystallinity of the remaining fibers after the pretreatment process. An indication that while hemicellulose was degraded, the thermal process had little effect on the degradation of cellulose below 240 ºC.

Similarly, the reduction in cellulose fraction of the pretreated cocoa pods fibers with increasing process severity could be due to the changing fraction of hemicellulose in the fibers of cocoa pods and limited hydrolysis of cellulose fraction. Cellulose is a complex polymeric substance comprising of several glucose monosaccharides. By convention, cellulose is degradable under anaerobic conditions. However, as stated earlier accessibility of the cellulose in the plant cell wall is limited by the presence of lignin in lignocellulosic materials. Aside this, cellulose is crystalline and thus difficult to degrade at subcritical conditions as reported by Fan et al. [207]. Due to this, limited hydrolysis has been reported using hydrothermal pretreatment.

The increase in lignin content of the pretreated samples should not be understood to mean an increase in the nominal amount of lignin in the pretreated cocoa pods samples but compositional changes of the structural carbohydrates. As reported by Harmsen et al. [114], lignin undergoes structural changes rather than solubilization during hydrothermal treatment below 200 ºC. Therefore, the chemical structure of lignin which is an amorphous polyphenol compound composed of three precursors – coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol [208] undergoes structural changes during thermal treatment resulting in its softening. The subsequent thermal degradation of lignin after softening is reported to begin at 200 ºC albeit slow at a rate of less than 0.15 wt%/ºC [86]. Further, an increase in temperature 200 - 275 ºC, is reported to lead to the depolymerization of lignin into aromatic hydrocarbons, phenolic, and hydroxyphenyl compounds [86]. However, the depolymerization of lignin to produce phenols [209] and furfural [210] and HMF at higher process severity is undesired in the anaerobic digestion process. This is because phenols [211] and furfurals [164] are known to be toxic to the anaerobic digestion process. Their presence could severely inhibit the digestion process resulting in total failure of the process or reduced biogas yield. Even when there is significant depolymerization at higher process severity, the possibility of repolymerization of some of the depolymerized monomers during cooling into pseudo lignin compounds as reported by Zhuang et al. [212] is a major drawback of hydrothermal pretreatment.

5.2.5 Effect of hydrothermal pretreatment on biogas yield

The biogas study experiment confirmed the efficacy of the hydrothermal pretreatment. No trend was observed between the biogas yield and the process severity over the entire range of process conditions of temperature and residence time considered. However, an interesting trend emerged in that the biogas yield of the cocoa pod residues increased significantly at treatment conditions below a severity of 3.0. This was largely expected due to the possibility of the lignin binding the hemicellulose and cellulose components of the cell wall thereby making the cellulose and hemicellulose less accessible. Further, the hydrolysis of hemicellulose during subcritical hydrothermal conditions has already been explained under section 5.2.4. These combined to enhance the biogas yield after pretreatment. The result is comparable to the result obtained by other researchers working on different substrates/residues. For instance Di Girolamo et al. [119], reported a 10%, 7%, 23% and 4% increase in yield at pretreatment conditions of 150 ºC/10 min, 150 ºC/20min, 180 ºC/10 min and 180 ºC/20 min respectively. Mendez et al. [213], also reported an increase of 64% in biogas yield after hydrothermal pretreatment of microalgae Chlorella vulgaris biomass at 160 ºC and 10 minutes corresponding to a process severity of 2.76. When the process severity was increased above 3.0, serious process inhibition resulting in either reduced biogas yield or complete cessation of the entire anaerobic digestion process was observed. At a process severity of 3.5 and 3.7 corresponding to process conditions of 185 ºC and reaction times of 10 minutes and 17 minutes was quite an anomaly. The completely failed biogas assay could only be explained as being due to the length of the treatment time. During higher process severity (4.23), even though the biogas assay did not fail, the biogas yield was only 25% of the actual biogas yield of the untreated samples. This was largely expected due to the start of the lignin degradation at 220 ºC. The degradation of the lignin could have led to the production of toxins (phenols and furfural) which inhibited the process. However, at the process severity of 4.71 corresponding to a temperature of 200 ºC and a reaction time of 15 minutes resulted in a 10% increase in biogas yield. This was an anomaly as one would have expected biogas yield to further reduce due to lignin degradation and the production of toxins. Other researchers like Ferreira [214], also reported greater solubility at a temperature of 220 ºC but shorter reaction time (1 min) resulting in a 21% increase in the biogas yield of pre-treated sample.

5.2.6 Continuous co-digestion and mono digestion studies

5.2.6.1 Effect of feed composition on biogas yield, process stability, and synergetic effect

The promotional effect of cocoa pods, cashew peduncle, and cashew bagasse when co-digested with maize silage was studied. The result shows that the higher biogas yield from the co-digested cashew peduncle when compared with the co-digested cashew bagasse and co-digested cocoa pods, could be due to the presence of the readily digestible sugars in the cashew peduncle as explained earlier. The readily digestible sugars decompose into volatile fatty acids under anaerobic conditions. As a result of the fast acidogenesis reaction of the carbohydrate leading to the production of volatile fatty acids, an acidic medium was created that could have resulted in speeding up the hydrolysis of the fibers in the maize silage into their basic monomers. This could explain why the specific biogas yield for cashew peduncle was higher than that of cashew bagasse at all feed composition investigated. This can also explain the antagonistic effect observed for cashew bagasse:maize silage feed composition. In the case of the cashew bagasse, the juice containing the readily digestible sugars had already been extracted leaving behind the fibrous material which then digested slowly. Despite the general increase in the specific biogas yield of the co-digested cashew peduncles, the dependence of the synergetic index on the feed composition was striking even though it could not be easily explained, as no clear trend was established. The statistically significant specific biogas yield for 50:50, 70:30 and 90:10 cashew peduncle-maize silage feed composition could be due to several possible reasons such as;

1. Some sort of chemical balance between the hydrolysis reaction and acidogenesis reaction was established at these feed compositions,
2. The mineral balance between mineral release and absorption could have been enhanced at these feed compositions leading to significantly higher biogas yield.

The insignificant promotional effect of cocoa pods at feed composition of 50:50, 60:40, and 70:30 could largely be attributed to the promotional effect of the Co, Mo, Ni, and Fe found in cocoa pods which are lacking in maize silage [215]. The antagonistic effect observed at 80:20 and 90:10 feed composition could be due to the overloading of the reactor, which resulted in an increase in the TS concentration. This shows that the promotional effect of cocoa pods as a co-substrate for maize silage digestion was limited by the percentage of cocoa pods in the feed composition. The results are comparable to reported synergetic effect but the insignificant gas yield from co-digested maize silage and red chicory waste by Cortesi et al. [182], who attributed the promotional effect to improvement in the kinetics of the digestion process instead.

The digestion process stability observed for all the three residues could be due in part to the low OLR that was chosen for the co-digestion experiment. The presence of micronutrients in the cocoa pods, cashew bagasse, and cashew peduncle residues could have also contributed to ensuring that the bacteria community had an insitu source of essential trace elements to enhance their growth thus requiring no trace element supplementation even though the hydraulic retention time and the duration of the experiment were short. It remains to be seen the effect of long-term digestion at higher organic loading rate will have on process stability without external trace element supplement on the co-digestion of cocoa pods, cashew peduncle, and cashew bagasse with maize silage.

5.2.6.2 Effect of increasing the organic loading rate (OLR) on specific biogas yield and process stability of mono digested substrates.

Prabhudessai et al. [216], reported a failed BMP test for cashew peduncle residues due to extreme acidification as a result of rapid hydrolysis during the initial phase of the digestion process at an OLR of 3.0 kgVS/m^3-day in a tubular flow digester. The result obtained in this study showed that the digestion of cashew peduncle residues was possible in a CSTR reactor at OLR of 3.0 kgVS/m^3.day. Despite the rapid hydrolysis of the cashew peduncle, the gas production rate was observed to be relatively stable at OLR of 2.5 and 3.0 kgVS/m^3-day with a cumulative specific biogas potential of 410 and 421 l(N)/kgVS-added and corresponding methane content of 51% and 52% respectively. Process inhibition was only observed when the OLR was increased to 3.5 kgVS/m^3-day, which plunged gas production from a peak of 14.9 l(N) on day 61 to 0.81 l(N) on day 81. 4.4. On the contrary, biogas production was stable at OLR of 3.5 and 4.0 kgVS/m^3-day for cashew bagasse and up to 5 kgVS/m^3-day for cocoa pods. This supports the findings of Prabhudessai [217], who reported stable digestion of phase-separated cashew peduncle (cashew bagasse) at OLR of 3.0 and 4.0 in a tubular flow reactor. Additionally, as noted earlier in section 5.2.6.1 of this thesis, the accumulation of minerals in the cashew bagasse and cocoa pods as compared to the cashew peduncle could have contributed to the process stability. The minerals probably served as a major source of trace elements for the bacteria community at higher OLR. Whereas phase separation led to a more stable digestion process, specific biogas yield was lower when compared with the digestion of the whole cashew peduncle, thus requiring some sort of balance to be found. In the case of the cocoa pods, the stable digestion process of cocoa pods at higher OLR could be attributed to the following reasons;

1. The balance between acidogenesis and acetogenesis reaction was primarily due to the relatively slow hydrolysis of the carbohydrates. This could be due to the high amount of structured carbohydrates in the fibers (54%) when compared to the cashew peduncle and cashew bagasse. Thus, the rate of production and consumption of the VFAs were in harmony.
2. The presence of major and minor minerals in cocoa pods could have served as a readily available source of trace minerals for the growth of the bacteria community. Thus, unlike maize silage [215] and other agricultural residues that experiences process instability at higher OLR due to lack of trace element, the high concentration of major and minor minerals in cocoa pods ensured that no external trace metal supplementation was required.
3. The absence of inhibitory minerals in the cocoa pods such as mercury and lead could have also contributed to the stable digestion of the cocoa pods.

5.2.5 Comparison between specific biogas and biomethane yield of batch and continuous study

The result of the semi-continuous study confirmed the specific biogas and biomethane yield of the cashew peduncle, cashew bagasse, and cocoa pods albeit with some notable differences. A reduction of about 16% was observed between the specific biogas yield of cocoa pods at OLR of 2.5 kgVS/m^3-day and the batch studies. However, the methane content of the biogas was similar (50%). As the OLR was increased from 2.5 – 5.0 kgVS/m^3.day-added, marginal decrease in specific biogas yield was observed. The decrease in biogas yield with increasing OLR could be predicted with a linear regression equation (Equation 5.1) with a coefficient of linear regression (R^2) of 0.8472.

$$Y = -20.205x + 333.25 \qquad 5.1$$

Where Y is the biogas yield, and X is the OLR

This notwithstanding, the biomethane content remained relatively constant (50%) except at OLR of 4.0 and 4.5 kgVS/m^3-day where a marginal increase in biomethane content to 52% was observed.

Similarly, the specific biogas yield for cashew peduncle and cashew bagasse in semi-continuous mode differed with the result obtained during the bench-scale studies. Substantial increase in specific biogas yield was observed when compared with the results obtained with the 500 ml Ankom bottles. For instance, at OLR of 2.5 kgVS/m^3-day, the specific biogas yield for cashew bagasse and cashew peduncle increased by 36.11 and 22.6% respectively. This as explained earlier could be due to the source of the inoculum as different inocula were used in both cases. In comparison with the large reactor (30 l) study, a decrease in specific biogas yield was observed. The specific biogas yield decreased by about 13% and 19% respectively. However, in both cases, the reduction in biogas yield could not be easily predicted with a regression model, unlike cocoa pods. The specific biomethane yields were also similar in both cases.

The reduction in specific biogas and biomethane yields for all the three residues as OLR was increased could be attributed directly to the hydraulic retention time that stayed constant as OLR was increased. This is consistent with literature that an increase in the organic loading rate at the expense of hydraulic retention time leads to a reduction in gas output.

5.3 Hydrothermal carbonization

5.3.1 Yield of hydrochar

The trend of decreasing yield at higher process severity observed in the result was generally expected. This could be because an increase in process temperature first of all acts to quickly dry up the moisture entrained in the cell wall of the substrate and catalyze solubilization of the hemicellulose component between 180-200 ºC and cellulose at a higher temperature above 200 ºC. Even though higher temperatures up to 240 may not be able to solubilize the lignin component, the softening of the lignin components aids the solubilization of the hemicellulose and cellulose component leading to higher solubilization. Thus, at higher process temperatures, increased solubilization as a result of increased hydrolysis is expected. Subsequently, dehydration and increase in residence time led to the carbonization reaction where multiple simultaneous reactions (decarboxylation, condensation polymerization, and aromatization) take place to modify the mainly C-H-O chemical bonds to become C-H at higher temperature thus reducing the molecular weight of the char. Similar results of decreasing yield as a result of temperature and reaction time increase were obtained by Danso-Boateng et al. [218], Donar et al. [91] and Saqib et al. [181] who worked on hydrothermal carbonization of fecal sludge, hazel nutshells, and olive residues and food waste respectively. This notwithstanding, the correlation between the process severity and the yield response factor was weak. This could be because due to the effect heating rate has on the whole process. For instance, at process severity of 6.55 attained with a temperature of 240 ºC and 4.5 hrs but at different heating rates of 10 K/min and 2 K/min resulted in hydrochar yields of 28 and 40% respectively. A higher heating rate affected the yield of the hydrochar due probably to the increased hydrolysis during the heating phase of the reaction. The rapid temperature increase has been reported to aid the hydrolysis of cellulose and hemicellulose through the softening of the lignin. This is evident from the model equation of the response factor for the cashew peduncle. Apart from process temperature and heating rate, the 2nd order polynomial function (Equation 5.5) also depends on the heating rate and is also seen to have multiple interactions with process temperature although the predictions were not significant. However, the high R^2 value of the model equation makes the model equation reliable in predicting the response factor. Contrary to results obtained for the cashew peduncle, the linear function (Equation 5.4) obtained for the response factor for cocoa pods could not be relied upon. This is due to the low R^2 value which is less than 0.8. The significant interaction between process temperature and reaction time of both cocoa pods and cashew peduncle hydrochar yield supports the general theory.

5.3.2 Higher heating value

The strong linear correlation between the HHV response factors for both cocoa pods and cashew peduncle hydrochar and the process severity was expected and did not deviate from the general theory. Higher process severity as a result of higher process temperature and longer reaction time has been reported to have a direct effect on the heating value of the hydrochar. This is supported by the theory that higher process severity results in the polymerization and aromatization reaction which leads to the C-H-O bonds becoming C-H bonds. The expulsion of the oxygen molecule from the C-H-O bonding does not only lead to the loss of molecular weight, but it also leads to a relatively higher heating value. Further the enrichment of carbon due to the migration of oxygen and hydrogen molecules into the liquid phase as reported by Basso et al. [219], potentially also increases the higher heating value of the hydrochars. Result of the higher heating value of the cocoa pods and cashew peduncle residues were in agreement with results reported by other researchers such as Kim et al. [87], who reported increasing higher heating values for hydrochars from pure hemicellulose, cellulose, and lignin with increasing process temperature. Similar results of increasing HHV at higher treatment severity were also reported by Basso et al. [101,219], working on organic municipal waste and Grape marc agricultural residues respectively and Zhang et al. [220], working on fruit waste.

5.3.3 Ash content

The ash content of the hydrochar is an important fuel property which indicates the amount of slag which is expected after combustion. The result of the ash content of cocoa pods and cashew peduncle hydrochars was anomalous to some reported literature. Generally, the ash content of the hydrochar is expected to increase with increased process severity as a result of the increased hydrolysis of cellulose and hemicellulose leading to a higher concentration of the minerals in the resulting hydrochar [101,219]. However, the result obtained showed a negative linear correlation between the ash content and process severity. Thus, an increase in process severity for both substrate (cocoa pods and cashew peduncle) resulted in lower ash content. This could be explained by the fact that the pH of the hydrolysate after the carbonization process was acidic in the range of 3.50 – 4.84 (Appendix B, Table B-3 and Table B-4). An increase in process severity resulted in lower pH values which could be due to the formation of volatile fatty acids due to the increased hydrolysis of the feedstock. Further, at the start of the carbonization processes, the measured pH of the substrates inside the reactor after the addition of the process water were all found to be in the acidic region. It is thus hypothesized that the acidic medium before, during, and after (cooling) the reaction phase could have resulted in leaching of some of the minerals into the liquid phase. This hypothesis is supported by the fact that an acidic medium in the range of (3.5 – 8.0) has been reported to aid the leaching of phosphorus from solid-phase fecal matter into the hydrolysate. Lievens et al. [221], also reported the reduced leaching rate with an increase in the pH of the solvent. Further, the successful leaching of potassium into the liquid phase of water at room temperature has been reported by Afrane [49], who used water at room temperature to leach out 92.73%, 7.13% and 0.14% respectfully of potassium, calcium and sodium ions from cocoa pods ash. Thus, the combined effect of low pH of the hydrolysate and water as a solvent could account for the leaching of the minerals into the liquid phase especially after the carbonization which resulted in lower ash content of the hydrochar.

5.3.4 Chemical oxygen demand (COD) of hydrolysate

The COD which is a measure of the amount of oxygen required to chemically oxidize organic and inorganic compounds is a particularly important indicator of the safety level of wastewater discharged into the biosphere. A high COD level is an indicator that the wastewater must be further treated before discharge. The measured COD levels of the hydrolysate varied 25.19 – 45.25 g/l for cashew peduncle HTC hydrolysate and 22.67 – 34.97 g/l for cocoa pods HTC hydrolysate. The COD of the hydrolysate of both cocoa pods and cashew peduncles were found to be variable with no clear trend. This variability in the COD of the hydrolysate is corroborated by Basso [222], who also reported variable TOC results when he investigated the hydrolysate from HTC of grape marc, grape skin and grape seeds. This is partly due to the high level of reactivity of some of the intermediates formed in the liquid phase which could result in the formation of gaseous compounds. This notwithstanding, a marginal increase in COD levels of cocoa pods HTC hydrolysate with respect to increasing the process temperature was observed which was similar to the results obtained by Danso-Boateng et al. [218]. A similar result of increasing COD with increasing process temperature was obtained by Mäkelä et al. [223] when they investigated the process water qualities after HTC of chemical sludge from pulp and board mill. This was however different for the cashew peduncles, where a general decrease in COD levels was observed. The marginal increase in COD levels of cocoa pods HTC hydrolysate could be due to increased leachate of the inorganic compounds from the solid phase hydrochar into the liquid phase as explained earlier in section 5.3.3. This undoubtedly will increase the COD of the hydrolysate. This is not the case with the COD of the cashew peduncle hydrolysate. The generally negative correlation between process severity and the COD of the hydrolysate partially agreed with the results obtained by Basso [222], decreasing TOC at 180 ºC and varying reaction time for grape marc seeds and grape marc whole fruit. The high COD at low process severity for the cashew peduncle could be due to the low level of carbonization at low process severity such that limited hydrolysis has taken place especially with the hemicellulose fraction leading to increased dissolved organic compounds in the liquid phase. This is consistent with the theory that the low carbonization takes place at low process severity characterized by especially short reaction time. As the process severity increases, multiple reactions leading to carbon densification as well as the formation of gaseous compounds is expected to rob the liquid phase of some of the intermediates leading to lower COD. Further, the low amount of the minerals in the cashew peduncle as compared to cocoa pods could explain the reason behind the marked difference in the COD levels of their respective hydrolysate. As pointed out in section 4.19, cocoa pods had significantly higher quantities of major and minor minerals thus any effect of leaching is expected to be more prominent in cocoa pods than in the cashew peduncle.

6. Conclusion and recommendations

6.1 Local and regional Impact of study on access to electricity

Cocoa beans export is the mainstay of two of West Africa's largest economies – Ghana and Cote d'Ivoire, accounting for a significant fraction of their Gross Domestic Product (GDP), and in the process providing employment for many people. Lately, cashew nut cultivation and export have in both countries seen an upsurge, driven by the high demand for the nuts on the international market. From all indications, the cultivation of cocoa beans and cashew nut will continue to increase in response to strong demand for natural confectionery products, food, and cosmetic products in general. Due to this, cocoa pods and cashew peduncles will most likely see an increase in its generation leading to serious consequential effects such as an increase in their greenhouse emission potential [175]. Using the same methodology as described under section 3.14, emissions from untreated cocoa pods could reach about 6,000 kt $CO_{2eq.}$ and 30,000 kt $CO_{2eq.}$ by 2030 in Nigeria and Cote d'Ivoire, respectively. Similarly, Ghana's emission from cocoa pods could reach about 15,100 kt $CO_{2eq.}$ by the same year if left untreated. Ironically, access to modern fuels for cooking in Ghana and Cote d'Ivoire as of 2016 according to the World Bank open-source data was 21.71% and 18.23% respectively. This means many people in both countries do not have access to modern fuels to meet their domestic fuel needs. This could explain in part the high annual deforestation rate in Ghana (2%) and Cote d'Ivoire (3%) which are driven primarily by the direct or indirect use of woodfuels as a major source of fuel in these countries. The continuous expansion of agricultural lands could also be a leading course of deforestation in both countries.

Further, access to electricity is a major challenge in the sub-region. Even though Ghana has an impressive high population with access to electricity (86%) as of 2018, a third of the rural population in Ghana do not have access to electricity (Worldbank data). The situation in Cote d'Ivoire is even worse. Close to 2/3rd (64%) of the rural population do not have access to electricity. Given the nexus between access to modern energy and access to electricity in attaining most of the sustainable development goals, action must be taken towards ensuring the rural population in these countries have access to modern fuels for cooking and access to electricity.

Results of the anaerobic digestion of cocoa pods and cashew peduncle residues present a bright opportunity in harnessing modern, clean, and sustainable energy for utilization at the national level or in rural communities in the Sub-region. Using the results obtained for the continuous mono-digestion of the cocoa pods and cashew peduncle residues at OLR of 2.5 $kgVS/m^3$-day and the resource assessment the electricity generation potential of cocoa pods and cashew peduncle residues is estimated for four countries in West Africa where cocoa and cashew are cultivated (Table 6.1) based on the following assumptions;

1. The regional climate conditions and crop yield are similar thus the calculated RCR could apply to the countries cultivating cocoa and cashew
2. Similar cultivars of Theobroma cacao and cashew Anacardium occidentale species are cultivated in the Sub-region.

The energetic potential is calculated based on the heating value of biogas with 50% methane content (6 kWh/m^3) [224] using Equation 6.1

$$E = \sum_{i}^{n} M_i \, y_i H_i \eta \qquad (6.1)$$

Where M is the resource potential of residue (kgVS), y is the biogas yield, and H is the heating value of the biogas with 50% methane content and i is the type of crop residue and ŋ is the electrical conversion efficiency (0.3) for biogas.

The impact of using cocoa pods and cashew peduncle as a substrate for biogas production is significant in Ghana and Cote d'Ivoire than in Nigeria and Cameroun. About a quarter (26%) of the rural population in Ghana without access to electricity can be potentially fed with electricity from biogas generated from only cocoa pods and cashew peduncles. This is significant in many respects. Firstly, the decentralized nature of cocoa beans and cashew nut cultivation means that isolated grid systems can be set up in hard to reach or remote communities without access to electricity. Further, any increase in access to electricity in rural communities will also impact on access to electricity at the national level. Thus, the attainment of universal access to electricity in Ghana can be achieved. Meanwhile, Cote d'Ivoire is seen to have the largest impact due to high production figures of cocoa beans and cashew nuts. The power generated from the cocoa pods and cashew peduncles can potentially meet the per capital power needs of about 44% of the rural population without access to electricity in Cote d'Ivoire. Nigeria and Cameroun have the least impact due in part to the low production of cocoa beans and cashew nuts and by extension cocoa pods and cashew peduncles and the significantly higher population of Nigeria. However, given the low per capita consumption of electricity in Nigeria, about 2 million people could be potentially impacted when cocoa pods and cashew peduncle residues are utilized.

In the alternative scenario of using all the technical resource potential of cocoa pods and cashew peduncle residues to produce hydrochar, the impact on access to electricity in rural communities does not change much in all three countries when compared with biogas. The potential of hydrochars to replace charcoal as an alternative domestic fuel was evaluated. As shown in Table 6.1, about 24% of the charcoal produced in Ghana annually can be replaced with hydrochars from cocoa pods and cashew peduncle residues. This is important for two reasons. Firstly, given that the conversion factor of fuelwood to charcoal is about 5:1 (Energy Commission, 2019), the potential savings of forestry product's use in charcoal production is 5 folds. Secondly, the potential emissions savings will be double in that the saved forest will act as a buffer for carbon sequestration, even as the utilization of the residues also saves carbon dioxide emissions arising from the untreated residues. Cote d'Ivoire has the greatest impact where the annual production of charcoal could be entirely substituted with hydrochar from cocoa pods and cashew peduncles. Even though the impact of charcoal substitution is marginal in Nigeria, the other benefit of reducing greenhouse gas emissions should at least serve as a driving force.

Table 6. 1: Impact of energetically valorizing cocoa pods and cashew peduncle residues in Ghana, Nigeria, and Cameroun (Data from world bank open-source and FAOstat).

	unit	Ghana	Cote d'Ivoire	Nigeria	Cameroun
Average (2008 – 2018) cocoa beans production	t	805,061	1,581,714	350,728	269,136
Average (2008 – 2018) cashew nuts production	t	49,151	519,844	356,858	-
per capita electricity consumption	kWh	351	276	144	280
Rural population, 2018	%	43.94%	49.22%	50%	43.63%
Total population, 2019		29,767,000	25,069,000	130,000,000	25,216,000
Rural population without access to electricity, 2017	%	33%	63%	78%	79%
Biogas potential of cocoa pods	m^3/a	206,368,582	405,455,083	96,672,351	68,990,070
Biogas potential of cashew peduncle	m^3/a	12,252,856	129,591,946	88,961,155	-
Electricity generation potential of cocoa pods and cashew peduncle	kWh/a	393,518,588	963,084,652	334,140,311	124,182,126
Potential population that could be impacted		1,121,136	3,489,437	2,320,419	443,508
Actual population without access to electricity		4,316,274	7,773,545	76,390,860	8,691,375
Impact on the population without access to electricity	%	26	45	3	5
Impact of using cocoa pods and cashew peduncle residues to produce hydrochar					
Hydrochar potential of cocoa pods	t/a	288,776	567,362	125,806	96,539
hydrochar potential of cashew peduncle	t/a	10,206	107,948	72,830	0
Electricity generation potential of cocoa pods and cashew peduncle (kWh)	kWh	385,746,047	866,204,594	252,329,612	124,751,766
Potential population that could be impacted		1,098,992	3,138,422	1,752,289	445,542
Actual population without access to electricity		4,316,274	7,773,545	76,390,860	8,691,375
Impact on the population without access to electricity	%	25	40	2	5
Total hydrochar potential	kt	299	675	199	97
charcoal consumption in 2018	kt	1265	488	4,550	503
potential charcoal substitution	%	24	138	4	19

6.2 Prospects of setting up a bioenergy production facility in Ghana

Several government of Ghana's policy instruments are replete with renewable energy production specific strategies and targets. The target as pointed out under section 2.1 of this thesis were driven in part by the lack of adequate capacity to produce electricity in the recent past and greenhouse gas emission abatement. The success of achieving the targets was hinged on the passage of the renewable energy law which brought into effect the feed-in tariff (Act 832). Apart from mandating the public utility regulatory commission to fix the feed-in tariff, the law also mandated the purchase of electricity from renewable energy sources by both the generation and distribution companies. The passing of the renewable energy law and the fixing of the feed-in tariff generated some initial excitement in the renewable energy space leading a lot of prospective renewable energy companies to sign power purchasing agreement with government. The excitement generated did not live up to expectation as the hard reality of the solvency of the generating and distribution companies were called into serious question. The state organizations in charge of generation and distribution were saddled with huge debt, thus calling into question their ability and capacity to pay. Several of the project are therefore still on the drawing board failing to take off. As a result, the achievement of the government targets have been called into serious question. Further, because of overcapacity in the electricity generation space currently forcing government of Ghana to issue a caveat on the issuance of new power purchasing agreement (PPA) means new projects in renewable energy may be difficult to take off in the immediate future. However, in issuing the caveat, government made a special case for waste to energy project. This means bioenergy projects such as the conversion of cocoa pods and or cashew bagasse into biogas or hydrochar could be considered and benefit from the feed-in tariff of 18.45/kWh (US cent). In addressing some of the key challenges of signing individual PPAs, government since 2020 has reverted to the subjecting all future PPAs to competitive bidding. In a situation like that, procurement notice for power blocs with special blocks for specific renewable energy technologies will be issued. The lowest bidder providing the lowest levelized cost of electricity generation will be selected.

In the specific instance of using cocoa pods and cashew residues as feedstock for a bioenergy production facility, the business model must be comprehensive to make it attractive. Depending on only the sales of power as the only revenue stream may not be attractive enough considering the huge investment cost needed to setup the plant. The levelized cost of electricity (LCOE) generated from biogas from cocoa pods and cashew peduncle in Ghana was determined using Equation 6.2 [225].

$$\mathrm{LCOE} = \left[\frac{\mathrm{I} + \sum_{t=1}^{n} \frac{\mathrm{M}}{(1+r)^{t}}}{\sum_{t=1}^{n} \frac{\mathrm{E}}{(1+r)^{t}}}\right] \tag{6.2}$$

Where LCOE is the levelized cost of electricity generation, GHS (Euro); I = fixed capital investment (Euro); M is the operation and maintenance cost (Euro); E is the Electricity generation rate (MWh); r is the discount rate, % per annum; n is the life of the plant, years.

In calculating the LCOE, the following assumptions were made.

1. In the absence of reference figures for utility scale biogas plant investment cost and annual operation and maintenance cost, German industry reference figures were used [225].

2. The exchange rate between the Euro and Ghana cedis was fixed at 1 Euro = 6.460 GHS as of 05.06.2020[2]
3. Bank of Ghana discount rate of 14% per annum was used.
4. A biogas plant is expected to last for about 30 years.
5. The plant capacity factor was fixed at 80%[3]
6. Grid emission factor of 0.46 in 2018 [5].
7. Revenue from sales of process heat and organic fertilizer are not considered.
8. Cost of feedstock was negligible.
9. Cost of transportation of feedstock was not considered.

Table 6.2: parameters used to determine the LCOE.

Parameter	Unit	Scenario 1	Scenario 2
Plant capacity	kW	1000	1000
CAPEX for biogas plant	GHS/kWh	26,000	26,000
Life of biogas plant	Years	30	30
Share of dept	%	100	80
Discount rate	%	30	30
OPEX for biogas plant	GHS/kWh	1,043.84	1,043.84
Share of equity	%	0	20
Expenditure on fuel	GHS/kg	0	0
LCOE	GHS/kWh	0.6753	0.5700
LCOE	Euro/kWh	0.1045	0.0882

In comparison with the prevailing cost of electricity in Ghana, the levelized cost of generating electricity from cocoa pods and cashew peduncle residues was about 100% above the current lifeline tariff. However, the cost was lower than the tariff for non-residential and the current feed-in tariff for bioenergy technologies (Table 6.3). This means even if the government finds it expensive to buy electricity generated from cocoa pods and cashew peduncle because of the peculiar situation of having a lot of residential users in the lifeline tariff consumption zone, private industry players may find it attractive to invest in it.

---

[2] https://www1.oanda.com/currency/converter/.

[3]

Table 6.3: Comparison between LCOE and tariff structure in Ghana.

	Power consumption	Amount (GHC/kWh)
LCOE cocoa pods and cashew peduncle power plant		0.6758
2019 lifeline tariff for residential consumers [226]	0 – 50 kWh/month	0.3078
2019 Non-residential [226]	0 – 300 kWh/month	0.7532
2019 Non-residential tariff [226]	301 – 600 kWh/month	0.8014
2016 feed-in tariff [227]		0.9667

Additional revenue stream apart from the sales of power, heat an organic fertilizer could be the sales of carbon emission credits. Emission reduction due to generating power from renewable energy sources could amount to about GHC 180,000 per annum. Sales of avoided emission from the treatment of cocoa pods and cashew residues could also amount to about 6 million Ghana cedis. When these are factored into a full feasibility study, it is likely to affect the profitability and sensitivity matrix leading to a more a successful project.

6.3 Conclusion

Cocoa pods and cashew peduncle residues generated in Ghana were investigated for the bioenergy energy production potential. The assessment took into consideration the resource potential of the residues. The result of the resource assessment study led to the following conclusions.

1. The recalculated RCR values of 9.3 (wet basis) and 2.5 (dry basis) resulted in a theoretical resource potential of about 7.2 x 10^6 t/a and 1.945 x 10^6 t/a of cocoa pods respectively. This represents a 250% increase over the previously reported estimate and a 60% increase in resource potential over the estimates by the Food and Agricultural Organization.
2. The RCR of cashew peduncle residues which had not been previously estimated resulted in an estimated RCR of 6.04 on a wet basis and 1.5 on an air-dried basis. The corresponding theoretical potential based on the current cashew nut production level in Ghana was estimated as 0.226 x 10^6 t/a (wet basis) and 0.075 x 10^6 t/a (dry basis). However due to competing demands for the resources locally and the possibility of recovering the biomass from the farm, the technical potential for cocoa pods was estimated to be about 3.564 x 10^6 t/a (wet basis). The technical potential of the cashew peduncle was estimated to be about 0.1017 x 10^6 t/a (wet basis).
3. The geographical spread of the resources, especially cocoa pods, was estimated on a regional basis and with the highest potential resources concentrated in the former Western, Ashanti, and former Brong Ahafo regions in order of magnitude, respectively. Due to the lack of regional segregated data on regional cashew production levels, the geographical spread of the cashew peduncle generation could not be readily assessed. This notwithstanding the map of cashew growing areas in Ghana suggest that the bulk of cashew residues could be in the former Brong Ahafo region of Ghana.

4. The combined effect of the resource potential and geographical spread of the residues point to some potential hotspots for the establishment of a bioenergy production facility. This means any potential bioenergy production facility with the intension of using cocoa and cashew residues as potential feedstock may consider siting the plant in either the Western Region were cocoa pods residues abound, or in the former Brong Ahafo Region where there is a high possibility of getting both residues.

The energetic pathways to produce bioenergy from cocoa pods and cashew residues were investigated. The selection of the pathways was heavily influenced by the physical and chemical characteristics of the cocoa pods and cashew peduncle residues. The high moisture content of the cocoa pods and cashew residues meant direct thermal combustion was not going to be a good option. Further analysis of the mineral content also showed the possibility of high quantities of slag and the added possibility of the slag being alkaline, in the case of cocoa pods due to the high presence of potassium which converts to potassium carbonate during combustion. The result of the physical and chemical characteristics thus served as a guide to reject the direct combustion of the residues. The choice of conversion pathways was also dependent on the possibility of utilizing the results in a developing country contest since this type of residues is generally found in developing countries. Thus, overly high-tech technologies were rejected. This resulted in the choice of anaerobic and subcritical hydrothermal carbonization pathways.

Based on the result of the anaerobic digestion study, the following conclusions can be drawn.

1. Cocoa pods and cashew peduncle are good substrates for anaerobic digestion albeit with notable difference in the biogas yield and process stability. The results showed that the digestion of cocoa pods was still possible despite the high C/N ratio without any significant inhibition. This notwithstanding, the lignin content of the cocoa pods especially limited the biodegradability and subsequently the biogas yield of the cocoa pods.
2. The kinetic data were found to fit both the modified Gompertz kinetic model and the dual-pool 2-step kinetic model with the latter having a better fit. The result of the bench-scale study (500 ml) was further confirmed by the result in a much larger reactor (30 l). Thus, the kinetic parameters established using the bench-scale apparatus could be directly applied to the model the digestion process is much bigger reactors. On the contrary, the biogas yield of cashew peduncle residues in its raw state and the fibers of the cashew peduncle (bagasse) differed under different experimental conditions. The biodegradability index in both cases significantly increased when a much larger digester (30 l) was used. Even though the dual pool 2-step model fitted the kinetic data better than the modified Gompertz model, using the model to predict the gas yield in the larger reactor was not possible due to the significant increase in biogas yield. This anomaly could be due to better adaptation of the methanogenic bacteria in the larger reactor or susceptibility of cashew peduncle residues to the change in the inoculum. Therefore, the kinetic parameters established using the bench-scale apparatus were of no significance and cannot be relied on for any design purpose.
3. The enhanced biodegradability of cashew peduncle residues in a larger reactor meant that pretreatment of the residues was not necessary since the main effect of pretreatment is to increase the biogas yield

4. The biogas yield of cocoa pods could be enhanced using hydrothermal process under mild process severity. Lower temperature and shorter retention/reaction time could be used to soften the lignin component of the lignocellulosic structure of the biomass leading to the hydrolysis of the hemicellulose and cellulose which would have otherwise been bound in the structural carbohydrate. The studies further confirmed the inhibitory potential of pretreating biomass at harsh process conditions characterized by higher heating temperature and longer retention time. The reported failure of the anaerobic digestion process after pretreatment of cocoa pods at higher process severity in this thesis confirmed earlier reports by other authors. The optimum process condition found to enhance the biogas yield was process temperature of 150 ºC and treatment 15 minutes resulting in a biogas yield of 526 l(N)/kgVS which represents 57% of the theoretical yield and an 47% increase over the biogas yield of the untreated cocoa pods. Using the lignin content of the pretreated samples and the cumulative specific biogas yield as response factors, two regression models were developed. The linear regression model (Equation 4.14) which was developed can be used to predict the lignin content of cocoa pods pretreated under hydrothermal conditions, while the quadratic model (Equation 4.15) can also be used to predict the biogas yield of the pretreated cocoa pods substrates under hydrothermal conditions.
5. The result of the semi-continuous studies in mono digestion mode of the individual substrate showed that while cocoa pods could be digested as a mono substrate at an organic loading rate up till 5 kgVS/m^3.day without any process inhibition, the same cannot be said of cashew peduncle. The digestion of cashew peduncle residues was strongly influenced by the hydrolysis constant. Thus, at higher OLR above 3.0 kgVS/m^3.day, the anaerobic digestion process could not be sustained resulting in serious process inhibition which led to a cessation of biogas production. On the contrary, the bagasse of the cashew peduncle could be digested above an OLR of 4.0 kgVS/m3.day.
6. Notable reductions in specific biogas yield of the bench-scale studies, large scale digester (30 l) and the semi-continuous studies were observed in the case of cocoa pods residues at OLR of 2.5 kgVS/m^3.day. Further reduction in biogas yield was observed when the OLR was increased from 2.5 – 5.0 kgVS/m^3.day and this could be predicted with linear regression equation (Equation 4.16). On the contrary, while an increase in the biogas yield of cashew peduncle and cashew bagasse was observed between the semi-continuous studies and the bench-scale experiments, a reduction in biogas yield was observed between results of the larger reactor and the semi-continuous reactor. The methane content was found to be similar in all cases.
7. The suitability of cocoa pods and cashew peduncle residues as co-substrates for maize silage digestion studies confirmed that while cashew peduncle could serve as a promoter of biogas yield, the promotional effect was dependent on the feed composition. In other words, the fraction of the cashew peduncle in the feed composition was important to obtain a significant increase in biogas yield. On the contrary, even though no significant change in biogas yield was observed, cocoa pods residues could serve as an important source of insitu mineralization of the digestion process resulting in no need for external mineral supplementation.

Similarly, the following conclusions can be drawn from the results of the hydrothermal carbonization study.

1. Result of the hydrothermal carbonization study shows that cocoa pods and cashew peduncle residues can be successfully carbonized into solid fuels.
2. The carbonization of the cocoa pods and cashew residues were heavily affected by the process conditions. The effect of three process parameters studied and the characteristics of the hydrochar produced showed varied response to changing process parameters. Additionally, the interactive effect of the process parameters on selected process response variables differed among the selected process variables and differed between the substrates (cocoa pods and cashew peduncle).
3. While the yield of the hydrochar from cocoa pods correlated linearly with the process temperature and reaction time, the yield of hydrochar from the cashew peduncle could be correlated with a quadratic model. Further, while the heating rate did not influence the yield of cocoa pods hydrochar, the heating rate was found to not only influence the yield of cashew peduncle hydrochar but also involved in multiple interactive effects with both the process temperature and reaction time. Thus, the effect of heating rate cannot be ignored in predicting the yield of hydrochar from the cashew peduncle.
4. The carbonized cocoa pods and cashew peduncle residues resulted in generally increased higher heating values when compared to the higher heating of the untreated substrates. While the higher heating value response factor correlated positively with the process temperature and reaction time in the case of both substrates, the heating rate was found to influence the higher heating value response factor in the cocoa pods. Additionally, no interactive effect was observed between the process parameters in the case of the cashew peduncle. However, in the case of cocoa pods, a significant interactive effect was found between process temperature and heating rate.
5. The ash content of the hydrochar reduced with increasing process severity. Further, the ash content of the hydrochar can be modeled by a linear equation in both cases. The effect of heating rate was minimal in both cases and thus was not factored into any of the resulting equations. Additionally, the interactive effect between the process temperature and reaction time was insignificant.
6. In both cases, the dependence of the COD of the hydrolysate and the severity of treatment were weak. However, both model equations can adequately predict the COD of their respective hydrolysate. The interactive effect of the process temperature and the heating rate for both models pointed to significantly different predictions.
7. Different optimum operating conditions were obtained for cocoa pods and cashew peduncle residues. Optimum operating conditions for the production of hydrochar from cashew peduncle were a temperature of 240 ºC, heating rate of 2.26 K/min, and reaction time of 7 hrs. On the other hand, the optimum operating conditions for cocoa pods were temperature of 240 ºC, heating rate of 9.16 K/min, and reaction time of 6.3 hrs.

6.4.2 Recommendations

Based on the results obtained from the investigation carried out and the limitations of the study, the following are recommendations for further research.

1. Time and resource constraints could not allow the study of the synergetic effect or otherwise of co-digesting cocoa pods and cashew peduncle residues. Semi-continuous co-digestion of cocoa pods and cashew peduncles could be interesting due to the fact that the rapidly digesting cashew peduncle residues could serve as an insitu catalyst to increase the

digestibility of the cocoa pods thus having a promotional effect on the amount of biogas produced. Additionally, the balanced utilization of the VFAs by the cocoa pods could ensure process stability, while the process could also benefit from the insitu mineral content of cocoa pods. The synergetic or antagonistic effect of co-digestion can serve a particularly good design purpose in any future cocoa pods and cashew peduncle residues combined with bioprocess engineering.

2. Continuous mono digestion studies could only be carried to up to 5 kgVS/m^3.day for cocoa pods and 4 kgVS/m^3.day for cashew bagasse. Continuous mono digestion studies especially for cocoa at higher OLR as well as cashew bagasse to determine the failure point will serve good design purpose.
3. Further studies to determine the effect of the hydrothermal pretreatment on continuous digestion assay was severely limited by the size of the hydrothermal process equipment used for the experiments. Using 1 l reactor for the experiment did not offer much in terms of quantities of substrate that could be treated especially for continuous experiments. Using a large reactor could have served a better purpose. Further studies to evaluate the enhanced biogas yield of hydrothermal pretreatment of cocoa pods will inform industrial application of the hydrothermal pretreatment process especially for cocoa pods.
4. To date, not much is known about the effect of particle size on the carbonization of lignocellulosic substrates. The current study could not evaluate the effect of particle size on the fuel properties of the hydrochar. Even though the particle size has been correlated to the degree of hydrolysis in past experiments, its direct effect on hydrochar formation and subsequent characteristic of the fuel is not well investigated.
5. A study using 100 l pilot-scale batch hydrothermal process was planned. However, resource constraints did not that that possible within the life of this study. Results of pilot studies on hydrothermal carbonization are scarce in literature. Besides, in moving from laboratory scale to industrial scale, results of pilot scale studies are needed to validate laboratory/bench-scale results and inform critical design parameters. It will therefore be interesting to validate the results of the bench-scale studies carried on cocoa pods and cashew peduncle residues. Further studies on semi-continuous hydrothermal carbonization studies will go further to inform the choice of critical design parameters.

References

[1] B. Kummamuru, WBA Global Bioenergy Statistics 2018, World Bioenergy Assoc. (2018) 43. https://doi.org/10.1016/0165-232X(80)90063-4.

[2] IRENA, Global Bioenergy supply and demand projections. A working paper for REmap 2030, GCB Bioenergy. 5 (2014) 88. https://doi.org/10.1111/j.1757-1707.2012.01207.x.

[3] International Energy Agency, Africa Energy Outlook 2019 World Energy Outlook Special Report, (2019) 288. www.iea.org/t&c/.

[4] F.S. Fabiani Appavou, Adam Brown, Bärbel Epp, Duncan Gibb, Bozhil Kondev, Angus McCrone, Hannah E. Murdock, Evan Musolino, Lea Ranalder, Janet L. Sawin, Kristin Seyboth, Jonathan Skeen, REN21 - 2019 Global Status Report, 2019. https://wedocs.unep.org/bitstream/handle/20.500.11822/28496/REN2019.pdf?sequence=1&isAllowed=y%0Ahttp://www.ren21.net/cities/wp-content/uploads/2019/05/REC-GSR-Low-Res.pdf.

[5] Energy Commission, National Energy Statistics: 2009 - 2018, Accra, 2019. http://energycom.gov.gh/files/Energy Statistics_2015Final_1.pdf.

[6] Ministry of Environment Science Technology and Innovation, Environmental Protection Agency, Ghana ’ s Second Biennial Update Report, (2018).

[7] Energy Commission, Energy Demand Projections for the Economy of Ghana, 2019.

[8] IEA, Sustainable Production of Second-Generation Biofuels, 2010.

[9] E. Allen, D.M. Wall, C. Herrmann, J.D. Murphy, A detailed assessment of resource of biomethane from fi rst , second and third generation substrates, Renew. Energy. 87 (2016) 656–665. https://doi.org/10.1016/j.renene.2015.10.060.

[10] N.S. Bentsen, P. Lamers, C. Lalonde, M. Wellisch, V.H. Dale, I. Bonner, J. Jacobson, I. Stupak, J. Gan, P. Girouard, Mobilisation of agricultural residues for bioenergy and higher value bio-products: Resources, barriers and sustainability. (IEA Bioenergy), (2017) 1–125.

[11] C. Heidecke, H. Montgomery, H. Stalb, L. Wollenberg, International Conference on Agricultural GHG Emissions and Food Security - Connecting research to policy and practice, Berlin, 2018.

[12] P. Bhattacharyya, D. Barman, Crop Residue Management and Greenhouse Gases Emissions in Tropical Rice Lands, Elsevier Inc., 2018. https://doi.org/10.1016/B978-0-12-812128-3.00021-5.

[13] GSS, Statistics for Development and Progress Gross Domestic Product 2014, 2014.

[14] GSS, Ghana Living Standards Survey Round 6, Accra, 2014.

[15] M.H. Duku, S. Gu, E. Ben Hagan, A comprehensive review of biomass resources and biofuels potential in Ghana, Renew. Sustain. Energy Rev. 15 (2011) 404–415. https://doi.org/10.1016/j.rser.2010.09.033.

[16] M.H. Duku, S. Gu, E. Ben Hagan, Biochar production potential in Ghana — A review, 15 (2011) 3539–3551. https://doi.org/10.1016/j.rser.2011.05.010.

[17] F. Kemausuor, A. Kamp, S.T. Thomsen, E.C. Bensah, H. Stergård, Assessment of biomass residue availability and bioenergy yields in Ghana, Resour. Conserv. Recycl. 86 (2014) 28–37. https://doi.org/10.1016/j.resconrec.2014.01.007.

[18] MoFA, Agriculture in Ghana, facts and figures. Ministry of Food and Agriculture, Statistics, Research and Information Directorate (SRID), Accra, 2016. https://www.agrofood-westafrica.com/fileadmin/user_upload/messen/agrofood-Westafrica/Brochure/AGRICULTURE-IN-GHANA-Facts-and-Figures-2015.pdf%0Ahttp://www.eep.gov.et/index.php?option=com_content&view=article&id=47&Itemid=264&lang=en%0Ahttp://www.agrofood-.

[19] FAO, FAOSTAT_data_1-5-2018, (2018). http://www.fao.org/faostat/en/#data/QC.

[20] C. Huber, I. Knoke, P. Morazán, M.M. Bonn, Strengthening the competitiveness of cocoa production and improving the income of cocoa producers in West and Central Africa, 49 (2016). https://suedwind-institut.de/files/Suedwind/Publikationen/2017/2017-06 Strengthening the competitiveness of cocoa production and improving the income of cocoa producers in West and Central Africa.pdf.

[21] C. Fidelis, B.K.R. Rao, Enriched cocoa pod composts and their fertilizing effects on hybrid cocoa seedlings, Int. J. Recycl. Org. Waste Agric. 6 (2017) 99–106. https://doi.org/10.1007/s40093-017-0156-8.

[22] C. Rabany, N. Rullier, P. Ricau, The African Cashew Sector In 2015, (2015).

[23] I. Das, A. Arora, Post-harvest processing technology for cashew apple e A review, J. Food Eng. 194 (2017) 87–98. https://doi.org/10.1016/j.jfoodeng.2016.09.011.

[24] I. Owiredu, D. Laryea, J. Barimah, Evaluation of cashew nut flour in the production of biscuit, (2014). https://doi.org/10.1108/NFS-06-2013-0067.

[25] P. Moreira, G. Colato, F. Elizabeth, X. Murr, Effect of concentration on the physical properties of cashew juice, 66 (2005) 413–417. https://doi.org/10.1016/j.jfoodeng.2004.04.008.

[26] F. Pinto, D. Abreu, M. Dornier, A. Paula, M. Carail, C. Caris-veyrat, C. Dhuique-mayer, Cashew apple (Anacardium occidentale L .) extract from by-product of juice processing : A focus on carotenoids, Food Chem. 138 (2013) 25–31. https://doi.org/10.1016/j.foodchem.2012.10.028.

[27] E. Gyedu-akoto, Utilization of some cashew by-products, Nutr. Food Sci. Vol. 4 (2011) 393–400. https://doi.org/10.1108/00346651111181949.

[28] ECREEE, Regional potential assessment of novel bio energy crops in fifteen ECOWAS countries, (2012) 25.

[29] J. Aline, J. Edvan, M. Jr, L. Rocha, B. Gonçalves, M. Valderez, P. Rocha, Bioresource Technology Enhanced enzymatic hydrolysis and ethanol production from cashew apple bagasse pretreated with alkaline hydrogen peroxide, Bioresour. Technol. 179 (2015) 249–259. https://doi.org/10.1016/j.biortech.2014.11.010.

[30] M. Syamsiro, H. Saptoadi, B.H. Tambunan, N.A. Pambudi, Energy for Sustainable Development A preliminary study on use of cocoa pod husk as a renewable source of energy in Indonesia, Energy Sustain. Dev. 16 (2012) 74–77. https://doi.org/10.1016/j.esd.2011.10.005.

[31] J.K. Ogunjobi, L. Lajide, The Potential of Cocoa Pods and Plantain Peels as Renewable Sources in Nigeria The Potential of Cocoa Pods and Plantain Peels as Renewable Sources in Nigeria, Int. J. Green Energy. 12 (2016) 440–445. https://doi.org/10.1080/15435075.2013.848403.

[32] S.T. Thomsen, J.E.G. Londoño, J.E. Schmidt, Z. Kádár, Comparison of Different Pretreatment Strategies for Ethanol Production of West African Biomass, Appl. Biochem. Biotechnol. 175 (2015) 2589–2601. https://doi.org/10.1007/s12010-014-1444-7.

[33] D. Maleka, Assessment of the implementation of alternative process technologies for rural heat and power production from cocoa pod husks, Royal Institute of Technology, 2016.
[34] S.T. Thomsen, Z. Kadar, J.E. Schmidt, ScienceDirect Compositional analysis and projected biofuel potentials from common West African agricultural residues, Biomass and Bioenergy. 3 (2014) 1–8. https://doi.org/10.1016/j.biombioe.2014.01.045.
[35] United Nations Economic Commission for Africa, Africa Bioenergy Policy Framework and Guidelines: Towards Harmonizing Sustainable Bioenergy Development in Africa, (2013) 1–15.
[36] K. Stecher, A. Brosowski, D. Thrän, Biomass Potential in Africa, n.d.
[37] Energy Commission, Energy Supply to the Economy: Woodfuels and Renewables, 2006.
[38] Energy Commission, Bioenergy Policy for Ghana, (2010) 1–29.
[39] A. Ahmed, B.B. Campion, A. Gasparatos, Biofuel development in Ghana: policies of expansion and drivers of failure in the jatropha sector, Renew. Sustain. Energy Rev. 70 (2017) 133–149. https://doi.org/10.1016/j.rser.2016.11.216.
[40] I. Nygaard, S. Bolwig, The rise and fall of foreign private investment in the jatropha biofuel value chain in Ghana, Environ. Sci. Policy. 84 (2018) 224–234. https://doi.org/10.1016/j.envsci.2017.08.007.
[41] E. Antwi, E. Cudjoe Bensah, D. Ato Quansah, R. Arthur, J. Ahiekpor, Ghana's biofuels policy: challenges and the way forward, Int. J. Energy Environ. 1 (2010) 805–814. https://doi.org/10.1098/rstb.2010.0134.
[42] F. Kemausuor, M.S. Adaramola, J. Morken, A Review of Commercial Biogas Systems and Lessons for Africa, Energies. 11 (2018) 1–21. https://doi.org/10.3390/en11112984.
[43] C.L. Vriesmann, R.D. de M.C. Amboni, C.L.D.O. Petkowicz, Cacao pod husks (Theobroma cacao L .): Composition and hot-water-soluble pectins, 34 (2011) 1173–1181. https://doi.org/10.1016/j.indcrop.2011.04.004.
[44] S.A. Osei, C.C. Atuahene, D. Heathcote, E.B. Frimpon, Cocoa pod-and-husk meal as a feed ingredient in layer diets, Anim. Feed Sci. Technol. 35 (1991) 283–288.
[45] R.N. Esong, K.A. Etchu, P.H. Bayemi, P.V. Tan, Effects of the dietary replacement of maize with sun-dried cocoa pods on the performance of growing rabbits, (2015) 1411–1416. https://doi.org/10.1007/s11250-015-0879-3.
[46] F. Alemawor, E. Okpoti, K. Oddoye, V.P. Dzogbefia, J.H. Oldham, A. Donkoh, Broiler performance on finisher diets containing different levels of either Pleurotus ostreatus - fermented dried cocoa pod husk or dried cocoa pod husk supplemented with enzymes, (2010) 933–939. https://doi.org/10.1007/s11250-009-9510-9.
[47] J.W. Hertrampf, F. Piedad-Pascual, J.W. Hertrampf, F. Piedad-Pascual, Cocoa-pod Husk Meal, Handb. Ingredients Aquac. Feed. (2000) 100–104. https://doi.org/10.1007/978-94-011-4018-8_10.
[48] C. Ofori-boateng, K.T. Lee, The potential of using cocoa pod husks as green solid base catalysts for the transesterification of soybean oil into biodiesel : Effects of biodiesel on engine performance, 220 (2013) 395–401. https://doi.org/10.1016/j.cej.2013.01.046.
[49] G. Afrane, Leaching of Caustic Potash From Cocoa Husk Ash, 41 (1992) 101–104.
[50] O.E. Taiwo, F.A.O. Osinowo, Evaluation of various agro-wastes for traditional black soap production, 79 (2001) 95–97.
[51] S. Khanahmadi, F. Yusof, O.H. Chyuan, A. Amid, H. Shah, Cocoa pod husk: a new source of CLEA-lipase for preparation of low-cost biodiesel: An optimized process, J. Biotechnol. (2016). https://doi.org/10.1016/j.jbiotec.2016.05.015.

[52] M. Adjin-Tetteh, N. Asiedu, D. Dodoo-Arhin, A. Karam, P.N. Amaniampong, Thermochemical conversion and characterization of cocoa pod husks a potential agricultural waste from Ghana, Ind. Crops Prod. 119 (2018) 304–312. https://doi.org/10.1016/j.indcrop.2018.02.060.

[53] S.O. Dahunsi, C.O. Osueke, T.M.A. Olayanju, A.I. Lawal, Co-digestion of Theobroma cacao (Cocoa) pod husk and poultry manure for energy generation: Effects of pretreatment methods, Bioresour. Technol. 283 (2019) 229–241. https://doi.org/10.1016/j.biortech.2019.03.093.

[54] M. Ward-Doria, J. Arzuaga-Garrido, K.A. Ojeda, E. Sánchez, Production of biogas from acid and alkaline pretreated cocoa pod husk (Theobroma cacao l.), Int. J. ChemTech Res. 9 (2016) 252–260.

[55] A. Donkoh, C.C. Atuahene, B.N. Wilson, D. Adomakob, Chemical composition of cocoa pod husk and its effect on growth and food efficiency in broiler chicks, 35 (1991).

[56] P. Sivagurunathan, S. Sivasankari, S.M. Muthukkarappan, Characterisation of cashew apple (An ac ard iu m o c c id e n tale L .) fruits collected from Ariyalur District ., 1 (2010) 101–107.

[57] J.D. Martínez-Ángel, A. Villamizar-Gallardo, O. Ortíz-Rodríguez, Pod Husk As a Renewable Energy Source, Agrociencia. (2015).

[58] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters, Renew. Sustain. Energy Rev. 57 (2016) 1126–1140. https://doi.org/10.1016/j.rser.2015.12.185.

[59] A. Nzihou, B. Stanmore, N. Lyczko, D.P. Minh, The catalytic effect of inherent and adsorbed metals on the fast/flash pyrolysis of biomass: A review, Energy. 170 (2019) 326–337. https://doi.org/10.1016/j.energy.2018.12.174.

[60] R. Van Poucke, R.W. Nachenius, K.E. Agbo, F. Hensgen, L. Bühle, M. Wachendorf, Y.S. Ok, F.M.G. Tack, W. Prins, F. Ronsse, E. Meers, Bioresource Technology Mild hydrothermal conditioning prior to torrefaction and slow pyrolysis of low-value biomass, (2016). https://doi.org/10.1016/j.biortech.2016.03.014.

[61] B.B. Krishna, B. Biswas, P. Ohri, J. Kumar, R. Singh, T. Bhaskar, Pyrolysis of Cedrus deodara saw mill shavings in hydrogen and nitrogen atmosphere for the production of bio-oil, Renew. Energy. 98 (2016) 238–244. https://doi.org/10.1016/j.renene.2016.02.056.

[62] H.S. Kambo, A. Dutta, A comparative review of biochar and hydrochar in terms of production , physico-chemical properties and applications, Renew. Sustain. Energy Rev. 45 (2015) 359–378. https://doi.org/10.1016/j.rser.2015.01.050.

[63] N. Rakesh, S. Dasappa, A critical assessment of tar generated during biomass gasification - Formation, evaluation, issues and mitigation strategies, Renew. Sustain. Energy Rev. 91 (2018) 1045–1064. https://doi.org/10.1016/j.rser.2018.04.017.

[64] I.L. Motta, N.T. Miranda, R. Maciel Filho, M.R. Wolf Maciel, Biomass gasification in fluidized beds: A review of biomass moisture content and operating pressure effects, Renew. Sustain. Energy Rev. 94 (2018) 998–1023. https://doi.org/10.1016/j.rser.2018.06.042.

[65] S. Safarian, R. Unnþórsson, C. Richter, A review of biomass gasification modelling, Renew. Sustain. Energy Rev. 110 (2019) 378–391. https://doi.org/10.1016/j.rser.2019.05.003.

[66] Y.A. Situmorang, Z. Zhao, A. Yoshida, A. Abudula, G. Guan, Small-scale biomass gasification systems for power generation (<200 kW class): A review, Renew. Sustain. Energy Rev. 117 (2020) 109486. https://doi.org/10.1016/j.rser.2019.109486.

[67] E.R. Widjaya, G. Chen, L. Bowtell, C. Hills, Gasification of non-woody biomass: A literature review, Renew. Sustain. Energy Rev. 89 (2018) 184–193. https://doi.org/10.1016/j.rser.2018.03.023.

[68] P.M. Bondesson, M. Galbe, G. Zacchi, Comparison of energy potentials from combined ethanol and methane production using steam-pretreated corn stover impregnated with acetic acid, Biomass and Bioenergy. 67 (2014) 413–424. https://doi.org/10.1016/j.biombioe.2014.05.025.

[69] L. Wang, C.L. Weller, D.D. Jones, M.A. Hanna, Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production, Biomass and Bioenergy. 32 (2008) 573–581. https://doi.org/10.1016/j.biombioe.2007.12.007.

[70] S.K. Sansaniwal, K. Pal, M.A. Rosen, S.K. Tyagi, Recent advances in the development of biomass gasification technology: A comprehensive review, Renew. Sustain. Energy Rev. 72 (2017) 363–384. https://doi.org/10.1016/j.rser.2017.01.038.

[71] S.K. Sansaniwal, M.A. Rosen, S.K. Tyagi, Global challenges in the sustainable development of biomass gasification: An overview, Renew. Sustain. Energy Rev. 80 (2017) 23–43. https://doi.org/10.1016/j.rser.2017.05.215.

[72] M. Crocker, Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals, Cambridge, 2010.

[73] F. Jin, Application of Hydrothermal Reactions to Biomass Conversion, Springer Berlin Heidelberg, Verlag, 2014.

[74] A. Funke, F. Ziegler, T.U. Berlin, Hydrothermal carbonization of biomass : A summary and discussion of chemical mecha- nisms for process engineering, (2010) 160–177. https://doi.org/10.1002/bbb.

[75] D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, Bioresource Technology Hydrothermal liquefaction of biomass : Developments from batch to continuous process, Bioresour. Technol. (2014). https://doi.org/10.1016/j.biortech.2014.09.132.

[76] E. Steurer, G. Ardissone, Hydrothermal Carbonization and Gasification Technology for Electricity Production using Biomass, Elsevier B.V., 2015. https://doi.org/10.1016/j.egypro.2015.11.473.

[77] T. Wang, Y. Zhai, Y. Zhu, C. Li, G. Zeng, A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties, Renew. Sustain. Energy Rev. 90 (2018) 223–247. https://doi.org/10.1016/j.rser.2018.03.071.

[78] M. Titirici, Hydrothermal Carbonisation : A Sustainable Alternative to Versatile Carbon Materials, Universität Potsdam von, 2012.

[79] D. Wang, F. Shen, G. Yang, Y. Zhang, S. Deng, J. Zhang, Y. Zeng, T. Luo, Z. Mei, Can hydrothermal pretreatment improve anaerobic digestion for biogas from lignocellulosic biomass?, Bioresour. Technol. 249 (2018) 117–124. https://doi.org/10.1016/j.biortech.2017.09.197.

[80] J. Baruah, B.K. Nath, R. Sharma, S. Kumar, R.C. Deka, D.C. Baruah, E. Kalita, Recent trends in the pretreatment of lignocellulosic biomass for value-added products, Front. Energy Res. 6 (2018) 1–19. https://doi.org/10.3389/fenrg.2018.00141.

[81] S. Sun, X. Cao, S. Sun, F. Xu, X. Song, R. Sun, G.L. Jones, Improving the enzymatic hydrolysis of thermo-mechanical fiber from Eucalyptus urophylla by a combination of hydrothermal pretreatment and alkali fractionation, (2014) 1–12.

[82] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschiri, K. Arai, Cellulose hydrolysis in subcritical and supercritical water, J. Supercrit. Fluids. 13 (1998) 261–268. https://doi.org/10.1016/S0896-8446(98)00060-6.

[83] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, Dissolution and hydrolysis of cellulose in subcritical and supercritical water, Ind. Eng. Chem. Res. 39 (2000) 2883–2890. https://doi.org/10.1021/ie990690j.

[84] K. Sheng, S. Zhang, J. Liu, S. E, C. Jin, Z. Xu, X. Zhang, Hydrothermal carbonization of cellulose and xylan into hydrochars and application on glucose isomerization, J. Clean. Prod. 237 (2019) 117831. https://doi.org/10.1016/j.jclepro.2019.117831.

[85] E. Dinjus, A. Kruse, N. Tröger, Hydrothermal carbonization - 1. Influence of lignin in lignocelluloses, Chem. Eng. Technol. 34 (2011) 2037–2043. https://doi.org/10.1002/ceat.201100487.

[86] M. Brebu, C. Vasile, Thermal degradation of lignin - A review, Cellul. Chem. Technol. 44 (2010) 353–363.

[87] D. Kim, K. Lee, K.Y. Park, Upgrading the characteristics of biochar from cellulose, lignin, and xylan for solid biofuel production from biomass by hydrothermal carbonization, J. Ind. Eng. Chem. 42 (2016) 95–100. https://doi.org/10.1016/j.jiec.2016.07.037.

[88] M. Sevilla, A.B. Fuertes, The production of carbon materials by hydrothermal carbonization of cellulose, Carbon N. Y. 47 (2009) 2281–2289. https://doi.org/10.1016/j.carbon.2009.04.026.

[89] A.M. Borrero-López, E. Masson, A. Celzard, V. Fierro, Modelling the reactions of cellulose, hemicellulose and lignin submitted to hydrothermal treatment, Ind. Crops Prod. 124 (2018) 919–930. https://doi.org/10.1016/j.indcrop.2018.08.045.

[90] C. Van Nguyen, D. Lewis, W. Chen, H. Huang, Z. Abdullah, Y. Yamauchi, K.C. Wu, Combined treatments for producing 5-hydroxymethylfurfural (HMF) from lignocellulosic biomass, Catal. Today. 278 (2016) 344–349. https://doi.org/10.1016/j.cattod.2016.03.022.

[91] Y.Os. Donar, E. Caglar, A. Sinag, Preparation and characterization of agricultural waste biomass based hydrochars, 183 (2016) 366–372. https://doi.org/10.1016/j.fuel.2016.06.108.

[92] K. Prapaiwatcharapan, S. Sunphorka, P. Kuchonthara, K. Kangvansaichol, Bioresource Technology Single- and two-step hydrothermal liquefaction of microalgae in a semi-continuous reactor : Effect of the operating parameters, Bioresour. Technol. 191 (2015) 426–432. https://doi.org/10.1016/j.biortech.2015.04.027.

[93] E. Sermyagina, J. Saari, J. Kaikko, E. Vakkilainen, Journal of Analytical and Applied Pyrolysis Hydrothermal carbonization of coniferous biomass : Effect of process parameters on mass and energy yields, J. Anal. Appl. Pyrolysis. 113 (2015) 551–556. https://doi.org/10.1016/j.jaap.2015.03.012.

[94] I. Hwang, H. Aoyama, T. Matsuto, T. Nakagishi, T. Matsuo, Recovery of solid fuel from municipal solid waste by hydrothermal treatment using subcritical water, Waste Manag. 32 (2012) 410–416. https://doi.org/10.1016/j.wasman.2011.10.006.

[95] Y. Lin, X. Ma, X. Peng, Z. Yu, S. Fang, Y. Lin, Y. Fan, Combustion , pyrolysis and char CO 2 -gasification characteristics of hydrothermal carbonization solid fuel from municipal solid wastes, Fuel. 181 (2016) 905–915. https://doi.org/10.1016/j.fuel.2016.05.031.
[96] P. Biller, R.B. Madsen, M. Klemmer, J. Becker, B.B. Iversen, M. Glasius, Bioresource Technology Effect of hydrothermal liquefaction aqueous phase recycling on bio- crude yields and composition, Bioresour. Technol. 220 (2016) 190–199. https://doi.org/10.1016/j.biortech.2016.08.053.
[97] Z. Song, D. Ren, T. Wang, F. Jin, Q. Jiang, Z. Huo, Highly selective hydrothermal production of cyclohexanol from biomass-derived cyclohexanone over Cu powder, Catal. Today. 274 (2016) 94–98. https://doi.org/10.1016/j.cattod.2015.11.016.
[98] H. Rasmussen, K.H. Mogensen, M.D. Jeppesen, H.R. Sørensen, A.S. Meyer, Biomass and Bioenergy 4-Hydroxybenzoic acid from hydrothermal pretreatment of oil palm empty fruit bunches e Its origin and in fl uence on biomass conversion, Biomass and Bioenergy. 93 (2016) 209–216. https://doi.org/10.1016/j.biombioe.2016.07.024.
[99] A. Jain, R. Balasubramanian, M.P. Srinivasan, Production of high surface area mesoporous activated carbons from waste biomass using hydrogen peroxide-mediated hydrothermal treatment for adsorption applications, 273 (2015) 622–629. https://doi.org/10.1016/j.cej.2015.03.111.
[100] M.K. Hrncic, G. Kravanja, Z. Knez, Hydrothermal treatment of biomass for energy and chemicals, (2016) 1–11. https://doi.org/10.1016/j.energy.2016.06.148.
[101] D. Basso, F. Patuzzi, D. Castello, M. Baratieri, E. Cristina, E. Weiss-hortala, L. Fiori, Agro-industrial waste to solid biofuel through hydrothermal carbonization, Waste Manag. 47 (2016) 114–121. https://doi.org/10.1016/j.wasman.2015.05.013.
[102] C. Falco, Sustainable biomass-derived hydrothermal carbons for energy applications, (2012).
[103] D.J. Batstone, J. Keller, I. Angelidaki, S. V Kalyuzhnyi, S.G. Pavlostathis, A. Rozzi, The IWA Anaerobic Digestion Model No 1 (ADM1), Water Sci. Technol. 45 (2002) 65–73.
[104] M. Eiroa, J.C. Costa, M.M. Alves, C. Kennes, M.C. Veiga, Evaluation of the biomethane potential of solid fish waste, Waste Manag. 32 (2012) 1347–1352. https://doi.org/10.1016/j.wasman.2012.03.020.
[105] F. Abouelenien, Y. Namba, M.R. Kosseva, N. Nishio, Y. Nakashimada, Enhancement of methane production from co-digestion of chicken manure with agricultural wastes, Bioresour. Technol. 159 (2014) 80–87. https://doi.org/10.1016/j.biortech.2014.02.050.
[106] M. Koyama, S. Yamamoto, K. Ishikawa, S. Ban, T. Toda, Anaerobic digestion of submerged macrophytes : Chemical composition and anaerobic digestibility, Ecol. Eng. 69 (2014) 304–309. https://doi.org/10.1016/j.ecoleng.2014.05.013.
[107] D. Ulrike, P. Karl-Heinz, G.N. Samira, Biogas in Ghana: Sub-Sector Analysis of Potential and Framework Conditions, (2014) 1–30.
[108] I. Angelidaki, M. Alves, D. Bolzonella, L. Borzacconi, J.L. Campos, A.J. Guwy, S. Kalyuzhnyi, P. Jenicek, J.B. Van Lier, Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays, Water Sci. Technol. 59 (2009) 927–934. https://doi.org/10.2166/wst.2009.040.
[109] T.L. Hansen, J.E. Schmidt, I. Angelidaki, E. Marca, J.L.C. Jansen, H. Mosbæk, T.H. Christensen, Method for determination of methane potentials of solid organic waste, Waste Manag. 24 (2004) 393–400. https://doi.org/10.1016/j.wasman.2003.09.009.

[110] S. Fujishima, T. Miyahara, T. Noike, Effect of moisture content on anaerobic digestion of dewatered sludge: Ammonia inhibition to carbohydrate removal and methane production, Water Sci. Technol. 41 (2000) 119–127. https://doi.org/10.2166/wst.2000.0063.

[111] A.G. Costa, G.C. Pinheiro, F.G.C. Pinheiro, A.B. Dos Santos, S.T. Santaella, R.C. Leit??o, Pretreatment strategies to improve anaerobic biodegradability and methane production potential of the palm oil mesocarp fibre, Chem. Eng. J. 230 (2013) 158–165. https://doi.org/10.1016/j.cej.2013.06.070.

[112] F. Ahmad, E.L. Silva, M.B.A. Varesche, Hydrothermal processing of biomass for anaerobic digestion – A review, Renew. Sustain. Energy Rev. 98 (2018) 108–124. https://doi.org/10.1016/j.rser.2018.09.008.

[113] G. Mancini, S. Papirio, P.N.L. Lens, G. Esposito, Increased biogas production from wheat straw by chemical pretreatments, Renew. Energy. 119 (2018) 608–614. https://doi.org/10.1016/j.renene.2017.12.045.

[114] P. Harmsen, W. Huijgen, L. Bermudez, R. Bakker, Literature review of physical and chemical pretreatment processes for lignocellulosic biomass Paulien, 2010.

[115] A. Chufo, H. Yuan, D. Zou, Y. Pang, X. Li, Bioresource Technology Biomethane production and physicochemical characterization of anaerobically digested teff (Eragrostis tef) straw pretreated by sodium hydroxide, Bioresour. Technol. 181 (2015) 214–219. https://doi.org/10.1016/j.biortech.2015.01.054.

[116] L. Janke, A.F. Leite, K. Batista, W. Silva, M. Nikolausz, M. Nelles, Bioresource Technology Enhancing biogas production from vinasse in sugarcane biorefineries : Effects of urea and trace elements supplementation on process performance and stability, Bioresour. Technol. (2016) 1–11. https://doi.org/10.1016/j.biortech.2016.01.110.

[117] L.D. Gottumukkala, A.K. Mathew, A. Abraham, R.K. Sukumaran, Biobutanol production: Microbes, feedstock, and strategies, 2nd ed., Elsevier Inc., 2019. https://doi.org/10.1016/B978-0-12-816856-1.00015-4.

[118] A.G. Costa, G.C. Pinheiro, F.G.C. Pinheiro, A.B. Dos Santos, S.T. Santaella, R.C. Leit??o, The use of thermochemical pretreatments to improve the anaerobic biodegradability and biochemical methane potential of the sugarcane bagasse, Chem. Eng. J. 248 (2014) 363–372. https://doi.org/10.1016/j.cej.2014.03.060.

[119] G. Di Girolamo, M. Grigatti, L. Barbanti, I. Angelidaki, Effects of hydrothermal pre-treatments on Giant reed (Arundo donax) methane yield, Bioresour. Technol. 147 (2013) 152–159. https://doi.org/10.1016/j.biortech.2013.08.006.

[120] D. Wang, F. Shen, G. Yang, Y. Zhang, S. Deng, J. Zhang, Y. Zeng, T. Luo, Z. Mei, Can hydrothermal pretreatment improve anaerobic digestion for biogas from lignocellulosic biomass?, Bioresour. Technol. (2017). https://doi.org/10.1016/j.biortech.2017.09.197.

[121] G. Ran, D. Li, T. Zheng, X. Liu, L. Chen, Q. Cao, Z. Yan, Hydrothermal pretreatment on the anaerobic digestion of washed vinegar residue, Bioresour. Technol. 248 (2018) 265–271. https://doi.org/10.1016/j.biortech.2017.06.068.

[122] A.M. Mustafa, H. Li, A.A. Radwan, K. Sheng, X. Chen, Effect of hydrothermal and Ca(OH)2 pretreatments on anaerobic digestion of sugarcane bagasse for biogas production, Bioresour. Technol. 259 (2018) 54–60. https://doi.org/10.1016/j.biortech.2018.03.028.

[123] E. Betiku, H.A. Emeko, B.O. Solomon, Fermentation parameter optimization of microbial oxalic acid production from cashew apple juice, HLY. (2016). https://doi.org/10.1016/j.heliyon.2016.e00082.

[124] E.D. Deenanath, K. Rumbold, S. Iyuke, The Production of Bioethanol from Cashew Apple Juice by Batch Fermentation Using Saccharomyces cerevisiae Y2084 and Vin13 , ISRN Renew. Energy. 2013 (2013) 1–11. https://doi.org/10.1155/2013/107851.
[125] K. Kucharska, P. Rybarczyk, I. Hołowacz, R. Łukajtis, M. Glinka, M. Kamiński, Pretreatment of lignocellulosic materials as substrates for fermentation processes, Molecules. 23 (2018) 1–32. https://doi.org/10.3390/molecules23112937.
[126] S.T. Thomsen, Z. Kádár, J.E. Schmidt, Compositional analysis and projected biofuel potentials from common West African agricultural residues, Biomass and Bioenergy. 63 (2014) 210–217. https://doi.org/10.1016/j.biombioe.2014.01.045.
[127] D. Shenoy, A. Pai, R.K. Vikas, H.S. Neeraja, J.S. Deeksha, C. Nayak, C.V. Rao, A study on bioethanol production from cashew apple pulp and coffee pulp waste, Biomass and Bioenergy. 35 (2011) 4107–4111. https://doi.org/10.1016/j.biombioe.2011.05.016.
[128] M.V.P. Rocha, T.H.T. Rodrigues, T. Lima de Albuquerque, L.R.B. Gonçalves, G. Ribeiro de Macedo, Evaluation of dilute acid pretreatment on cashew apple bagasse for ethanol and xylitol production, Chem. Eng. J. 243 (2014) 234–243. https://doi.org/10.1016/j.cej.2013.12.099.
[129] P.K. Halder, N. Paul, M.R.A. Beg, Assessment of biomass energy resources and related technologies practice in Bangladesh, Renew. Sustain. Energy Rev. 39 (2014) 444–460. https://doi.org/10.1016/j.rser.2014.07.071.
[130] N. Scarlat, J. Dallemand, F. Monforti, K. Bo, The possible contribution of agricultural crop residues to renewable energy targets in Europe : A spatially explicit study $, 19 (2013) 666–677. https://doi.org/10.1016/j.rser.2012.11.060.
[131] J. Singh, B.S. Panesar, S.K. Sharma, Energy potential through agricultural biomass using geographical information system — A case study of Punjab, 32 (2008) 301–307. https://doi.org/10.1016/j.biombioe.2007.10.003.
[132] K. Hilla, B. Deen, A. Weersink, V.R. Acker, K. Janovicek, A. De Laporte, Assessment Of The Availability Of Agricultural Biomass For Heat, (2010).
[133] H. Kludze, B. Deen, W. Alfons, R. van Acker, K. Janovicek, A. De Laporte, Assessment Of The Availability Of Agricultural Biomass For Heat, (2010).
[134] M. Hensley, S. Gu, E. Ben, A comprehensive review of biomass resources and biofuels potential in Ghana, Renew. Sustain. Energy Rev. 15 (2011) 404–415. https://doi.org/10.1016/j.rser.2010.09.033.
[135] S.N. Bentsen, C. Felby, J.B. Thorsen, Agricultural residue production and potentials for energy and materials services, Prog. Energy Combust. Sci. 40 (2014) 59–73. https://doi.org/10.1016/j.pecs.2013.09.003.
[136] Word Cocoa Foundation, Cocoa Market Update, (2014) 1–11.
[137] M. Laven, M. Boomsma, Incentives for sustainable cocoa production in Ghana, 2012.
[138] Cashewinfo, Cashew Handbook 2014, 2014.
[139] M. Wessel, P.M.F. Quist-wessel, NJAS - Wageningen Journal of Life Sciences Cocoa production in West Africa , a review and analysis of recent developments, NJAS - Wageningen J. Life Sci. 74–75 (2015) 1–7. https://doi.org/10.1016/j.njas.2015.09.001.
[140] R. Lal, World crop residues production and implications of its use as a biofuel, 31 (2012) 575–584. https://doi.org/10.1016/j.envint.2004.09.005.
[141] E. Anabire, F. Kemausuor, A. Addo, Resources , Conservation and Recycling Technical analysis of crop residue biomass energy in an agricultural region of Ghana, "Resources, Conserv. Recycl. 96 (2015) 51–60. https://doi.org/10.1016/j.resconrec.2015.01.007.

[142] E. Smeets, A. Faaij, I. Lewandowski, A quickscan of global bio-energy potentials to 2050: An analysis of the regional availability of biomass resources for export in relation to the underlying factors, 2004.
[143] E.L. Iye, P.E. Bilsborrow, Assessment of the availability of agricultural residues on a zonal basis for medium- to large-scale bioenergy production in Nigeria, Biomass and Bioenergy. 48 (2013) 66–74. https://doi.org/10.1016/j.biombioe.2012.11.015.
[144] M. Valk, Availability and cost of agricultural residues for bioenergy generation: International literature review and a case study for South Africa, (2014) 1–126.
[145] R. Pipatti, Q. Alves, Joao Wagner Silva Gao, K. Cabrera, Carlos Lopez Mareckova, H. Oonk, E. Scheehle, S. Chhemendra, A. Smith, P. Svardal, Yamada Masato, Chapter 4 Biological Treatment Of Solid, in: 2006.
[146] R. Pipatti, Q. Alves, Joao Wagner Silva Gao, K. Cabrera, Carlos Lopez Mareckova, H. Oonk, E. Scheehle, S. Chhemendra, A. Smith, P. Svardal, Y. Masato, CHAPTER 3, (2006) 1–40.
[147] P. Foster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Shulz, R. Van Dorland, Changes in Atmospheric Constituents and in Radiative Forcing Coordinating, United Kingdon and New York, 2007.
[148] IPCC, Module 6 - Waste, in: Intergovernmental Panel for Climate Change, 1996.
[149] EN 14774-1, Solid biofuels - Determination of moisture content -Oven dry method, 2009.
[150] EN 15148, Solid biofuels - Determination of the content of volatile matter, 2009.
[151] EN ISO 16948, Solid biofuels - Determination of total content of carbon and hydrogen and nitrogen, 2015.
[152] EN 14918, Solid Biofuels - Determination of calorific value, 2010.
[153] J. Liebetrau, D. Pfeiffer, D. Thrän, Collection of Methods for Biogas, 2016.
[154] P.J. Van Soest, J.B. Robertson, B.A. Lewis, Methods for Dietary Fiber, Neutral Detergent Fiber, and Nonstarch Polysaccharides in Relation to Animal Nutrition, J. Dairy Sci. 74 (1991) 3583–3597. https://doi.org/10.3168/jds.S0022-0302(91)78551-2.
[155] EN ISO 16967, Solid biofuels - Determination of major elements - Al, Ca, Fe, Mg, K, Si, Na and Ti, 2015.
[156] EN 15297, Solid biofuels — Determination of minor elements — As , Cd , Co , Cr , Cu , Hg , Mn , Mo , Ni , Pb , Sb , V and Zn, 2011.
[157] A. Ware, N. Power, Biogas from cattle slaughterhouse waste : Energy recovery towards an energy self-sufficient industry in Ireland, Renew. Energy. 97 (2016) 541–549. https://doi.org/10.1016/j.renene.2016.05.068.
[158] R.O. Shea, D. Wall, J.D. Murphy, Bioresource Technology Modelling a demand driven biogas system for production of electricity at peak demand and for production of biomethane at other times, Bioresour. Technol. 216 (2016) 238–249. https://doi.org/10.1016/j.biortech.2016.05.050.
[159] S. Park, Y. Yoon, S. Kuk, D. Kim, H. Kim, Effect of hydrothermal pre-treatment (HTP) on poultry slaughterhouse waste (PSW) sludge for the enhancement of the solubilization , physical properties , and biogas production through anaerobic digestion, Waste Manag. 64 (2017) 327–332. https://doi.org/10.1016/j.wasman.2017.03.004.
[160] Verein Deutscher Ingenieure (VDI), Vdi 4630, 2006. https://doi.org/2006.

[161] C. Liu, H. Li, Y. Zhang, C. Liu, Bioresource Technology Improve biogas production from low-organic-content sludge through high-solids anaerobic co-digestion with food waste, Bioresour. Technol. 219 (2016) 252–260. https://doi.org/10.1016/j.biortech.2016.07.130.

[162] T.A. Pozdniakova, J.C. Costa, R.J. Santos, M.M. Alves, R.A.R. Boaventura, Bioresource Technology Anaerobic biodegradability of Category 2 animal by-products : Methane potential and inoculum source, Bioresour. Technol. 124 (2012) 276–282. https://doi.org/10.1016/j.biortech.2012.08.022.

[163] M. Brulé, H. Oechsner, T. Jungbluth, Exponential model describing methane production kinetics in batch anaerobic digestion: A tool for evaluation of biochemical methane potential assays, Bioprocess Biosyst. Eng. 37 (2014) 1759–1770. https://doi.org/10.1007/s00449-014-1150-4.

[164] L.C. Ferreira, A. Donoso-Bravo, P.J. Nilsen, F. Fdz-Polanco, S.I. Pérez-Elvira, Influence of thermal pretreatment on the biochemical methane potential of wheat straw, Bioresour. Technol. 143 (2013) 251–257. https://doi.org/10.1016/j.biortech.2013.05.065.

[165] Z. Zahan, M.Z. Othman, W. Rajendram, Anaerobic Codigestion of Municipal Wastewater Treatment Plant Sludge with Food Waste : A Case Study, 2016 (2016).

[166] J. Kim, J. Kim, C. Lee, Anaerobic co-digestion of food waste, human feces, and toilet paper: Methane potential and synergistic effect, Fuel. 248 (2019) 189–195. https://doi.org/10.1016/j.fuel.2019.03.081.

[167] S. Román, J. Libra, N. Berge, E. Sabio, K. Ro, L. Li, B. Ledesma, A. Alvarez, S. Bae, Hydrothermal carbonization: Modeling, final properties design and applications: A review, Energies. 11 (2018) 1–28. https://doi.org/10.3390/en11010216.

[168] M. Usman, H. Chen, K. Chen, S. Ren, J.H. Clark, J. Fan, G. Luo, S. Zhang, Characterization and utilization of aqueous products from hydrothermal conversion of biomass for bio-oil and hydro-char production: A review, Green Chem. 21 (2019) 1553–1572. https://doi.org/10.1039/c8gc03957g.

[169] E. Ashitey, Ghana - Cocoa Report Annual, 2012.

[170] ACi, Background Information for Stakeholder Workshop on Cashew Master Plan Development, 2015.

[171] B.M. Heinrich, Case study of the African Cashew Initiative – Focus : Ghana Lessons from Working with New and Multiple Partners – Emerging Results, (2012).

[172] CRIG, Cocoa Research Institute of Ghana Annual Report, 2010/2011, 2011.

[173] Cashewinfo, Cashew week, 2016.

[174] COCOBOD, Cocoa production in Ghana, Accra, 2018. https://cocobod.gh/cocoa-purchases.

[175] E. Antwi, N. Engler, M. Nelles, A. Schüch, Anaerobic digestion and the effect of hydrothermal pretreatment on the biogas yield of cocoa pods residues, Waste Manag. 88 (2019) 131–140. https://doi.org/10.1016/j.wasman.2019.03.034.

[176] A. Eisentraut, Sustainable production of second-generation biofuels, 2010.

[177] F. Liotta, G. D'Antonio, G. Esposito, M. Fabbricino, L. Frunzo, E.D. Van Hullebusch, P.N. Lens, F. Pirozzi, Effect of moisture on disintegration kinetics during anaerobic digestion of complex organic substrates, Waste Manag. Res. 32 (2014) 40–48. https://doi.org/10.1177/0734242X13513827.

[178] P.D. Osborn, Data charts and tables, in: Handb. Energy Data Calc. Incl. Dir. Prod. Serv., 1960: pp. 1–67. https://doi.org/10.1016/B978-0-408-01327-7.50005-1.

[179] I. Amber, N. Gukop, Generation , characteristics and energy potential of solid municipal waste in Nigeria, 23 (2012) 47–51.

[180] G. Afrane, A. Ntiamoah, Analysis of the life-cycle costs and environmental impacts of cooking fuels used in Ghana, Appl. Energy. 98 (2012) 301–306. https://doi.org/10.1016/j.apenergy.2012.03.041.

[181] N.U. Saqib, S. Baroutian, A.K. Sarmah, Physicochemical, structural and combustion characterization of food waste hydrochar obtained by hydrothermal carbonization, Bioresour. Technol. 266 (2018) 357–363. https://doi.org/10.1016/j.biortech.2018.06.112.

[182] A. Cortesi, V. Gallo, D. Solinas, R. Vitanza, Assessing the synergistic effects of co-digestion of maize silage and red chicory waste, Chem. Biochem. Eng. Q. 32 (2018) 383–390. https://doi.org/10.15255/CABEQ.2018.1300.

[183] E. Song, S. Park, H. Kim, Hydrochar from Sewage Sludge, (2019) 1–9.

[184] I. Cabeza, M. Thomas, A. Vázquez, P. Acevedo, M. Hernández, Anaerobic Co-digestion of Organic Residues from Different Productive Sectors in Colombia: Biomethanation Potential Assessment, 5th Int. Symp. Ind. Biotechnol. (Ibic 2016). 49 (2016) 385–390. https://doi.org/10.3303/Cet1649065.

[185] Y. Li, R. Zhang, Y. He, C. Zhang, X. Liu, C. Chen, G. Liu, Anaerobic co-digestion of chicken manure and corn stover in batch and continuously stirred tank reactor (CSTR), Bioresour. Technol. 156 (2014) 342–347. https://doi.org/10.1016/j.biortech.2014.01.054.

[186] L.A. dos Santos, R.B. Valença, L.C.S. da Silva, S.H. de B. Holanda, A.F.V. da Silva, J.F.T. Jucá, A.F.M.S. Santos, Methane generation potential through anaerobic digestion of fruit waste, J. Clean. Prod. 256 (2020). https://doi.org/10.1016/j.jclepro.2020.120389.

[187] J.S. Silva, J.S. Mendes, J.A.C. Correia, M.V.P. Rocha, L. Micoli, Cashew apple bagasse as new feedstock for the hydrogen production using dark fermentation process, J. Biotechnol. 286 (2018) 71–78. https://doi.org/10.1016/j.jbiotec.2018.09.004.

[188] J. Poerschmann, I. Baskyr, B. Weiner, R. Koehler, H. Wedwitschka, F.D. Kopinke, Hydrothermal carbonization of olive mill wastewater, Bioresour. Technol. 133 (2013) 581–588. https://doi.org/10.1016/j.biortech.2013.01.154.

[189] M. Jeguirim, L. Limousy, Biomass chars: Elaboration, characterization and applications II, 2019. https://doi.org/10.3390/en12030384.

[190] N. Acosta, J. De Vrieze, V. Sandoval, D. Sinche, I. Wierinck, K. Rabaey, Cocoa residues as viable biomass for renewable energy production through anaerobic digestion, Bioresour. Technol. 265 (2018) 568–572. https://doi.org/10.1016/j.biortech.2018.05.100.

[191] L.C. Vriesmann, C.L.O. Petkowicz, Highly acetylated pectin from cacao pod husks (Theobroma cacao L.) forms gel, Food Hydrocoll. 33 (2013) 58–65. https://doi.org/10.1016/j.foodhyd.2013.02.010.

[192] X. Kang, Y. Zhang, B. Song, Y. Sun, L. Li, Y. He, X. Kong, X. Luo, Z. Yuan, The effect of mechanical pretreatment on the anaerobic digestion of Hybrid Pennisetum, Fuel. 252 (2019) 469–474. https://doi.org/10.1016/j.fuel.2019.04.134.

[193] Y. Tamaki, G. Mazza, Measurement of structural carbohydrates, lignins, and micro-components of straw and shives: Effects of extractives, particle size and crop species, Ind. Crops Prod. 31 (2010) 534–541. https://doi.org/10.1016/j.indcrop.2010.02.004.

[194] C. Dumas, G. Silva Ghizzi Damasceno, B. Abdellatif, H. Carrère, J.P. Steyer, X. Rouau, Effects of grinding processes on anaerobic digestion of wheat straw, Ind. Crops Prod. 74 (2015) 450–456. https://doi.org/10.1016/j.indcrop.2015.03.043.

[195] J.C. Motte, R. Escudié, N. Bernet, J.P. Delgenes, J.P. Steyer, C. Dumas, Dynamic effect of total solid content, low substrate/inoculum ratio and particle size on solid-state anaerobic digestion, Bioresour. Technol. 144 (2013) 141–148. https://doi.org/10.1016/j.biortech.2013.06.057.

[196] C.L.B. Reis, L.M.A. e Silva, T.H.S. Rodrigues, A.K.N. Félix, R.S. Santiago-aguiar, K.M. Canuto, M.V.P. Rocha, Bioresource Technology Pretreatment of cashew apple bagasse using protic ionic liquids : Enhanced enzymatic hydrolysis, Bioresour. Technol. (2016). https://doi.org/10.1016/j.biortech.2016.11.019.

[197] A. Mudhoo, S. Kumar, Effects of heavy metals as stress factors on anaerobic digestion processes and biogas production from biomass, Int. J. Environ. Sci. Technol. 10 (2013) 1383–1398. https://doi.org/10.1007/s13762-012-0167-y.

[198] H.I. Abdel-Shafy, M.S.M. Mansour, Biogas production as affected by heavy metals in the anaerobic digestion of sludge, Egypt. J. Pet. 23 (2014) 409–417. https://doi.org/10.1016/j.ejpe.2014.09.009.

[199] O. Thygesen, S.G. Sommer, S.G. Shin, J.M. Triolo, Residual biochemical methane potential (BMP) of concentrated digestate from full-scale biogas plants, Fuel. 132 (2014) 44–46. https://doi.org/10.1016/j.fuel.2014.04.062.

[200] D. Yadav, L. Barbora, D. Bora, S. Mitra, L. Rangan, P. Mahanta, International Biodeterioration & Biodegradation An assessment of duckweed as a potential lignocellulosic feedstock for biogas production, Int. Biodeterior. Biodegradation. (2016) 1–7. https://doi.org/10.1016/j.ibiod.2016.09.007.

[201] R.O. Shea, D.M. Wall, I. Kilgallon, J.D. Browne, J.D. Murphy, Assessing the total theoretical , and financially viable , resource of biomethane for injection to a natural gas network in a region, Appl. Energy. 188 (2017) 237–256. https://doi.org/10.1016/j.apenergy.2016.11.121.

[202] A. Nielfa, R. Cano, M. Fdz-Polanco, Theoretical methane production generated by the co-digestion of organic fraction municipal solid waste and biological sludge, Biotechnol. Reports. 5 (2015) 14–21. https://doi.org/10.1016/j.btre.2014.10.005.

[203] M.J. Odedina, B. Charnnok, K. Saritpongteeraka, S. Chaiprapat, Effects of size and thermophilic pre-hydrolysis of banana peel during anaerobic digestion, and biomethanation potential of key tropical fruit wastes, Waste Manag. 68 (2017) 128–138. https://doi.org/10.1016/j.wasman.2017.07.003.

[204] E. Elbeshbishy, G. Nakhla, H. Hafez, Biochemical methane potential (BMP) of food waste and primary sludge: Influence of inoculum pre-incubation and inoculum source, Bioresour. Technol. 110 (2012) 18–25. https://doi.org/10.1016/j.biortech.2012.01.025.

[205] A.A. Rajput, Z. Sheikh, Effect of inoculum type and organic loading on biogas production of sunflower meal and wheat straw, Sustain. Environ. Res. 29 (2019) 1–10. https://doi.org/10.1186/s42834-019-0003-x.

[206] B. Wirth, T. Reza, J. Mumme, Bioresource Technology Influence of digestion temperature and organic loading rate on the continuous anaerobic treatment of process liquor from hydrothermal carbonization of sewage sludge, Bioresour. Technol. 198 (2015) 215–222. https://doi.org/10.1016/j.biortech.2015.09.022.

[207] S. Fan, P. Zhang, F. Li, S. Jin, S. Wang, S. Zhou, A Review of Lignocellulose Change During Hydrothermal Pretreatment for Bioenergy Production, 2016. https://doi.org/10.2174/1385272820666160513154113.

[208] M. Drahansky, M.. Paridah, A. Moradbak, A.. Mohamed, F. abdulwahab taiwo Owolabi, M. Asniza, S.H.. Abdul Khalid, Compositional Variability of Lignin in Biomass, in: Lignin - Trends Appl., 2016: p. 13. https://doi.org/http://dx.doi.org/10.5772/57353.
[209] H.R. Holgate, J.C. Meyer, J.W. Tester, Glucose Hydrolysis and Oxidation in Supercritical Water, 41 (1995) 637–648.
[210] S. Paul, A. Dutta, Challenges and opportunities of lignocellulosic biomass for anaerobic digestion, Resour. Conserv. Recycl. 130 (2018) 164–174. https://doi.org/10.1016/j.resconrec.2017.12.005.
[211] F.C. Ertem, P. Neubauer, S. Junne, Environmental life cycle assessment of biogas production from marine macroalgal feedstock for the substitution of energy crops, J. Clean. Prod. 140 (2017) 977–985. https://doi.org/10.1016/j.jclepro.2016.08.041.
[212] J. Zhuang, X. Wang, J. Xu, Z. Wang, M. Qin, hot-water-treated wood during cooling process, Wood Sci. Technol. (2016). https://doi.org/10.1007/s00226-016-0872-7.
[213] L. Mendez, A. Mahdy, M. Ballesteros, C. González-fernández, Methane production of thermally pretreated Chlorella vulgaris and Scenedesmus sp . biomass at increasing biomass loads, Appl. Energy. 129 (2014) 238–242. https://doi.org/10.1016/j.apenergy.2014.04.110.
[214] A.J. Cavaleiro, T. Ferreira, F. Pereira, G. Tommaso, M.M. Alves, Biochemical methane potential of raw and pre-treated meat-processing wastes, Bioresour. Technol. 129 (2013) 519–525. https://doi.org/10.1016/j.biortech.2012.11.083.
[215] S. Myszograj, A. Stadnik, E. Płuciennik-Koropczuk, The Influence of Trace Elements on Anaerobic Digestion Process, Civ. Environ. Eng. Reports. 28 (2019) 105–115. https://doi.org/10.2478/ceer-2018-0054.
[216] V. Prabhudessai, A. Ganguly, S. Mutnuri, Biochemical Methane Potential of Agro Wastes, J. Energy. 2013 (2013) 1–7. https://doi.org/10.1155/2013/350731.
[217] V. Prabhudessai, Anaerobic Digestion of Food Waste in a Horizontal Plug Flow Reactor, PhD Thesis. (2013).
[218] E. Danso-Boateng, G. Shama, A.D. Wheatley, S.J. Martin, R.G. Holdich, Hydrothermal carbonisation of sewage sludge: Effect of process conditions on product characteristics and methane production, Bioresour. Technol. 177 (2015) 318–327. https://doi.org/10.1016/j.biortech.2014.11.096.
[219] D. Basso, E. Weiss-hortala, F. Patuzzi, D. Castello, M. Baratieri, L. Fiori, Bioresource Technology Hydrothermal carbonization of off-specification compost : A byproduct of the organic municipal solid waste treatment, Bioresour. Technol. 182 (2015) 217–224. https://doi.org/10.1016/j.biortech.2015.01.118.
[220] B. Zhang, M. Heidari, B. Regmi, S. Salaudeen, P. Arku, M. Thimmannagari, A. Dutta, Hydrothermal carbonization of fruit wastes: A promising technique for generating hydrochar, Energies. 11 (2018) 1–14. https://doi.org/10.3390/en11082022.
[221] C. Lievens, D. Mourant, X. Hu, Y. Wang, L. Wu, A. Rossiter, A case study : what is leached from mallee biochars as a function of pH ?, (2018).
[222] D. Basso, Hydrothermal carbonization of waste biomass, 2016.
[223] M. Mäkelä, J. Forsberg, C. Söderberg, S.H. Larsson, O. Dahl, Process water properties from hydrothermal carbonization of chemical sludge from a pulp and board mill, Bioresour. Technol. 263 (2018) 654–659. https://doi.org/10.1016/j.biortech.2018.05.044.

[224] J.C. Solarte-Toro, Y. Chacón-Pérez, C.A. Cardona-Alzate, Evaluation of biogas and syngas as energy vectors for heat and power generation using lignocellulosic biomass as raw material, Electron. J. Biotechnol. 33 (2018) 52–62. https://doi.org/10.1016/j.ejbt.2018.03.005.
[225] C. Kost, T. Schlegl, J. Thomsen, S. Nold, J. Mayer, N. Hartmann, C. Senkpiel, S. Philipps, S. Lude, N. Saad, Fraunhofer ISE: Levelized Cost of Electricity - Renewable Energy Technologies, March 2018, Fraunhofer ISE Levelized Cost Electr. - Renew. Energy Technol. (2018).
[226] PURC, Publication of electricity tariffs, (2019).
[227] Public Utility Regulatory Authority, Publication of feed-in tariff for electricity generation from renewable energy sources, 2016.

Theses on the dissertation

1. Cocoa pods and cashew peduncle residues are left untreated in Ghana and pose a significant environmental risk.
2. The RPR methodology was used to estimate the cocoa theoretical and technical potential of cocoa pods and cashew peduncle residues.
3. Anaerobic digestion assay shows that even though the digestion of cocoa pods and cashew peduncle was possible, digestibility of cocoa pods was low due to the high lignin content. Cashew peduncle residues on the other hand is readily digestible however its digestibility is sensitive to the inoculum used.
4. Kinetic parameters obtained for cocoa pods digestion are applicable to large reactors and can be used as useful design parameters. However, due to the sensitivity of the cashew peduncle to the choice of inoculum, the kinetic parameters obtained during the desktop batch anaerobic digestion is limited in its application especially when there is a change in inoculum.
5. Mild sub critical hydrothermal pretreatment of cocoa pods has the potential of increasing the biogas yield of cocoa pods by softening the lignin leading to enhanced hydrolysis and increased biogas yield. Sever sub critical hydrothermal pretreatment conditions above a severity of 3.5 is generally not good for cocoa pods and does not improve its digestibility, rather process inhibition is to be expected.
6. Mono digestion of cashew peduncle is only possible up to an OLR of 3.0 kgVS/m^3.day in a CSTR. However, phase separation of cashew peduncle will result in stable digestion up to an OLR 4.0 kgVS/m^3.day. Mono digestion of cocoa pods is stable up to an OLR of 5.0 kgVS/m^3.day.
7. Feed composition plays a significant role in the synergetic potential of cashew peduncle as a co-substrate to maize silage. However, no synergetic effect is expected when cocoa pods is codigested with maize silage.
8. Using surface response models, the effect of process temperature, reaction time and heating rate on the yield, heating value and ash content of the hydrochar was studied.
9. Hitherto not considered as an important process parameter, heating rate has an effect on the higher heating value of cocoa pods hydrochar, yield of cashew peduncle hydrochar and the COD of the hydrolysate after the carbonization of cocoa pods.
10. Influence of process parameters were specific to the both the substrate type and response factor
11. Hydrothermal carbonization can be used to valorize cocoa pods and cashew peduncle residues resulting lower ash content and higher HHV even though notable reduction in yield is observed.

Abschlussarbeiten zur Dissertation

1. Kakaofrüchte und Cashewstielreste werden in Ghana unbehandelt gelassen und stellen ein erhebliches Umweltrisiko dar.
2. Die RPR-Methode wurde verwendet, um das theoretische und technische Potenzial von Kakaofrüchten und Cashewstielresten für Kakao abzuschätzen.
3. Der anaerobe Verdauungstest zeigt, dass die Verdaulichkeit von Kakaofrüchten aufgrund des hohen Ligningehalts gering war, obwohl die Verdauung von Kakaofrüchten und Cashewstielen möglich war. Cashew-Stielreste sind dagegen leicht verdaulich, ihre Verdaulichkeit ist jedoch empfindlich gegenüber dem verwendeten Inokulum.
4. Kinetische Parameter, die für den Aufschluss von Kakaofrüchten erhalten wurden, sind auf große Reaktoren anwendbar und können als nützliche Entwurfsparameter verwendet werden. Aufgrund der Empfindlichkeit des Cashewstiels gegenüber der Wahl des Inokulums sind die kinetischen Parameter, die während des anaeroben Aufschlusses der Desktop-Charge erhalten werden, in ihrer Anwendung begrenzt, insbesondere wenn sich das Inokulum ändert.
5. Eine milde unterkritische hydrothermale Vorbehandlung von Kakaofrüchten hat das Potenzial, die Biogasausbeute von Kakaofrüchten durch Erweichen des Lignins zu erhöhen, was zu einer verbesserten Hydrolyse und einer erhöhten Biogasausbeute führt. Schwere unterkritische hydrothermale Vorbehandlungsbedingungen über einem Schweregrad von 3,5 sind im Allgemeinen nicht gut für Kakaofrüchte und verbessern ihre Verdaulichkeit nicht, vielmehr ist eine Prozesshemmung zu erwarten.
6. Eine Monoverdauung des Cashewstiels ist in einem CSTR nur bis zu einer OLR von 3,0 kgVS / m3 Tag möglich. Die Phasentrennung des Cashewstiels führt jedoch zu einer stabilen Verdauung bis zu einem OLR von 4,0 kgVS / m3. Tag. Die Monoverdauung von Kakaofrüchten ist bis zu einer OLR von 5,0 kgVS / m3 Tag stabil.
7. Die Futterzusammensetzung spielt eine wichtige Rolle für das synergetische Potenzial des Cashewstiels als Co-Substrat für Maissilage. Es wird jedoch kein synergetischer Effekt erwartet, wenn Kakaofrüchte mit Maissilage mitverdaut werden.
8. Unter Verwendung von Oberflächenreaktionsmodellen wurde der Einfluss von Prozesstemperatur, Reaktionszeit und Heizrate auf die Ausbeute, den Heizwert und den Aschegehalt des Hydrochars untersucht.
9. Bisher nicht als wichtiger Prozessparameter angesehen, hat die Heizrate einen Einfluss auf den höheren Heizwert von Kakaofrucht-Hydrochar, die Ausbeute an Cashewstiel-Hydrochar und den CSB des Hydrolysats nach der Carbonisierung von Kakaofrucht.
10. Der Einfluss der Prozessparameter war sowohl für den Substrattyp als auch für den Antwortfaktor spezifisch
11. Die hydrothermale Karbonisierung kann verwendet werden, um Kakaofrüchte und Cashewstielreste aufzuwerten, was zu einem niedrigeren Aschegehalt und einem höheren HHV führt, obwohl eine merkliche Verringerung der Ausbeute beobachtet wird.

List of publication and conference proceedings during my PhD study period

1. **Antwi, E**., Engler, N., Nelles, M. and Schuch, A., (2019), Anaerobic digestion and the effect of hydrothermal pretreatment on the biogas yield of cocoa pods, Waste Management, Vol. 88, 131 – 140, https://doi.org/10.1016/j.wasman.2019.03.034
2. **Antwi, E**., Engler, N., Nelles, M. and Schuch, A., (2019), Valorisation of cashew peduncle residues through anaerobic digestion, conference proceedings, 9th DGAW science congress, Amberg, 14th – 15th March, 2019.
3. **Antwi, E**., Engler, N., Nelles, M. and Schuch, A., (2019), Environmental effect of cocoa pods disposal in 3 West African Countries, Accepted abstract for the 13th International Rostocker Bioenergieforum, Germany.
4. **Antwi, E**., Schuch, A., Hakim, T., Engler, N., Latrache, H., Nelles, M. (2017), Agro waste management strategies in low income countries – future perspectives to use as a resource, conference proceedings, 16th Sardinia symposium on waste and landfill management, Margherita Di Pula, 2 – 6th October, 2017.

Edward Antwi

Date of birth	April 30th, 1979
Sex	Male
Citizenship	Ghanaian
Research interest	Bioenergy, (biodiesel, biogas, bioethanol, hydrochar) solar thermal applications, energy efficiency
Email	edwardantwi@ceesdghana.org; edwardantwi@hotmail.com

Education

2016 – date	PhD environmental Engineering University of Rostock
2006 - 2008	MSc – Mechanical Engineering – Thermofluids and Energy Systems, Kwame Nkrumah University of Science and Technology (KNUST), Kumasi, Ghana
1999 - 2003	BSc – Chemical Engineering, 2nd Class Upper, KNUST, Ghana

Employment record

09/2015 – 08/2016	Head of Department, Electrical and Electronic Engineering Department, Kumasi Polytechnic.
09/2015 – 12/2017	Managing partner, EO Utility – Project Developer for the development of Oblogo landfill gas capture and utilization project into a CDM project.
09/2013- 08/2014	Head of Department, Mechanical Engineering Department, Kumasi Polytechnic
09/2009 - Date	Snr. Lecturer, Mechanical Engineering Department, Kumasi Polytechnic Lecturer, Mechanical Engineering Department, Kumasi Polytechnic
10/2009 – date	Assistant Director, Centre for Energy, Environment and Sustainable Development (CEESD), Non-profit, Kumasi, Ghana (Volunteer)
06/2004 – 12/2005	Environmental Engineer, Waste Group Ghana Limited
07/2003 - 6/2004	Teaching and Research Assistant, Faculty of Chemical and Materials Engineering, KNUST, Ghana

Selected Project with involvement

Date	Location	Position	Project
01.2020 -	Germany	Supporting expert	Waste to energy as a sustainable solution for Ghana, funded by the Federal Ministry of Education and Research, Germany (6.2 million Euros)
08/2018 – 04/2019	Ghana/Germany	Supporting expert	Bioenergy for production and utilization in Ghana (BiograG, funding from Federal Ministry of Education and Research, Germany, 58,000 Euros
08/2016-10/2016	Ghana	Supporting expert	Prefeasibility study for cookstoves technology transfer from China to Ghana
08/2016-10/2016	Ghana	Lead expert	Prefeasibility studies for biogas technology transfer to Ghana from China

08/2016 -	Ghana	Supporting expert	Isolated solar mini grid for an Island community in the Afram Plains North District Assembly, a \$100,000 project funded by USADF under the Power Africa Initiative
08/2016 - 10/2016	Ghana	Lead expert	Biogas technology catalogue preparation and selection criteria for RETT from China to Ghana – UNDP/EC under the China – Ghana South South Cooperation on Renewable Energy
08/2011 - 12/2017	Ghana	Supporting expert	Project development for Oblogo landfill gas recovery and destruction. (Project successfully registered as a CDM project by the UNFCC on the 1st of April, 2016)
08/2016 – 10/2016	Ghana	Supporting expert	Pre-feasibility study of Improved cookstoves technology and fuels in Ghana - UNDP/EC under the China – Ghana South South Cooperation on Renewable Energy
09/2015- 11/2015	Ghana	Supporting consultant	Identification of Barriers to Renewable Energy Technology Transfer to Ghana – UNDP/EC under the China – Ghana South South Cooperation on Renewable Energy
01/2015 – 11/2015	Ghana	Co-principal Investigator	Environmental and Social Impact Assessment of Kumasi Polytechnic's proposed new campus at Kuntenase (EIA issued in 2017)
02/2012 – 03.2014	Ghana	Co-principal Investigator	Natural Science Workgroup, Integrated Assessment of Water Sustainability, Infrastructural Inequality, and Health in Small-Scale Gold Mining Communities in Ghana, University of Michigan and Ghana
02/2015- 08/2015	Kushea	Principal Investigator	Waste Characterization in Kushea and construction of waste incinerators for the township
09/2014 – 10/2014	Kumasi	Co-Principal Investigator	Characterization of household waste at the point of disposal – Umawa Arkolia
08/2014- 09/2014	Kumasi	Lead Principal Investigator	Biomethane Potential Determination for cassava peels, cocoa husk and spent grain – Umawa Arkolia
04/2014 - date	Kumasi	Co-coordinator	Establishment of the Renewable Energy and Energy Efficiency Centre at Kumasi Polytechnic
12/2013 - 01/2014	Brong-Ahafo	Supporting Expert	Mapping of clean cookstoves stakeholders in Ghana https://cleancookstoves.org/binary-data/RESOURCE/file/000/000/311-1.pdf
12/2013 – 05/2014	Domeabra	Lead expert	Design and construction of a 40 m^3 biogas digester to generate 3.5 kW of electricity (US\$60,000)
12/2013 – date	Kumasi	Coordinator	Design, construction and testing of efficient fish smokers for mass deployment and fish smoking areas in Ghana

09/2014	Domeabra	Coordinator	Design and construction of a 14 m^3 floating drum biodigester for cooking
8/2011 – Date	Ghana	Team member	First CDM programme activity on Envirofit cookstoves in Ghana
6/2010 – 6/2012	Kumasi Polytechnic	Team member	Research and development of solar dryers for large scale drying of agricultural produce in Ghana
10/2010 – 02/2013	Ghana, Nigeria, Senegal Cote D'Ivoire	Team member – KNUST	Integrated Waste Management in Western Africa (IWWA), 7th Framework Programme, European Commission, Policy review and recommendation for integrated solid waste management. www.iwwa.eu
08/2010 – Date	Kumasi Polytechnic	Team member	Research and development of decentralized biochar reactors and small-scale compost plants for agricultural applications in Ghana
05/2009 - Date	Ghana	Team member	Production and testing of gel ethanol (from sugarcane) as household fuel in Ghana
9/2010	Bongo	Coordinator	Design and installation of solar water distillers at Anaafo Bisi, Bongo, Upper East Region
09/2010	Kumasi Polytechnic	Team coordinator	Design and fabrication of gel-ethanol stoves

Relevant refereed publications

5. **Antwi, E**., Engler, N., Nelles, M. and Schuch, A., (2019), Anaerobic digestion and the effect of hydrothermal pretreatment on the biogas yield of cocoa pods, Waste Management, Vol. 88, 131 – 140, https://doi.org/10.1016/j.wasman.2019.03.034
6. **Antwi, E**., Engler, N., Nelles, M. and Schuch, A., (2019), Valorisation of cashew peduncle residues through anaerobic digestion, conference proceedings, 9th DGAW science congress, Amberg, 14th – 15th March, 2019.
7. **Antwi, E**., Engler, N., Nelles, M. and Schuch, A., (2019), Environmental effect of cocoa pods disposal in 3 West African Countries, Accepted abstract for the 13th International Rostocker Bioenergieforum, Germany.
8. **Antwi, E**., Schuch, A., Hakim, T., Engler, N., Latrache, H., Nelles, M. (2017), Agro waste management strategies in low income countries – future perspectives to use as a resource, conference proceedings, 16th Sardinia symposium on waste and landfill management, Margherita Di Pula, 2 – 6th October, 2017.
9. Rajee, M., Obiri, S., Green, A., Long, R., Cobbina., Nartey, V., Buck. David, **Antwi, E.,** and Basu, N. (2015), Integrated Assessment of Artisanal and Small-Scale Gold Mining in Ghana – Part 2: Natural Science Review, Int. Journal Environmental Research and Public Health, 12(8), 8971-9011. DOI: 10.3390/ijerph120808971
10. Samuel Obiri, Philip O. Yeboah, Shiloh Osae, Sam Adu-kumi, Samuel J. Cobbina, Frederick A. Armah, Benjamin Ason, **Edward Antwi** and Reginald Quansah, Int. J. Environ. Res. Public Health. 13(1): 139. doi: 10.3390/ijerph13010139
11. Ahiekpor J. C., **Antwi E.,** Bensah E. C., Ribeiro J. X. F. (2015). Determinants of urban household cooking fuel choice in Ghana. International Journal of Current Research, Vol. 7, Issue 06, pp.17203-17206
12. Obeng, G., Mensah, E. and **Antwi, E**. (2013). Engine Performance Evaluation Using Biodiesel Blends From Waste Palm Kernel Oil, Mixed WVOs And Diesel Fuel, IJES, Vol. 2, 19-25.
13. Bensah E. C., Mensah M., **Antwi E.** (2011). Status and prospects for household biogas plants in Ghana – lessons, barriers, potential, and way forward. International Journal on Energy and Environment, Volume 2, Issue 5, 2011 pp.887-898
14. **Antwi E**., Bensah E. C., Ahiekpor J. (2011). Use of solar water distiller for treatment of fluoride-contaminated water: the case of Bongo district of Ghana, Desalination, doi: 10.1016/j.desal.2011.05.044
15. Bensah E.C., **Antwi E**., Ahiekpor J. (2011). Promoting enterprise-based ecological public toilets in Ghana: technology and economics, 2nd National Environmental Sanitation Conference – NESCON 2011, Ministry of Local Government and Rural Development, Kumasi, Ghana
16. Bensah E.C**., Antwi E**., Ahiekpor J. Promoting decentralized solar water purification systems in Ghana: a case study at Bongo, 3rd Ghana Water Forum, Ministry of Water, Works and Housing, Accra
17. Arthur, R. Badoo, M. R. and **Antwi, E.,** (2011), Biogas as a Potential Renewable Energy Source: A Ghanaian Case study, Renewable Energy, vol. 36, issue 5, pp 1510 – 1516.

18. Mensah M., **Antwi E**., Bensah E. Integrated Waste Management in Western Africa (IWWA). National Environmental Sanitation Conference 2010, Kumasi, Ghana
19. **Antwi, E**., Quansah, A., Bensah, K., Arthur, R. And Ahiekpor, J. (2010). Ghana's Liquid Biofuel Policy: Challenges and The Way Forward', IJEE, Volume 1, Issue 5, 2010, pp.805-814

Conference presentations

1. **Antwi, E. (2019)** 1st German Doctoral Colloquium on "Bioenergy, Can hydrothermal Pretreatment of cocoa pods enhance biogas yield? 22nd -23rd September, Leipzig, Germany.
2. Bensah E. C., **Antwi E.** (2011). Anaerobic wastewater treatment plant for the treatment of organic waste and wastewater at Kumasi abattoir: A CDM project. Growing green through the rule of law: Capacity Building for carbon markets for Africa, ACDLP, GIMPA, Accra, Ghana, July.
3. **Antwi, E**. and Ahiekpor J. (2009), Gel fuel production as a possible substitute for fuelwood in Ghana. A paper presented at the Mondailogo Engineering Awards in Stuttgart, Germany, 6 - 9th December 2009.
4. **Antwi, E** and Brew- Hammond, A. (2008). Experimental Analysis of Vegetable oil blends in Compression Ignition Engines, presented at the 4th National Conference of the Society of Agricultural Engineers in 2008 at UCC, Ghana.
5. Mensah, M. and **Antwi, E.** (2004). Developing an Environmental Management Information System for Kumasi, presented at the 19th CODATA conference, 2004 in Germany.

Books and Thesis written

1. Idun, Y., Obiri, S., **Antwi, E** and Bensah, E. (2013). Training Africa's Youth in Waste Management and Climate Change: A Textbook for the Youth in Africa's Primary and Junior Secondary Schools, Xlibris publishers, ISBN 9781493139194
2. Co-Author, (2009). Guidebook of Modern Bioenergy Conversion Technologies in Africa. UNIDO project https://www.ctc-n.org/sites/d8uat.ctc-n.org/files/resources/106866899.pdf
3. Experimental Analysis of Vegetable oil blends with diesel in Compression Ignition (CI) Engines, (2008). Msc Thesis
4. Bensah, E. Kermaousour, F, **Antwi, E.** and Ahiekpor, J, Identification of Barriers to Renewable Energy Technology Transfer to Ghana, A report to UNDP, Ghana https://www.undp.org/content/dam/ghana/docs/Doc/Susdev/UNDP_GH_SUSDEV_C-G_Identification%20of%20barriers%20to%20renewable%20energy%20technology%20transfer.pdf

Awards

1. DAAD Award for PhD studies in Germany
2. Bronze Medalist, Mondialogo Engineering Awards. UNESCO/Diamler, 2009 (http://www.unesco.org/new/en/natural-sciences/priority-areas/sids/science-technology/mondialogo-engineering-awards/)
3. Research Excellence Award, Kumasi Polytechnic
4. Young African Leader, BMW stiftung) (http://www.bmw-stiftung.de/en/

Membership in professional and other bodies

Corporate Member: Ghana Institution of Engineers (GhIE)

Founding member: Center for Renewable Energy and Energy Efficiency (CEESD)
Center for Renewable Energy and Eenergy Efficiency, Kumasi Technical University (CREK)

Selected relevant training courses

Bioenergy training course for engineers and technicians	May 25 – 29, 2011	KNUST, Kumasi
IAEA training on modeling national energy policy	May 12, 2009	Energy Commission, Accra
Solar water pump installation	Jan 4 – 8, 2008	Deng Limited, Accra

Reviewer

1. Waste Management Journal, Elsevier
2. BioEnergy Research Journal, Springer
3. GMSARN International Journal, Thailand

Appendices

Appendix A: Hydrothermal pretreatment of cocoa pods

A-1: Design of the hydrothermal pretreatmnet experiment.

A	Temperature	ºC	Numeric	135.50	234.50	-1 ↔ 150.00	+1 ↔ 220.00	185.00	28.58
B	Reaction time	min	Numeric	2.93	17.07	-1 ↔ 5.00	+1 ↔ 15.00	10.00	4.08

A-2: Fiber analysis after hydrothermal pretreatment.

Temperatue ºC	Residence time, min	Severity	Final PH	NDF	ADF	ADL	cellulose %	Hemicellulose, %
220	5	4.23	4.13	71.30	68.62	35.64	32.98	2.68
150	5	2.17	4.91	74.24	64.98	29.07	35.91	9.26
135	10	2.03	5.11	71.64	66.47	29.75	36.71	5.18
185	3	2.98	4.51	74.27	69.07	32.94	36.13	5.20
220	15	4.71	4.25	71.36	68.88	36.21	32.67	2.48
234	10	4.95	4.26	70.23	67.88	34.99	32.90	2.35
185	10	3.50	4.36	71.05	70.07	33.14	36.93	0.98
185	10	3.50	4.47	69.92	67.82	31.60	36.21	2.10
150	15	2.65	4.81	73.43	69.01	32.16	36.85	4.41
185	10	3.50	4.51	71.36	65.59	31.03	34.56	5.77
185	17	3.73	4.34	72.53	66.00	31.59	34.41	6.53
185	10	3.50	4.42	70.78	66.52	31.75	34.77	4.26
185	10	3.50	4.49	71.25	68.29	32.02	36.27	2.96

Appendix B: Experimental design of Hydrothermal carbonization study

B-1: Box Behnken HTC experimental Design with 3 central position.

Std	Run	Process temperature (ºC)	Heating rate (K/min)	Reaction time (hrs)
4	1	240	10	4.5
14	2	210	6	4.5
1	3	180	2	4.5
6	4	240	6	1
7	5	180	6	8
5	6	180	6	1
15	7	210	6	4.5
10	8	210	10	1
11	9	210	2	8
12	10	210	10	8
8	11	240	6	8
13	12	210	6	4.5
2	13	240	2	4.5
3	14	180	10	4.5
9	15	210	2	1

B-2: Factor coding for HTC RSM design.

Factor	**Name**	**Units**	**Type**	**Minimum**	**Maximum**	**Coded Low**	**Coded High**	**Mean**	**Std. Dev.**
A	Temperature	ºC	Numeric	180.00	240.00	-1 ↔ 180.00	+1 ↔ 240.00	210.00	22.68
B	Heating rate	k/min	Numeric	2.00	10.00	-1 ↔ 2.00	+1 ↔ 10.00	6.00	3.02
C	Reaction time	hrs	Numeric	1.00	8.00	-1 ↔ 1.00	+1 ↔ 8.00	4.50	2.65

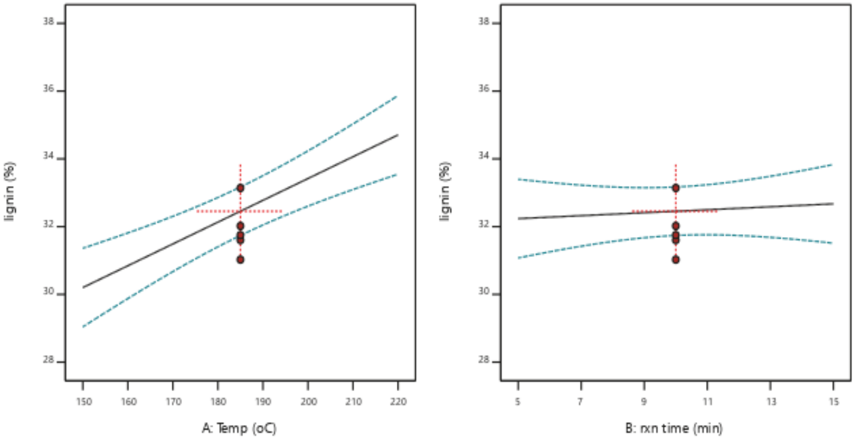
B-3: Raw data on yield, heating value ash content and yield after hydrothermal carbonization of cashew peduncle.

Temperature	Heating rate	Reaction time	Yield	HHV	Ash	COD	Energy intensity	Final pH	Initial pH
ºC	K/min	hr	% TS	MJ/kg	% Yield	g/l			
0	0	0.0	100	16.71	8.0	-	1.00	-	-
240	10	4.5	0.32	26.99	3.29	25.80	1.61	4.16	3.91
210	6	4.5	0.37	24.79	4.95	31.50	1.48	3.89	4.15
180	2	4.5	0.32	23.82	5.81	32.60	1.43	3.65	4.13
240	6	1.0	0.26	25.93	4.95	24.40	1.55	3.90	4.18
180	6	8.0	0.38	23.88	3.65	27.50	1.43	3.52	4.03
180	6	1.0	0.24	21.95	6.82	48.90	1.31	3.40	4.07
210	6	4.5	0.36	25.12	3.85	27.20	1.50	3.98	4.10
210	10	1.0	0.34	23.97	4.75	28.75	1.43	4.18	4.40
210	2	8.0	0.43	25.46	4.11	29.70	1.52	3.94	3.93
210	10	8.0	0.40	25.07	3.40	22.20	1.50	3.56	4.38
240	6	8.0	0.30	26.86	2.91	23.30	1.61	3.87	3.95
210	6	4.5	0.36	24.55	4.68	31.10	1.47	4.10	4.46
240	2	4.5	0.35	26.32	2.93	29.00	1.58	4.37	4.45
180	10	4.5	0.32	24.63	4.20	33.15	1.47	3.50	4.20
210	2	1.0	0.39	24.82	4.05	39.80	1.49	3.68	4.13

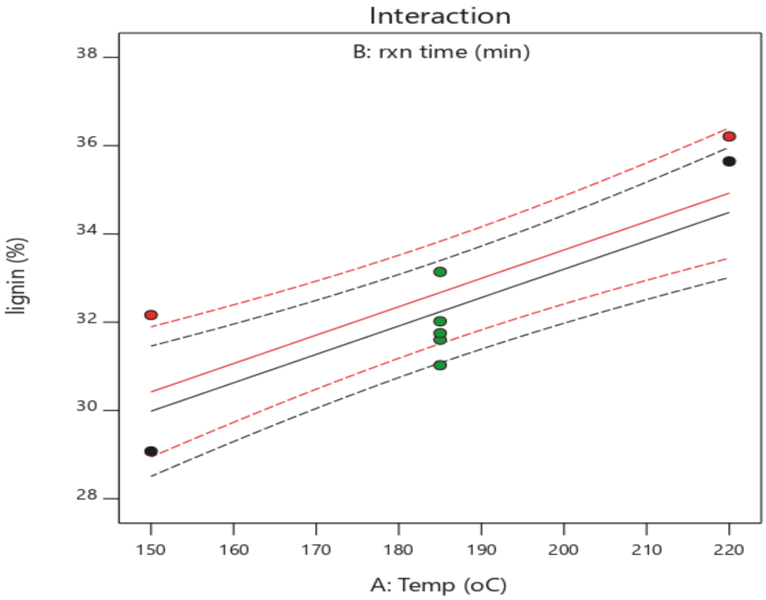
B-4: Raw data on yield, HHV and Ash content of hydrochar from cocoa pods.

Temperature	Heating rate	Reaction time	Yield	HHV	Ash	Energy content	Energy intensity	Final pH	Initial pH
ºC	K/min	hr	% TS	MJ/kg	% Yield	MJ			
0	0	0.0	100	16.71		17.30	1.00	-	--
240	10	4.5	28	27.00	3.29	7.70	1.55	4.84	5.47
210	6	4.5	39	24.79	4.95	9.00	1.31	4.61	5.71
180	2	4.5	46	23.82	5.81	9.50	1.17	4.45	7.29
240	6	1.0	49	25.93	4.95	11.70	1.35	4.60	5.85
180	6	8.0	57	23.88	3.65	11.80	1.17	4.52	5.13
180	6	1.0	44	21.95	6.82	6.40	1.06	4.60	5.74
210	6	4.5	39	25.12	3.85	9.11	1.31	4.60	5.82
210	10	1.0	53	23.97	4.75	11.70	1.25	4.30	5.26
210	2	8.0	49	25.46	4.11	12.11	1.40	4.59	5.52
210	10	8.0	47	25.07	3.99	11.80	1.41	4.62	5.39
240	6	8.0	38	26.86	2.91	10.70	1.59	4.82	5.77
210	6	4.5	49	24.55	4.68	11.30	1.30	4.57	5.46
240	2	4.5	40	26.32	2.93	9.50	1.35	4.82	5.17
180	10	4.5	58	24.63	4.20	12.70	1.27	4.35	5.35
210	2	1.0	54	24.82	4.06	11.70	1.22	4.36	5.30

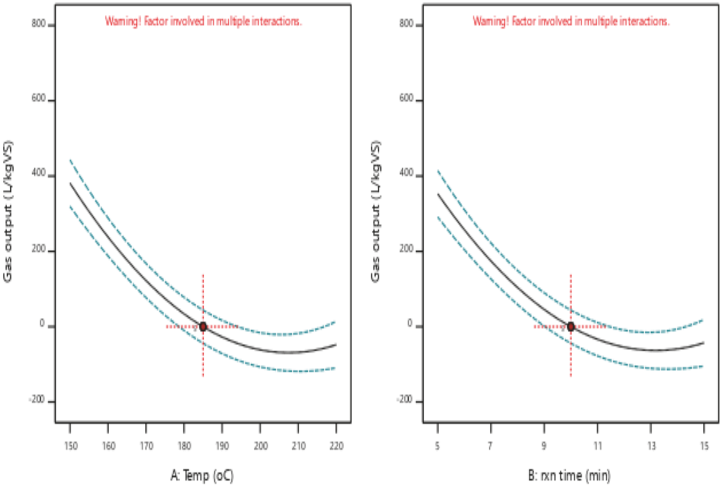
Appendix C: Surface response models for hydrothermal pretreatment of cocoa pods.



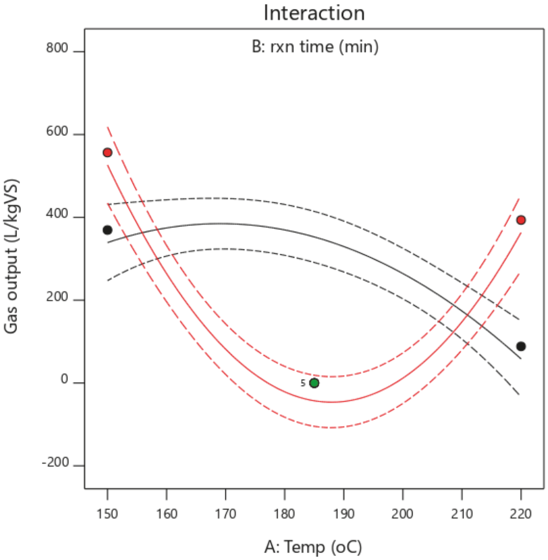
C-1: Perturbation plot of lignin response factor after hydrothermal pretreatment of cocoa pods.



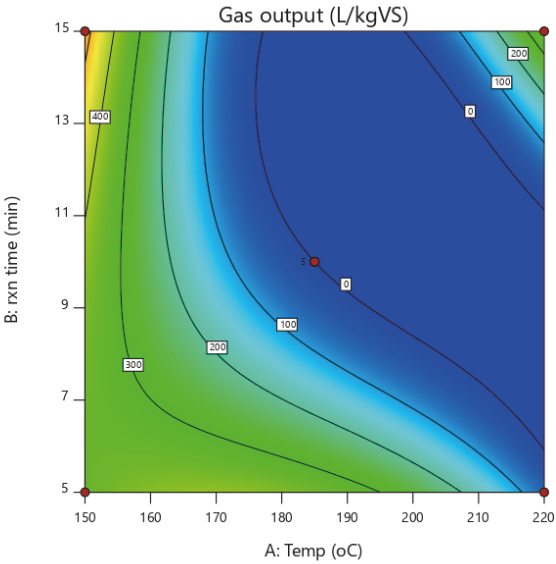
C-2: Factor interactions between lignin content of the pretreated samples and the reaction.



C-3: Perturbation plot of specific biogas yield response factor after hydrothermal pretreatment of cocoa pods.

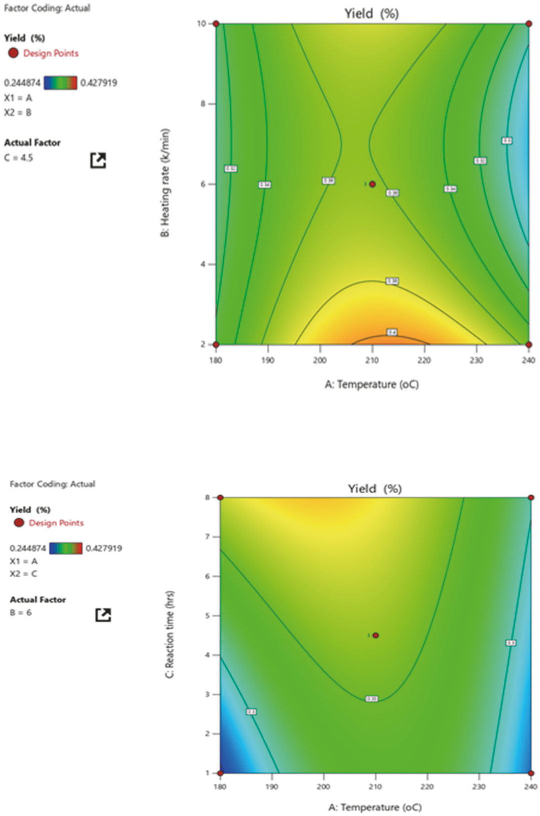


C-4: Factor interaction between process temperature and reaction time for specific biogas yield of hydrothermally pretreated cocoa pods.

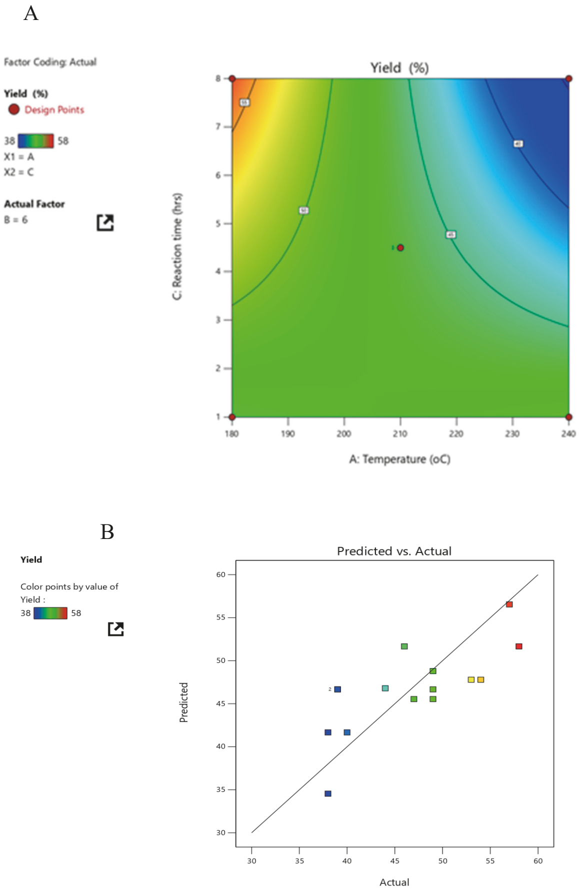


C-5: 2D surface response plot of specific biogas output response factor against the reaction time and process temperature.

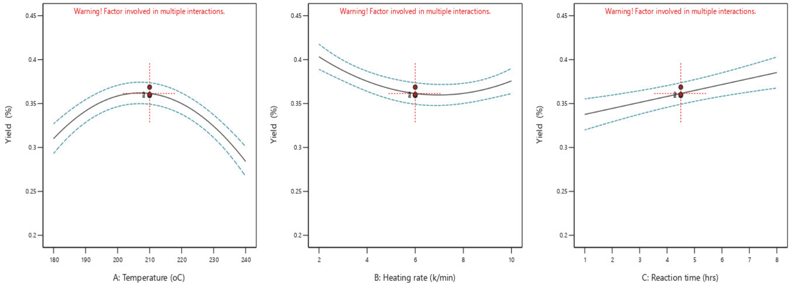
Appendix D: Surface response models for hydrothermal carbonization of cocoa pods and cashew peduncle residues

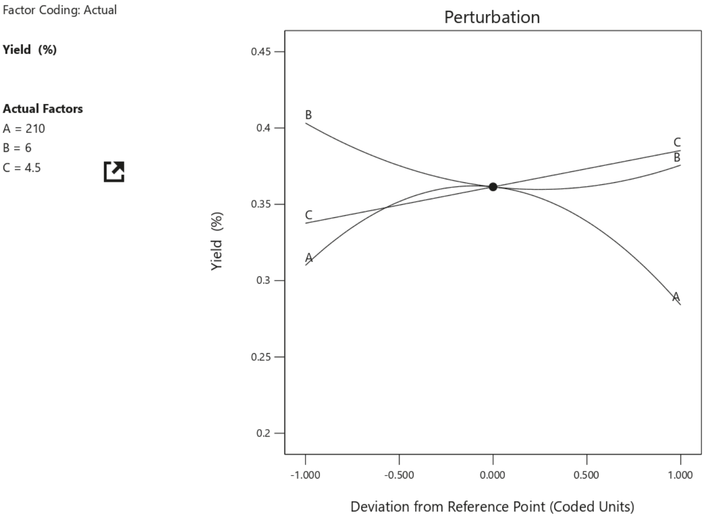


D-1: 2-D surface response plot for the yield of cashew peduncle hydrochar during varying process conditions.

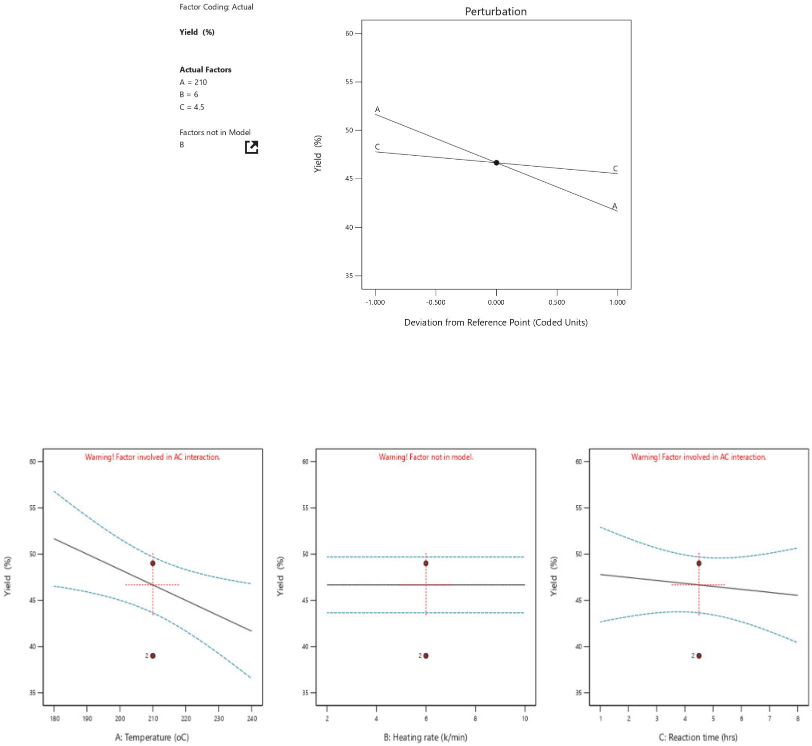


D-2: 2-D response surface models (A) and plot of actual and predicted yield response values (B) for cocoa pods hydrochar.

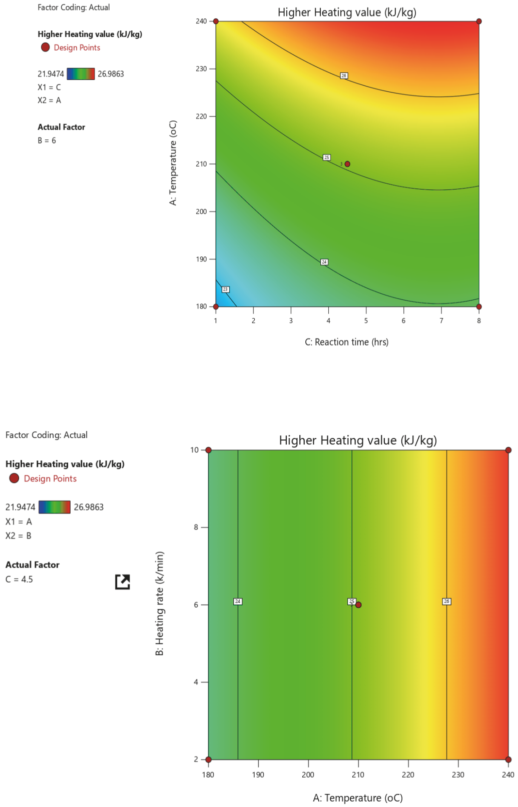




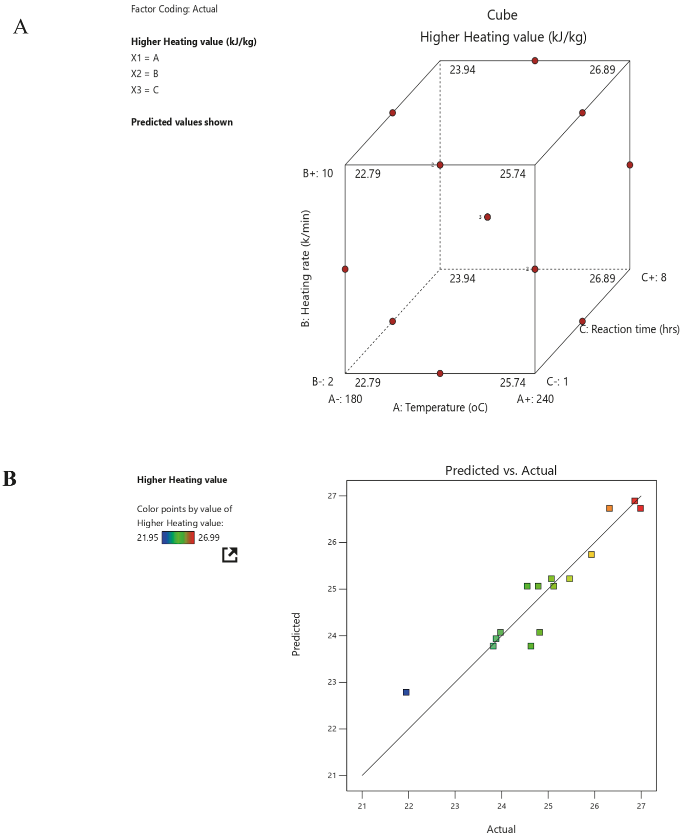
D-3: Perturbation plot of the process parameters with respect to cashew peduncle hydrochar yield.



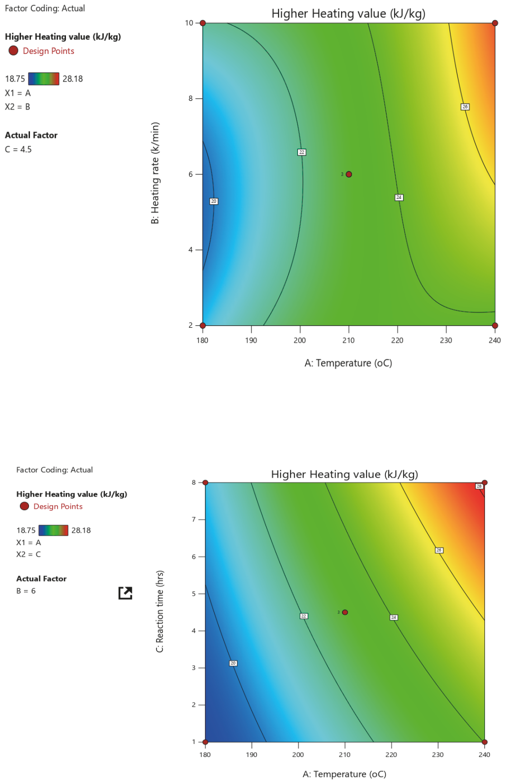
D-3: Perturbation plot of the process parameters with respect to the yield of cocoa pods hydrochar.



D-4: 2-D surface response plot for the HHV of cashew peduncle hydrochar.

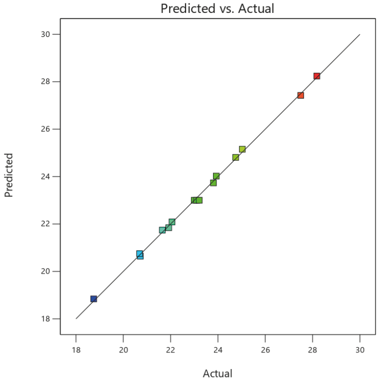


D-5: Box plot of HHV of cashew peduncle hydrochar (A) and plot of predicted HHV response values vrs the actual HHV response values.

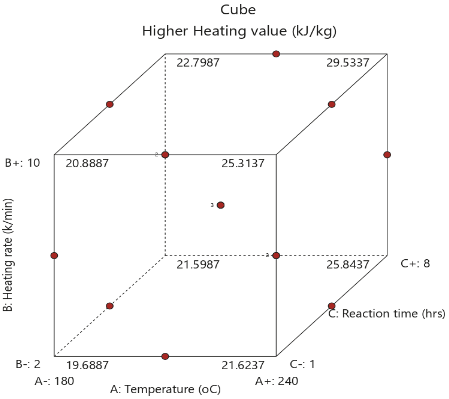


D-6: 2-D Surface response models for HHV of cocoa pods hydrochar.

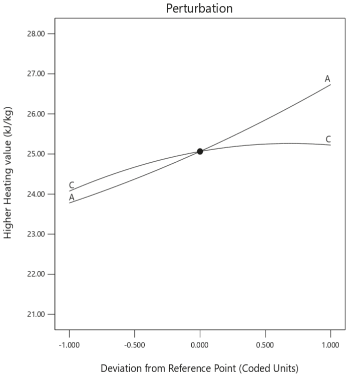
A



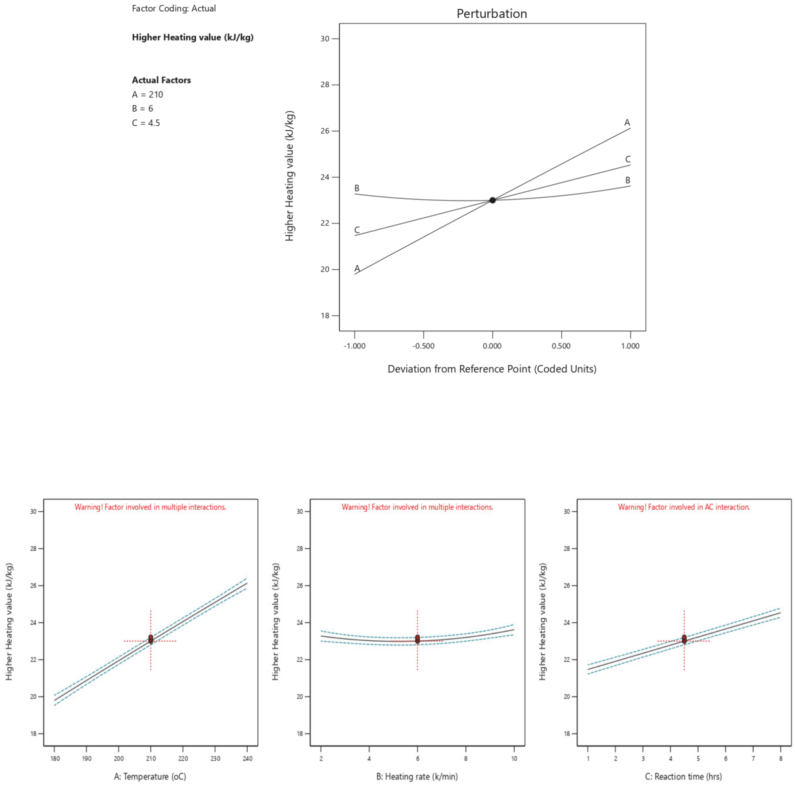
B



D-7: Plot of predicted vrs atual (A) and box plot HHV response factor for cocoa pods hydrochar.

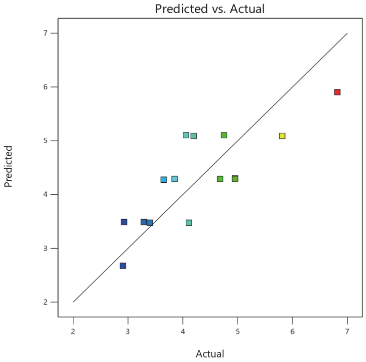


D-8: Perturbation plat of process parameters for HHV of cashew peduncle hydrochars.

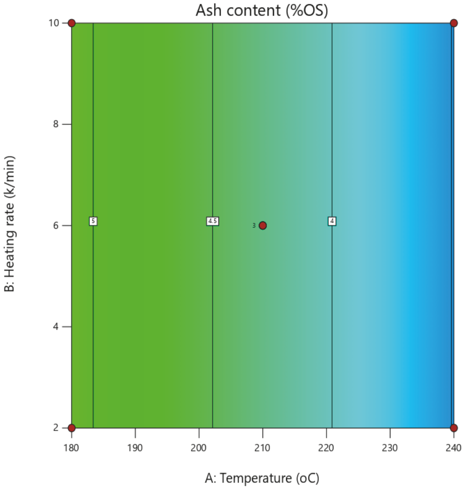


D-9: Perturbation plot of process parameters for HHV of cocoa pods.

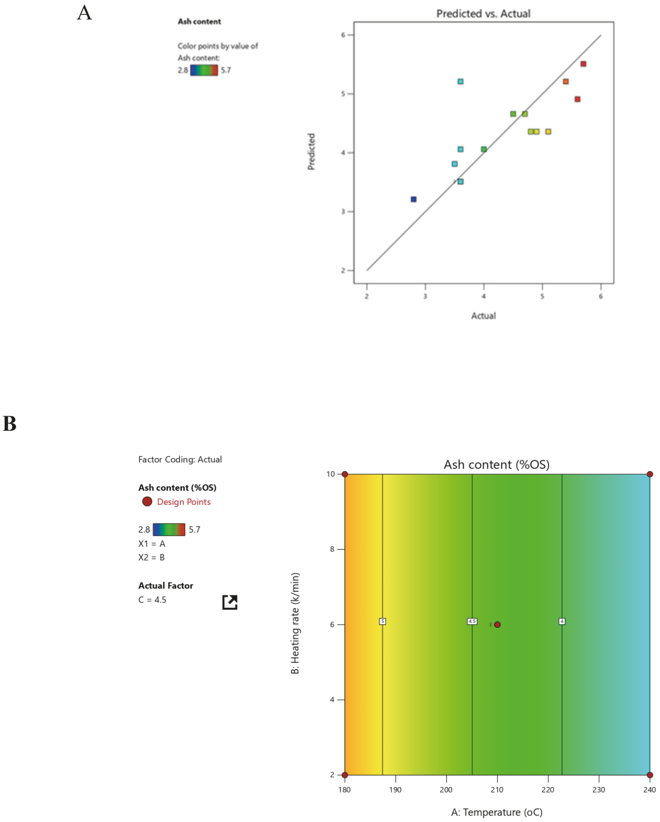
A



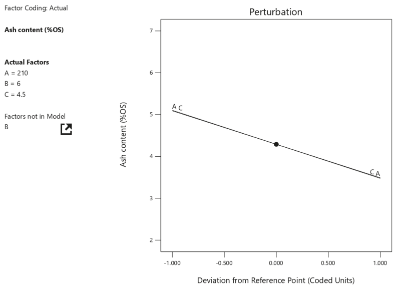
B



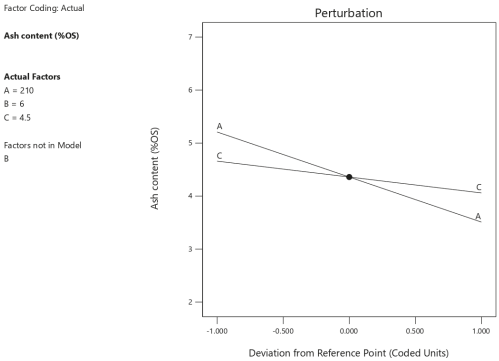
D-10: Predicted vrs actual values for ash content response factor (A) and 2-D surface response plot for ash content response factor for cashew peduncle hydrochar.



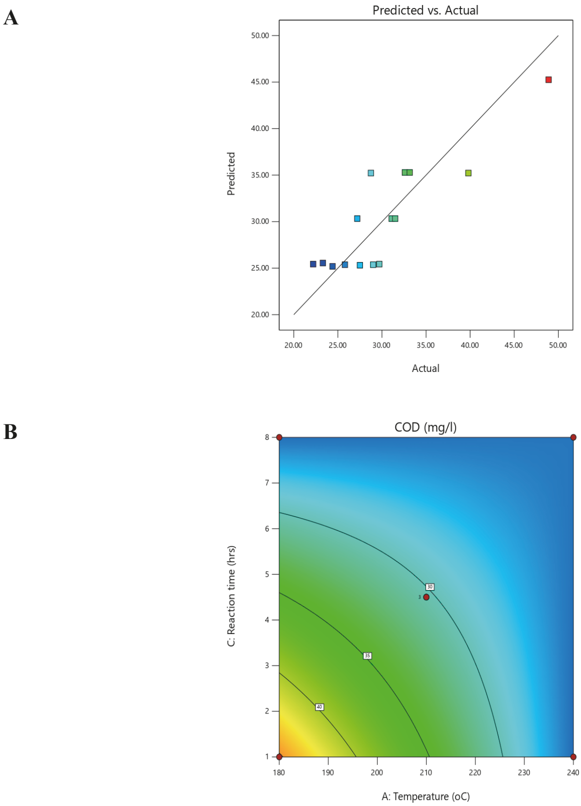
D-11: Predicted vrs actual values for ash content response factor (A) and 2-D surface response plot for ash content response factor for cocoa pods hydrochar.



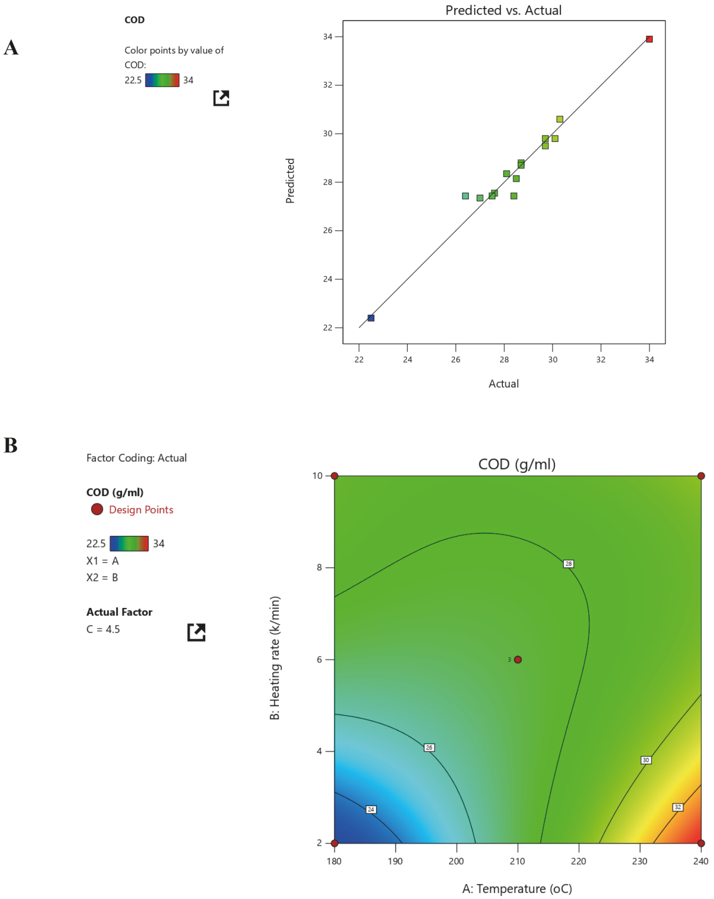
D-12: Perturbation plot of process parameters for cashew ash content of cashew peduncle hydrochar.



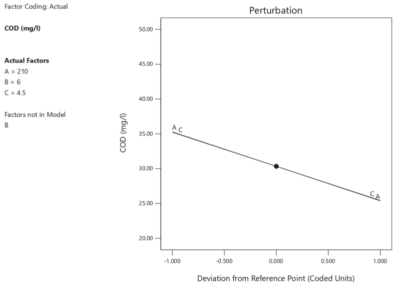
D-13: Perturbation plot of process parameters for cocoa pods ash content of cocoa pods hydrochar.



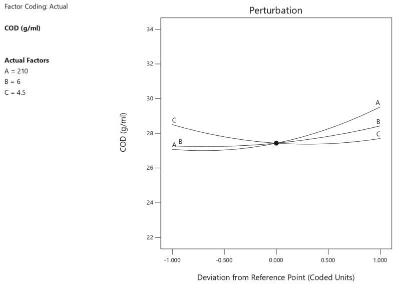
D-14: Predicted vrs actual values for the COD response factor (A) and 2-D surface response plot for ash content response factor for cashew peduncle hydrolysate after hydrothermal carbonization.



D-15: Predicted vrs actual values for ash content response factor (A) and 2-D surface response plot for ash content response factor for cocoa pods hydrolysate after hydrothermal carbonization.

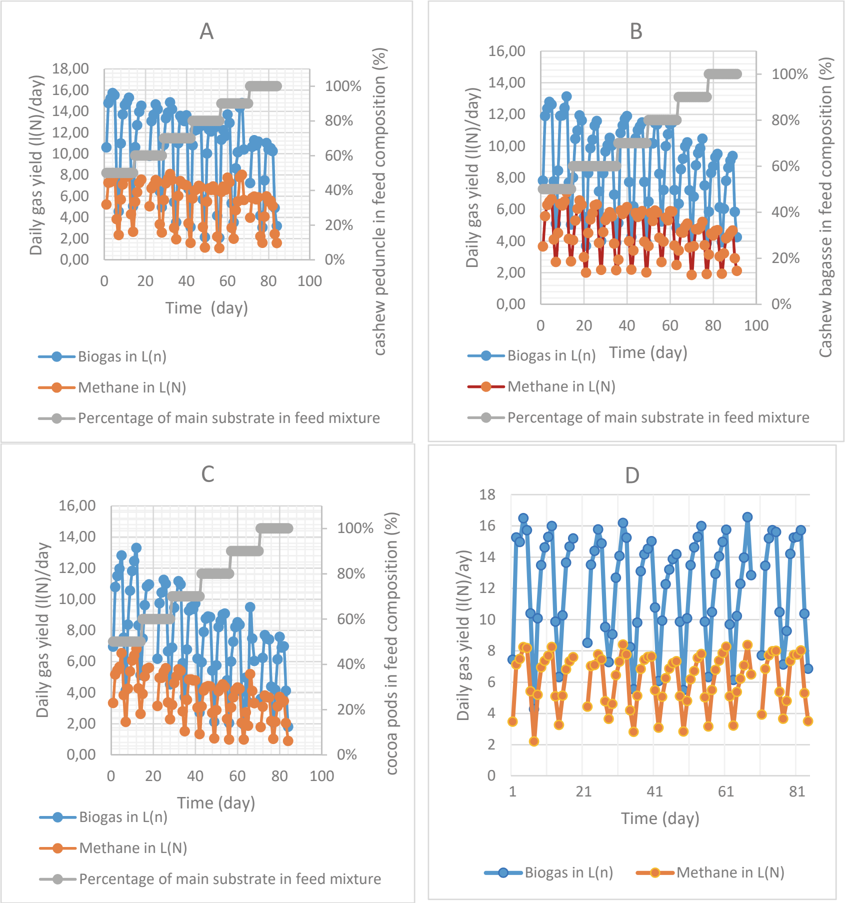


D-16: Perturbation plot of process parameters for cashew Ash content of cashew peduncle after hydrothermal carbonization.



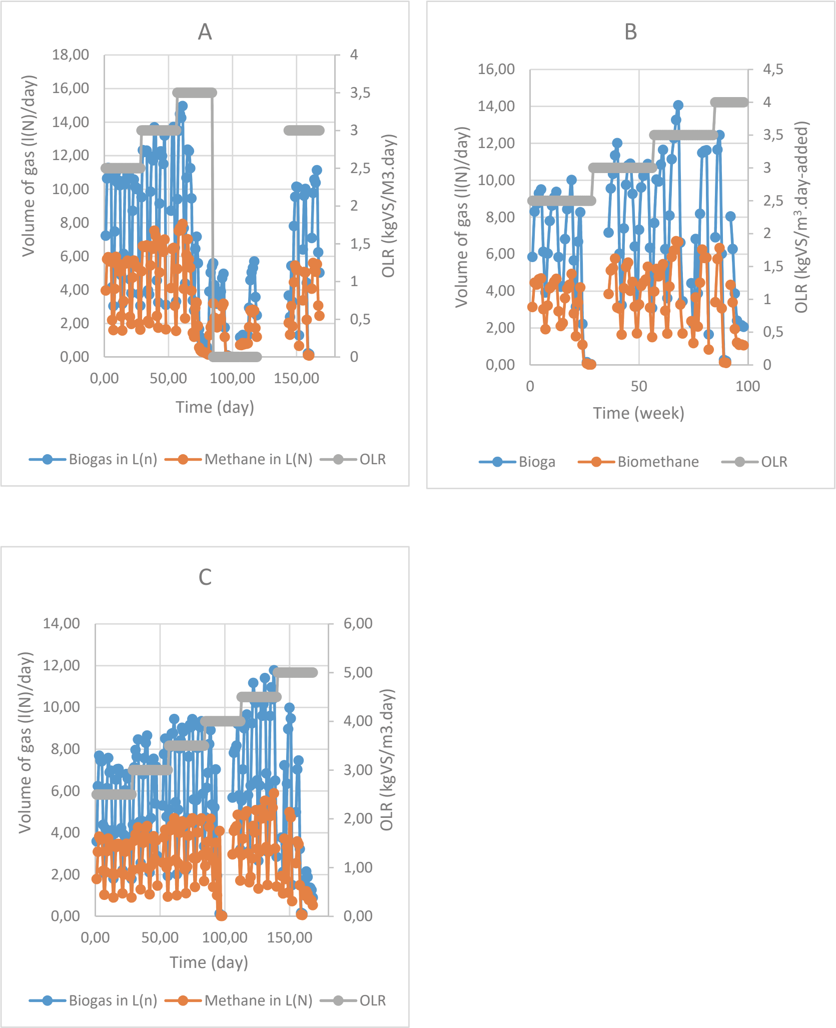
D-17: Perturbation plot of process parameters for COD content of cocoa pods hydrolysate after hydrothermal carbonization.

Appendix E: Continuous digestion results



E-1: Daily biogas and biomethane production from co-digested cashew peduncle (A), cashew bagasse (B) and cocoa pods (C) with maize silage and mono digested maize silage (D).

Biogas production from mono digested cashew peduncle, cashew bagasse and cocoa pods at varying OLR starting at 2.5 kgVS/m^3.day but constant hydraulic retention time.



E-2: Daily biogas and biomethane production from mono digested cashew peduncle (A), cashew bagasse (B) and cocoa pods (C).

In dieser Reihe bisher erschienen

Band I
10. DIALOG Abfallwirtschaft MV
– Von der Abfallwirtschaft zur Energiewirtschaft.
Tagungsband, erschienen im Juni 2007, ISBN 987-3-86009-004-6

Band II
Ellen-Rose Trübger
Entwicklung eines Ansatzes zur Berücksichtigung der ungesättigten Zone bei der Grundwassersimulation von Feuchtgebieten.
Dissertation, erschienen im August 2007, ISBN 978-3-86009-006-0

Band III
René Dechow
Untersuchungen verschiedener Ansätze der Wasserhaushalts- und Stofftransportmodellierung hinsichtlich ihrer Anwendbarkeit in Stickstoffhaushaltsmodellen.
Dissertation, erschienen im September 2007, ISBN 978-3-86009-016-9

Band IV
Carolin Wloczyk
Entwicklung und Validierung einer Methodik zur Ermittlung der realen Evapotranspiration anhand von Fernerkundungsdaten in Mecklenburg-Vorpommern.
Dissertation, erschienen im September 2007, ISBN 978-3-86009-009-1

Band 5
1. Rostocker Bioenergieforum.
Bioenergieland Mecklenburg-Vorpommern.
Tagungsband, erschienen im Oktober 2007, ISBN 978-3-86009-013-8

Band 6
Kulturtechniktagung 2007.
Ostseeverschmutzung und Flächenentwässerung.
Tagungsband, erschienen im Januar 2008, ISBN 978-3-86009-018-3

Band 7
Enrico Frahm
Bestimmung der realen Evapotranspiration für Weide (Salix spp.) und Schilf (Phragmites australis) in einem nordostdeutschen Flusstalmoor.
Dissertation, erschienen im Mai 2008, ISBN 978-3-86009-023-7

Band 8
Jenny Haide
Methode zur Quantifizierung der Einflüsse auf Vorgangsdauern lohnintensiver Arbeiten am Beispiel von Pflasterarbeiten.
Dissertation, erschienen im Juni 2008, ISBN 978-3-86009-024-4

Band 9
11. DIALOG Abfallwirtschaft MV
Chancen und Risiken für die deutsche Abfallwirtschaft im Ausland.
Tagungsband, erschienen im Juni 2008, ISBN 978-3-86009-029-9

Band 10
Stefan Cantré
Ein Beitrag zur Bemessung geotextiler Schläuche für die Entwässerung von Baggergut.
Dissertation, erschienen im Juni 2008, ISBN 978-3-86009-032-9

Band 11
Birgit Wüstenberg
Praxis der Standortwahl von Sportboothäfen im Küstenbereich Mecklenburg-Vorpommerns und Entwicklung einer Bewertungsmethode als Planungshilfe.
Dissertation, erschienen im Juli 2008, ISBN 978-3-86009-033-6

Band 12
André Clauß
Erhöhung der Trinkwasserversorgungssicherheit in Havarie- und Krisensituationen durch neue Handlungsalgorithmen sowie Einbeziehung bisher ungenutzter Ressourcen am Beispiel von Bergbaugrubenwasser.
Dissertation, erschienen im September 2008, ISBN 978-3-86009-037-4

Band 13
Peter Degener
Sickerwasserkreislauf zur Behandlung von Sickerwässern der aerob-biologischen Restabfallbehandlung (Restabfallrotte).
Dissertation, erschienen im Oktober 2008, ISBN 978-3-86009-043-5

Band 14
2. Rostocker Bioenergieforum
Innovationen für Klimaschutz und wirtschaftliche Entwicklung.
Tagungsband, erschienen im Oktober 2008, ISBN 978-3-86009-044-2

Band 15
7. Rostocker Abwassertagung
Fortschritte auf dem Gebiet der Abwasserentsorgung.
Tagungsband, erschienen im November 2008, ISBN 978-3-86009-045-9

Band 16
Christian Noß
Strömungsstrukturen kleiner naturnaher Fließgewässer unter Berücksichtigung von Turbulenztheorie und Dispersionsmodellen.
Dissertation, erschienen im Januar 2009, ISBN 978-3-86009-054-1

Band 17
Ralf Schröder
Entwicklung von Möglichkeiten zur Messung der N2-Übersättigung sowie Methoden zur Reduzierung der Schwimmschlammbildung.
Dissertation, erschienen im Februar 2009, ISBN 978-3-86009-055-8

Band 18
Elmar Wisotzki
Bodenverfestigungen mit Kalk-Hüttensand-Gemischen.
Dissertation, erschienen im April 2009, ISBN 978-3-86009-059-6

Band 19
Ramez Mashkouk
Untersuchungen zur Adsorption und biologischen Aktivität an Aktivkohlefilter unter den Bedingungen der Wasseraufbereitung im Wasserwerk Rostock.
Dissertation, erschienen im April 2009, ISBN 978-3-86009-060-2

Band 20
Torsten Birkholz
Handlungserfordernisse und Optimierungsansätze für kommunale Ver- und Entsorgungsunternehmen im Zusammenhang mit demografischen Veränderungen im ländlichen Raum aufgezeigt an einem Beispiel in Mecklenburg-Vorpommern.
Dissertation, erschienen im Mai 2009, ISBN 978-3-86009-061-9

Band 21
12. DIALOG Abfallwirtschaft MV
Aktuelle Entwicklungen in der Abfallwirtschaft.
Tagungsband, erschienen im Juni 2009, ISBN 978-3-86009-062-6

Band 22
Thomas Fritz
Entwicklung, Implementierung und Validierung eines praxisnahen Verfahrens zur Bestimmung von Biogas- bzw. Methanerträgen.
Dissertation, erschienen im Oktober 2009, ISBN 978-3-86009-065-7

Band 23
3. Rostocker Bioenergieforum
Bioenergie – Chance und Herausforderung für die regionale und globale Wirtschaft.
Tagungsband, erschienen im Oktober 2009, ISBN 978-3-86009-065-8

Band 24
Muhammad Mariam
Analyse von Gefahrenpotenzialen für die Trinkwasserversorgung der Stadt Rostock unter besonderer Berücksichtigung von Schadstoffausbreitungsvorgängen in der Warnow.
Dissertation, erschienen im Februar 2010, ISBN 978-3-86009-078-7

Band 25
Manja Steinke
Untersuchungen zur Behandlung von Abwässern der Fischverarbeitungsindustrie.
Dissertation, erschienen im Juni 2010, ISBN 978-3-86009-085-5

Band 26
13. DIALOG Abfallwirtschaft MV
Die Kreislauf- und Abfallwirtschaft im Wandel. Wohin gehen die rechtlichen und technischen Entwicklungen?
Tagungsband, erschienen im Juni 2010, ISBN 978-3-86009-087-9

Band 27
4. Rostocker Bioenergieforum
Zukunftstechnologien für Bioenergie
Tagungsband, erschienen im Oktober 2010, ISBN 978-3-940364-12-8

Band 28
Dirk Banemann
Einfluss der Silierung und des Verfahrensablaufs der Biomassebereitstellung auf den Methanertrag unter Berücksichtigung eines Milchsäurebakteriensiliermittel
Dissertation, erschienen im Januar 2011, ISBN 978-3-86009-087-9

Band 29
14. DIALOG Abfallwirtschaft MV
Abfall als Wertstoff- und Energiereserve
Tagungsband, erschienen im Juni 2011, ISBN 978-3-940364-18-0

Band 30
5. Rostocker Bioenergieforum
Tagungsband, erschienen im November 2011, ISBN 978-3-940364-20-3

Band 31
8. Rostocker Abwassertagung
Erhöhung der Effektivität von Abwasserentsorgungsanlagen
Tagungsband, erschienen im November 2011, ISBN 978-3-86009-120-3

Band 32
6. Rostocker Bioenergieforum
Tagungsband, erschienen im Juni 2012, ISBN 978-3-940364-27-2

Band 33
Ishan Machlouf
Untersuchungen zur Nitratelimination bei der Trinkwasseraufbereitung unter Berücksichtigung syrischer Verhältnisse
Dissertation, erschienen im März 2013, ISBN 978-3-86009-204-0

Band 34
Ralph Sutter
Analyse und Bewertung der Einflussgrößen auf die Optimierung der Rohbiogasproduktion hinsichtlich der Konstanz von Biogasqualität und -menge
Dissertation, erschienen im März 2013, ISBN 978-3-86009-202-6

Band 35
Wolfgang Pfaff-Simoneit
Entwicklung eines sektoralen Ansatzes zum Aufbau von nachhaltigen Abfallwirtschaftssystemen in Entwicklungsländern vor dem Hintergrund von Klimawandel und Ressourcenverknappung
Dissertation, erschienen im Mai 2013, ISBN 978-3-86009-203-3

Band 36
7. Rostocker Bioenergieforum
Tagungsband, erschienen im Juni 2013, ISBN 978-3-86009-207-1

Band 37
Markus Helftewes
Modellierung und Simulation der Gewerbeabfallaufbereitung vor dem Hintergrund der Outputqualität, der Kosteneffizienz und der Klimabilanz
Dissertation, erschienen im Oktober 2013, ISBN 978-3-86009-402-0

Band 38
Jan Stefan Riha
Detektion und Quantifizierung von Cyanobakterien in der Ostsee mittels Satellitenfernerkundung
Dissertation, erschienen im Oktober 2013, ISBN 978-3-86009-403-7

Band 39
Peter Helmke
Optimierung der Verarbeitungs-, Gebrauchs- und Entsorgungseigenschaften eines naturfaserverstärkten Kunststoffes unter Berücksichtigung automobiler Anforderungen
Dissertation, erschienen im November 2013, ISBN 978-3-86009-404-4

Band 40
Andrea Siebert-Raths
Modifizierung von Polylactid (PLA)für technische Anwendungen
Verfahrenstechnische Optimierung der Verarbeitungs- und Gebrauchseigenschaften
Dissertation, erschienen im Januar 2014 ISBN 978-3-86009-405-1

Band 41
Fisiha Getachew Argaw
Agricultural Machinery Traffic Influence on Clay Soil Compaction as Measured by the Dry Bulk Density
Dissertation, erschienen im Januar 2014 ISBN 978-3-86009-406-8

Band 42
Tamene Adugna Demissie
Climate change impact on stream flow and simulated sediment yield to Gilgel Gibe 1 hydropower reservoir and the effectiveness of Best Management Practices
Dissertation, erschienen im Februar 2014 ISBN 978-3-86009-407-5

Band 43
Paul Engelke
Untersuchungen zur Modellierung des Feststofftransports in Abwasserkanälen: Validierung in SIMBA®
Dissertation, erschienen im Februar 2014 ISBN 978-3-86009-408-2

Band 44
16. DIALOG Abfallwirtschaft MV
Aktuelle Entwicklungen in der Abfall- und Ressourcenwirtschaft
Tagungsband, erschienen im April 2014, ISBN 978-3-86009-410-5

Band 45
8. Rostocker Bioenergieforum, 19.-20. Juni 2014 an der Universität Rostock
Tagungsband, erschienen im Juni 2014, ISBN 978-3-86009-412-9

Band 46
Abschlussbericht Projekt CEMUWA − Climate protection, natural resources management and soil improvement by combined Energetic and Material Utilization of lignocellulosic agricultural WAstes and residues
Projektbericht, erschienen im September 2014, ISBN 978-3-86009-413-6

Band 47
8. Rostocker Baggergutseminar, 24.-25. September 2014 in Rostock
Tagungsband, erschienen im September 2014, ISBN 978-3-86009-414-3

Band 48
Michael Kuhn
Mengen und Trockenrückstand von Rechengut kommunaler Kläranlagen
Dissertation, erschienen im Oktober 2014 ISBN 978-3-86009-415-0

Band 49
9. Rostocker Abwassertagung, Infrastruktur- und Energiemanagement –
ein Geschwisterpaar der Wasserwirtschaft 12. November 2014 in Rostock
Tagungsband, erschienen im November 2014, ISBN 978-3-86009-416-7

Band 50
Mulugeta Azeze Belete
Modeling and Analysis of Lake Tana Sub Basin Water Resources Systems, Ethiopia
Dissertation, erschienen im Dezember 2014 ISBN 978-3-86009-422-8

Band 51
Daniela Dressler
Einfluss regionaler und standortspezifischer Faktoren auf die Allgemeingültigkeit ökologischer und primärenergetischer Bewertungen von Biogas
Dissertation, erschienen im Oktober 2014 ISBN 978-3-86009-424-2

Band 52
9. Rostocker Bioenergieforum, 18.-19. Juni 2015 in Rostock
Tagungsband, erschienen im November 2014, ISBN 978-3-86009-425-9

Band 53
Nils Engler
Spurenelementkonzentrationen und biologische Aktivität in NaWaRo-Biogasfermentern
Dissertation, erschienen im September 2015 ISBN 978-3-86009-427-3

Band 54
Thomas Schmidt
Möglichkeiten der Effizienzsteigerung bei der anaeroben Vergärung
von Weizenschlempe
Dissertation, erschienen im Oktober 2015 ISBN 978-3-86009-428-0

Band 55
Thomas Dorn
Principles, Opportunities and Risks associated with the transfer of environmental technology between Germany and China using the example of thermal waste disposal
Dissertation, erschienen im Dezember 2015 ISBN 978-3-86009-429-7

Band 56
Uwe Holzhammer
Biogas in einer zukünftigen Energieversorgungsstruktur mit hohen Anteilen fluktuierender Erneuerbarer Energien
Dissertation, erschienen im Dezember 2015 ISBN 978-3-86009-430-3

Band 57
17. DIALOG Abfallwirtschaft MV
Aktuelle Entwicklungen in der Abfall- und Ressourcenwirtschaft,
15. Juni 2016 in Rostock,
Tagungsband, erschienen im Juni 2016, ISBN 978-3-86009-432-7

Band 58
10. Rostocker Bioenergieforum, 16.-17. Juni 2016 in Rostock
Tagungsband, erschienen im Juni 2016, ISBN 978-3-86009-433-4

Band 59
Michael Friedrich
Adaptation of growth kinetics and degradation potential of organic material in activated sludge
Dissertation, erschienen im Juli 2016 ISBN 978-3-86009-434-1

Band 60
Nico Schulte
Entwicklung von Qualitätsprüfungen für die haushaltsnahe Abfallsammlung im Holsystem
Dissertation, erschienen im Juli 2016 ISBN 978-3-86009-435-8

Band 61
Ullrich Dettmann
Improving the determination of soil hydraulic properties of peat soils at different scales
Dissertation, erschienen im September 2016 ISBN 978-3-86009-436-5

Band 62
Anja Schreiber
Membranbasiertes Verfahren zur weitergehenden Vergärung
von feststoffreichen Substraten in landwirtschaftlichen Biogasanlagen
Dissertation, erschienen im Oktober 2016 ISBN 978-3-86009-446-4

Band 63
André Körtel
Entwicklung eines selbstgängigen statischen Verfahrens zur biologischen Stabilisierung und Verwertung organikreicher Abfälle unter extrem ariden Bedingungen für Entwicklungs- und Schwellenländer, am Beispiel der Stadt Teheran
Dissertation, erschienen im Oktober 2016 ISBN 978-3-86009-447-1

Band 64
Ayman Elnaas
Actual situation and approach for municipal solid waste treatment in the Arab region
Dissertation, erschienen im Oktober 2016 ISBN 978-3-86009-448-8

Band 65
10. Rostocker Abwassertagung, Wege und Werkzeuge für eine zukunftsfähige Wasserwirtschaft im norddeutschen Tiefland, 8. November 2016 in Rostock
Tagungsband, erschienen im November 2016, ISBN 978-3-86009-449-5

Band 66
Gunter Weißbach
Mikrowellen-assistierte Vorbehandlung lignocellulosehaltiger Reststoffe
Dissertation, erschienen im November 2016 ISBN 978-3-86009-450-1

Band 67
Leandro Janke
Optimization of anaerobic digestion of sugarcane waste for biogas production in Brazil
Dissertation, erschienen im Mai 2017 ISBN 978-3-86009-454-9

Band 68
11. Rostocker Bioenergieforum, 22.-23. Juni 2017 in Rostock
Tagungsband, erschienen im Juni 2017, ISBN 978-3-86009-455-6

Band 69
Claudia Demmig
Einfluss des Erntezeitpunktes auf die anaerobe Abbaukinetik der Gerüstsubstanzen im Biogasprozess
Dissertation, erschienen im Juli 2017, ISBN 9978-3-86009-456-3

Band 70
Christian Koepke
Die Ermittlung charakteristischer Bodenkennwerte der Torfe und Mudden Mecklenburg-Vorpommerns als Eingangsparameter für erdstatische Berechnungen nach Eurocode 7 / DIN 1054
Dissertation, erschienen im Juni 2017, ISBN 978-3-86009-457-0

Band 71
Sven-Henning Schlömp
Geotechnische Untersuchung und Bewertung bautechnischer Eignung
von Müllverbrennungsschlacken und deren Gemischen mit Böden
Dissertation, erschienen im Juni 2017, ISBN 978-3-86009-458-7

Band 72
Anne-Katrin Große
Baggergut im Deichbau – Ein Beitrag zur geotechnischen Charakterisierung
und Erosionsbeschreibung feinkörniger, organischer Sedimente
aus dem Ostseeraum zur Einschätzung der Anwendbarkeit
Dissertation, erschienen im Juni 2017, ISBN 978-3-86009-459-4

Band 73
Thomas Knauer
Steigerung der Gesamteffizienz von Biogasanlagen durch thermische
Optimierung
Dissertation, erschienen im Juli 2017, ISBN 978-3-86009-460-0

Band 74
Mathhar Bdour
Electrical power generation from residual biomass by combustion
in externally fired gas turbines (EFGT)
Dissertation, erschienen im August 2017, ISBN 978-3-86009-468-6

Band 75
Johannes Dahlin
Vermarktungsstrategien und Konsumentenpräferenzen für Dünger und Erden
aus organischen Reststoffen der Biogasproduktion
Dissertation, erschienen im September 2017, ISBN 978-3-86009-469-3

Band 76
Sören Weinrich
Praxisnahe Modellierung von Biogasanlagen
Systematische Vereinfachung des Anaerobic Digestion Model No. 1 (ADM1)
Dissertation, erschienen im März 2018, ISBN 978-3-86009-471-6

Band 77
18. DIALOG Abfallwirtschaft MV
Aktuelle Entwicklungen in der Abfall- und Ressourcenwirtschaft
Tagungsband, erschienen im Juni 2018, ISBN 978-3-86009-472-3

Band 78
12. Rostocker Bioenergieforum
Tagungsband, erschienen im Juni 2018, ISBN 978-3-86009-473-0

Band 79
Tatyana Koegst
Screening approaches for decision support in drinking water supply
Dissertation, erschienen im Juni 2018, ISBN 978-3-86009-474-7

Band 80
Liane Müller
Optimierung des anaeroben Abbaus stickstoffhaltiger Verbindungen durch den Einsatz von Proteasen
Dissertation, erschienen im September 2018, ISBN 978-3-86009-475-4

Band 81
Projektbericht Wasserwirtschaft
KOGGE – **Ko**mmunale **G**ewässer **G**emeinschaftlich **E**ntwickeln
Ein Handlungskonzept für kleine urbane Gewässer am Beispiel
der Hanse- und Universitätsstadt Rostock
Projektbericht, erschienen im September 2018, ISBN 978-3-86009-476-1

Band 82
Adam Feher
Untersuchungen zur Bioverfügbarkeit von Mikronährstoffen für den Biogasprozess
Dissertation, erschienen im Oktober 2018, ISBN 978-3-86009-477-8

Band 83
Constanze Uthoff
Pyrolyse von naturfaserverstärkten Kunststoffen zur Herstellung eines kohlenstoffhaltigen Füllstoffs für Thermoplasten
Dissertation, erschienen im November 2018, ISBN 978-3-86009-478-5

Band 84
Ingo Kaundinya
Prüfverfahren zur Abschätzung der Langzeitbeständigkeit von Kunststoffdichtungsbahnen aus PVC-P für den Einsatz in Dichtungssystemen
von Straßentunneln
Dissertation, erschienen im Dezember 2018, ISBN 978-3-86009-484-6

Band 85
Eric Mauky
A model-based control concept for a demand-driven biogas production
Dissertation, erschienen im Januar 2019, ISBN 978-3-86009-485-3

Band 86
Michael Kröger
Thermochemical Utilization of Algae with Focus on hydrothermal Processes
Dissertation, erschienen im Februar 2019, ISBN 978-3-86009-486-0

Band 87
13. Rostocker Bioenergieforum
Tagungsband, erschienen im Juni 2019, ISBN 978-3-86009-487-7

Band 88
12. Rostocker Abwassertagung
Tagungsband, erschienen im September 2019, ISBN 978-3-86009-488-4

Band 89
Philipp Stahn
Wasser- und Nährstoffhaushalt von Böden unter Mischkulturen und Trockenstress
Dissertation, erschienen im Juli 2019, ISBN 978-3-86009-489-1

Band 90
BioBind: Luftgestützte Beseitigung von Verunreinigungen durch Öl mit biogenen Bindern
Projektbericht, erschienen im September 2019, ISBN 978-3-86009-490-7

Band 91
Jürgen Müller
Die forsthydrologische Forschung im Nordostdeutschen Tiefland: Veranlassung, Methoden, Ergebnisse und Perspektiven
Habilitation, erschienen im Oktober 2019, ISBN 978-3-86009-491-4

Band 92
Marcus Siewert
Bewertung der Ölhavarievorsorge im deutschen Seegebiet auf Grundlage limitierender Randbedingungen – Ein Beitrag zur Verbesserung des Vorsorgestatus
Dissertation, erschienen im November 2019, ISBN 978-3-86009-492-1

Band 93
Camilo Andrés Wilches Tamayo
Technical optimization of biogas plants to deliver demand oriented power
Dissertation, erschienen im Februar 2020, ISBN 978-3-86009-493-8

Band 94
Robert Kopf
Technisches Benchmarking mit Standortqualifikationsstudie biochemischer Energieanlagenprojekte (Beispiel Biogas)
Dissertation, erschienen im Februar 2020, ISBN 978-3-86009-494-5

Band 95
14. Rostocker Bioenergieforum und 19. DIALOG Abfallwirtschaft MV
Tagungsband, erschienen im Juni 2020, ISBN 978-3-86009-507-2
DOI https://doi.org/10.18453/rosdok_id00002650

Band 96
Safwat Hemidat
Feasibility Assessment of Waste Management and Treatment in Jordan
Dissertation, erschienen im Juli 2020, ISBN 978-3-86009-509-6

Band 97
Andreas Heiko Metzing
Verdichtung von ungebundenen Pflasterdecken und Plattenbelägen - Untersuchungen zur Lagerungsdichte des Fugenmaterials
Dissertation, erschienen im Juli 2020, ISBN 978-3-86009-510-2

Band 98
Ying Zhou
Research on Utilization of Hydrochars Obtained by the Organic Components of Municipal Solid Waste
Dissertation, erschienen im November 2020, ISBN 978-3-86009-515-7

Band 99
Mathias Gießler
Ein prozessbasiertes Modell zur wirtschaftlich-technischen Abbildung von Abwasserunternehmen – Beispielhafte Anwendung für eine ländliche Region mit Bevölkerungsrückgang
Dissertation, erschienen im November 2020, ISBN 978-3-86009-516-4

Band 100
Dodiek Ika Candra
Development of a Virtual Power Plant based on a flexible Biogas Plant and a Photovoltaic-System
Dissertation, erschienen im Dezember 2020, ISBN 978-3-86009-518-8

Band 101
Thomas Zeng
Prediction and reduction of bottom ash slagging during small-scale combustion of biogenic residues
Dissertation, erschienen im Dezember 2020, ISBN 978-3-86009-519-5

Universität
Rostock
Traditio et Innovatio

ISBN 978-3-86009-520-1
https://doi.org/10.18453/rosdok_id00002818

Schriftenreihe Umweltingenieurwesen ▪ Abfall- und Stoffstromwirtschaft

Bd.
102

Schriftenreihe Umweltingenieurwesen

Agrar- und Umweltwissenschaftliche Fakultät

Band 102

Dissertation

Edward Antwi

Pathways to sustainable bioenergy production from cocoa and cashew residues from Ghana

PROFESSUR **Abfall- und Stoffstromwirtschaft**

Universität
Rostock
Traditio et Innovatio