Effects of Biomass Addition and Fermentation on the Energy Content of Hydrochar Produced by Hydrothermal Carbonization (HTC) with Faecal Sludge

by

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Abstract

At a global level, faecal sludge management (FSM) is in need of the effective technologies that have to accomplish the basic sanitation problems such as pathogen removals, pre/post treatment, large foot print etc. Additionally, the proposed technology has to overwhelm all the deficiencies from the current practices. Hydrothermal carbonization (HTC) successfully aids to solve the issues, which effectively converts the feedstock into a char coal like hydrochar within few hours at high temperature. Moreover, HTC is most favorable for the wet biomass that produces hydrochar with its energy content. Previous studies were carried out to investigate the effects of faecal sludge (FS) as feedstock, which generally holds higher moisture content. The results prove that HTC is also effective for FS. Although, it shows good results to treat FS, the energy content of hydrochar produced is quiet low while compared with other biomass. Therefore, external biomass such as cassava pulp (CP), dried leaves/grass cuttings (DL), pig manure (PM) and rice husk (RH) were added with FS. It was investigated its effects on the energy content for different mixing ratio at 220°C for 5h. Relatively, all the biomasses used in this study helped to increase the energy content from 3 – 16%. From the results, an effective biomass of cassava pulp had selected that increase the energy content from 19.50 MJ/kg to 22.66 MJ/kg.

In the second phase, to unravel the effects of process parameters on the maximum energy content that can be yielded when FS and CP are involved in the HTC process, parameters such as temperature and operation time were varied and studied the results obtained. As a result, FS: CP produced hydrochar with 23.75 MJ/kg at 250°C for 3 h. Furthermore, the research was extended to examine the characteristics of the produced hydrochar and validated with previous studies. Apart from the energy content, biomass addition also significantly enhanced the carbon content up to 7.23% in hydrochar. Moreover, the emission of CO_2 from HTC was extremely lower, when compared with other technologies. In order to satisfy the economic beneficial aspects, energy balance were carried out for the optimum conditions.

Apart from the biomass addition, HTC is also capable to increase the energy content in the presence of catalyst. Literature reviews revealed that acetic acid as a catalyst significantly gains the energy content. Therefore, in order to produce acetic acid from acidogenesis process, fermentation process was studied by using FS: CP for 35 days as total SRT. HTC experiments were conducted to study the performance of digested sludge, which segregated acetic acid during fermentation. Expected results could not be achieved in this phase, since produced acetic acid through fermentation is too lower. But, HTC was also effective to convert the digested sludge into hydrochar by varying its energy content from 21 - 17.36 MJ/kg. In conclusion, increment on energy content was achieved by addition of biomass with FS and its optimum process parameters were also found. Finally, recommendations for the further research were suggested.

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List of Abbreviations

AD	Anaerobic digestion
ADS	Anaerobically digested sludge
AIT	Asian Institute of technology
BOD	Biochemical oxygen demand
C	Carbon
CAPEX	Capital expenditures
cfu	Colony forming unit
CH_4	Methane gas
CO	Carbon monoxide gas
CO_2	Carbon-di-oxide gas
COD	Chemical oxygen demand
CP	Cassava pulp
DL	Dried leaves/grass cuttings
EEM	Environmental engineering and management
FS	Faecal sludge
FSM	Faecal sludge management
GHG	Green House Gas
H	Hydrogen
H:C	Hydrogen to carbon ratio
H_2S	Hydrogen sulphide gas
HMF	Hydroxy methyl furfural
HTC	Hydrothermal carbonization
kg	Kilogram
kJ	Kilojoules
MC	Moisture content
MJ	Mega joules
N	Nitrogen
N_2	Nitrogen gas
NH_3	Ammonia gas
O	Oxygen
O&M	Operation and maintenances
O:C	Oxygen to carbon ratio
O_2	Oxygen gas
OSS	On-site sanitary system
PM	Pig manure
RH	Rice husk
S	Sulphur
SRT	Sludge retention time
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
TP	Total Phosphorous
TS	Total solids
TSS	Total suspended solids
TVS	Total volatile solids
VM	Volatile matter
WHO	World Health Organization
WWTP	Waste water treatment plant

Chapter 1

Introduction

1.1 Background/Rationale for the Thesis

World Health Organization (WHO, 2004) reports that worldwide 2.7 billion people are lacking proper sanitation. In regions, which are not served by sewers, on-site sanitation system (OSS) is implemented for faecal sludge (FS) collection. Various OSS such as pit-latrines, unsewered public toilets, septic tanks, aqua privies, dry toilets etc., are successfully equipped. FS collected from these have to be treated and safely disposed. Otherwise, the pathogens and microorganisms are the major culprits that causes serious water-borne diseases (Drewko, 2007). Conversely in most of the developing countries they are left untreated into the environment, resulting in adverse impact on human health and natural resources (Ingallinella et al., 2002). WHO (2004) states that every year nearly 1.8 million people perish due to diarrheal disease. Among this 90% are children under age of five from developing countries. Therefore, implementation of a sustainable faecal sludge management (FSM) is the utmost importance in environmental studies.

FSM involves the storage, collection, transport and treatment to safe end uses or disposal of FS (Bassan, 2014a). However, application of these tasks in practical is challenging. Recent rapid urbanization in developing countries does not follow these ecologically sustainable methods regularly. As a result, dumping sites or open defecation grounds are widely noticed in large urban cities of Africa, Asia and parts of Latin America. Deterioration of water quality also degradation of agricultural lands are primarily affected. Therefore, a better, affordable technology is in need in FSM.

1.2 Statement of the Problems

Every year, approximately 0.6 - 1 billion tons of human excreta is generated and probably only 10% is treated (Danso-Boateng et al., 2013). Settling/thickening tanks, unplanted/planted drying beds, co-composting, deep row entrenchment, anaerobic digestion, vermicomposting etc. are generally practiced in developing countries to treat FS. These practices are not flawless since removal of pathogens, pre/post treatment, large foot print, odour problem, leachate infiltration, ground water contamination, Green House gas (GHG) emission, climatic problems are not effectively addressed within a system (Dodane et al., 2014; Ronteltap et al., 2014). Thus, FSM requires an advanced technology that overwhelms all the deficiency. Though advance technologies in wastewater treatment are implemented easily in developing countries, there is a procrastination to accept/adopt the new technologies in FS treatment (Ingallinella et al., 2002). Thus, seeking the affordable technologies is broadly under in research.

FS is treated either physical/chemical/biological mechanisms. Municipal wastewater sludge has been extensively treated by using anaerobic digestion (AD), in order to produce renewable energy. Although it produces the biogas potentially, still it has been revealed the complications for the disposal of digested sludge (Appels et al., 2008; McCarty, 1964). It requires additional treatment such as solar/thermal drying and sludge incineration (Ambulkar et al., 2014). The main drawbacks are listed out that supply of external energy is necessary in the drying process and solar drying is entirely decided by the regional climate. According to Turovskiy and Mathai (2006), burning of sludge with >70%

moisture content is difficult, which requires additional pretreatment (combustion) before drying. Moreover, the products from these technologies are getting low market value (Ambulkar et al., 2014). Hence, thermo-chemical processes have been introduced to produce coal-like material from any biomass waste. Pyrolysis, gasification, torrefaction and hydrothermal carbonization (HTC) are the various techniques involved. These technologies have been discovered based on the natural coal formation. Among theses, HTC has number of advantages compared with the others.

HTC principally converts the feedstocks inside a closed vessel suspended in water, where high pressure and oxygen free environment are maintained. As a result of thermo-chemical reactions yield a coal-water-slurry product (Guiotoku et al., 2011). HTC is a novel technology that produces renewable bio energy substance within several minutes to hours (Libra et al., 2011). The advantage of HTC over pyrolysis process is it is ready to treat wet biomass without any pretreatment. Additionally, HTC is very effective at low temperature range (<300°C) whereas, liquefaction and gasification processes require higher temperature range (>800°C) (Shrestha, 2014). Comparatively, HTC is a better solution in FSM, which converts wet biomass waste including FS into coal-like product.

Hydrochar, the solid achieved from HTC, has gained energy content with rich carbon content and can be used as a sustainable bio-energy (Libra et al., 2011). Fossil fuels can be substituted by hydrochar biofuels (Child, 2014). Thus, it improves the environmental quality by reducing leachate losses, pollutant controls, carbon sequestration in terms of controlling GHG emissions and increasing the soil fertility (Ippolito et al., 2012). The applications of the products include in the field of ion-binding, pollutant absorbent, particle binding, catalysts etc,. The liquid by product from the process can also be applicable in many fields. Overall, HTC is overwhelmed by its compact reactor design, processing time, minimal pre/post treatment while comparing with the conventional/ biological treatment (Titirici et al., 2007).

Many experiments have been carried out in HTC process by using different types of biomass or agricultural residues for different temperature and reaction time. It significantly increases the energy and carbon content. Ramke et al., (2009) used various organic wastes such as municipal solid waste, commercial waste, industrial waste/residues, agricultural residues and silvicultral residues in HTC. From the results, the energy content approximately varies from 10 – 30 MJ/kg depending on the feedstocks. According to Lubeck (2011), primary sewage sludge (PSS) from the treatment plant is also capable to produce the energy content of 19 – 23 MJ/kg. The hydrochar gained higher energy content when fresh human excreta is used as feedstock (Afolabi and Wheatley, 2014). It is evident that HTC is capable of transforming any type of biomass into a carbonized material. Additionally, it carbonizes the digested sludge effectively sludge (Ramke et al., 2009; Lubeck 2011). Mixing of different agricultural residues as a feedstock in HTC process is also yielded higher energy content (Oliveria et al., 2013; Ramke et al., 2009). Henceforth, to accomplish the sustainable sanitary in FSM, HTC can be involved to treat the FS very effectively.

The purpose of this study is to enhance the energy content of hydrochar produced from FS by adding different types of biomass. Investigations the optimum conditions on process parameters (temperature, reaction time) were determined from the effective biomass. Additionally, the effects of fermentation on HTC were also studied.

1.3 Objectives of the Research

To investigate the effects of hydrochar produced by addition of different type of biomass with FS.

1.3.1 Specific Objectives

- To investigate the effects of biomass addition with FS in HTC process for different mixing ratio.
- To determine the optimum process parameters for the effective biomass with FS for different temperature and reaction time.
- To analyze the effects of digested sludge from fermentation process in HTC process.

1.4 Scope of the Study

A 1-L high-pressure HTC reactor was utilized for batch experiments at Environmental Engineering and Management (EEM), ambient laboratory in the Asian Institute of Technology (AIT), Pathumthani, Thailand. FS was collected from pathumthani municipal emptying truck. Biomass such as cassava pulp (CP), dried leaves/grass (DL), pig manure (PM), rice husk (RH) were sourced locally. The effects on the energy content of hydrochar were investigated at 220°C, 5 hours by mixing of biomass with FS for different mixing ratio (0:1, 1:0, 1:1, 3:1). The effective biomass was chosen compared on their energy contents and proceeded to find the optimum process parameters by varying temperature and reaction time. The characteristics of the products from optimum condition were analyzed and compared. In order to inspect the energy content of digested sludge, the effective biomass and FS were involved in fermentation process. 1L reagent bottle with 700ml mixture of sample were incubated at 35°C for 35 days. HTC experiments were conducted for every 7days and the results were analyzed.

1.5 Framework of the Thesis

Chapter1 - states the general background, statement of the problem and proposes the objectives of the research with its scope.

Chapter2 - reviews the previous literatures about HTC technologies in detail and highlights the results so far done.

Chapter 3 - explains the step by step methodology followed in this study.

Chapter 4 - interprets and presents the actual results with the discussions.

Chapter 5 - provides the conclusions with recommendations for future research.

Chapter 2

Literature Review

2.1 Faecal Sludge

Faecal sludge (FS) is the combination of excreta (faeces & urine) and blackwater either alone or mixed with grey water. FS differs in their concentration, consistency and quantity (Strauss, 2002). It is like slurry or semisolid, based on the stabilization of the biodegradable organic matter (Strande et al., 2014). The characteristics of the excreta are dependent on the dietary habits of people, which vary from place to place. It is important to estimate the quantity and quality of FS, in order to select the suitable treatment and management based on socio-economic levels.

2.2 Characteristics of FS

FS normally contains very high moisture, pathogens, organic matter, and nutrients. Traces of heavy metals are also found. The characteristics mainly depends on its source of collection (OSS) as well as type of toilets used, filling rate of FS, storage duration, frequency of collection, method of collection, inflow and infiltration of leachate and climatic conditions. Furthermore, mixing of domestic wastewater especially from kitchen waste seriously hinders the microbial activity due to scum (fat, oil and grease). This microbial activity improves the degradation of organic matter biologically. It is essential to manage its stability. Thus, FS characteristics are extremely varied from unstabilized to stabilized state (Table 2.1).

Table 2.1 Characteristics of FS from Different Facilities (Charles et al., 2014)

Parameter	FS source		*WWTP sludge	Reference
	Public toilet sludge	Septage		
pH	1.5 - 12.6	-	-	USEPA (1994)
	6.55 - 9.34	-	-	(Kengne et al., 2014)
TS (mg/L)	52,500	12,000-35,000	-	Koné and Strauss (2004)
	30,000	22,000	-	NWSC (2008)
		34,106	-	
TVS (%TS)	≥ 3.5%	< 3%	<1%	Heinss, (1998)
	68	50-73	-	Koné and Strauss (2004)
	65	45	-	NWSC, (2008)
COD (mg/L)	49,000	1,200-7,800	-	Koné and Strauss (2004)
	30,000	10,000	7 - 608	NWSC (2008)
	20,000-50,000	< 10,000	500 - 2500	Heinss (1998)
BOD (mg/L)	7,600	840-2,600	-	Koné and Strauss (2004)
			20 - 229	NWSC (2008)

Parameter	FS source		*WWTP sludge	Reference
	Public toilet sludge	Septage		
TN (mg/L)	-	190-300	-	Koné and Strauss (2004)
	-	-	32 - 250	NWSC (2008)
TKN (mg/L)	3400	1000	-	Katukiza et al., (2012)
NH_4-N (mg/L)	3,300	150-1,200	-	Koné and Strauss, (2004)
	2,000	400	2 - 168	NWSC (2008)
	2,000-5,000	< 1,000	30 - 70	Heinss,(1998)
NO_3_N (mg/L)	-	0.2 - 2.1	-	Koottatep et.al., (2005)
TP (mg P/L)	450	150	09 - 063	NWSC (2008)
Faecal coliforms (cfu/100 mL)	1×10^5	1×10^5	6.3×10^4	NWSC (2008)
			6.6×10^5	
Helminth eggs	2,500	4,000-5,700	-	Heinss (1994)
	20,000-60,000	4,000	300 - 2,000	Heinss (1998)
	-	600-6,000	-	Ingallinella et al., (2002)
	-	16,000	-	Yen-Phi et al., (2010)

*WWTP – Waste water treatment plant

2.3 What is FSM?

A complete sanitation service chain absolutely demands an integrated system level approach including technology, management and planning. Figure 2.1 shows the different steps involved in FSM. Manual/mechanical desludging is the first step in FSM from various OSS and is followed by ideal/professional transportation to the treatment plant. Selection of appropriate treatment technology is reinforced by socio-economic conditions of local communities. At the end, disposal or reuse of the end products are accomplished (Parkinson et al., 2013).

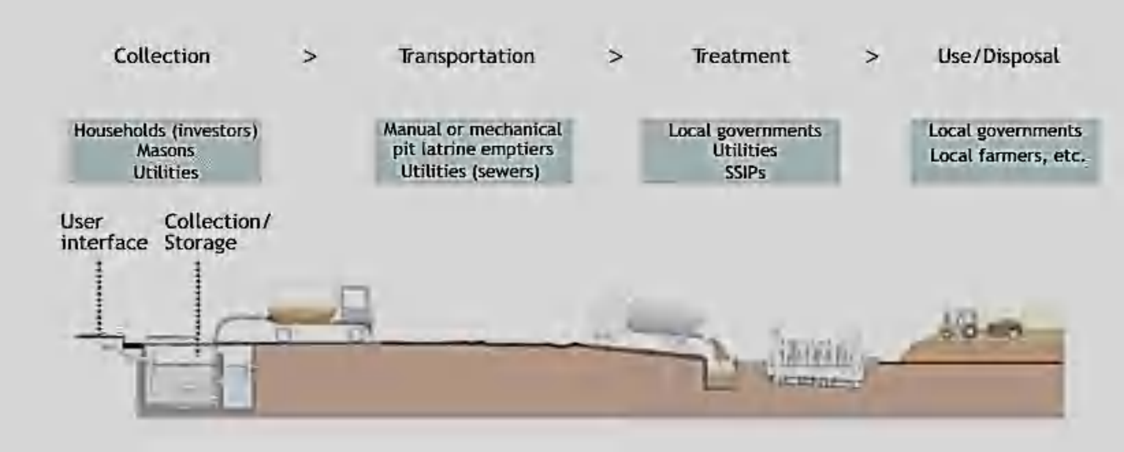
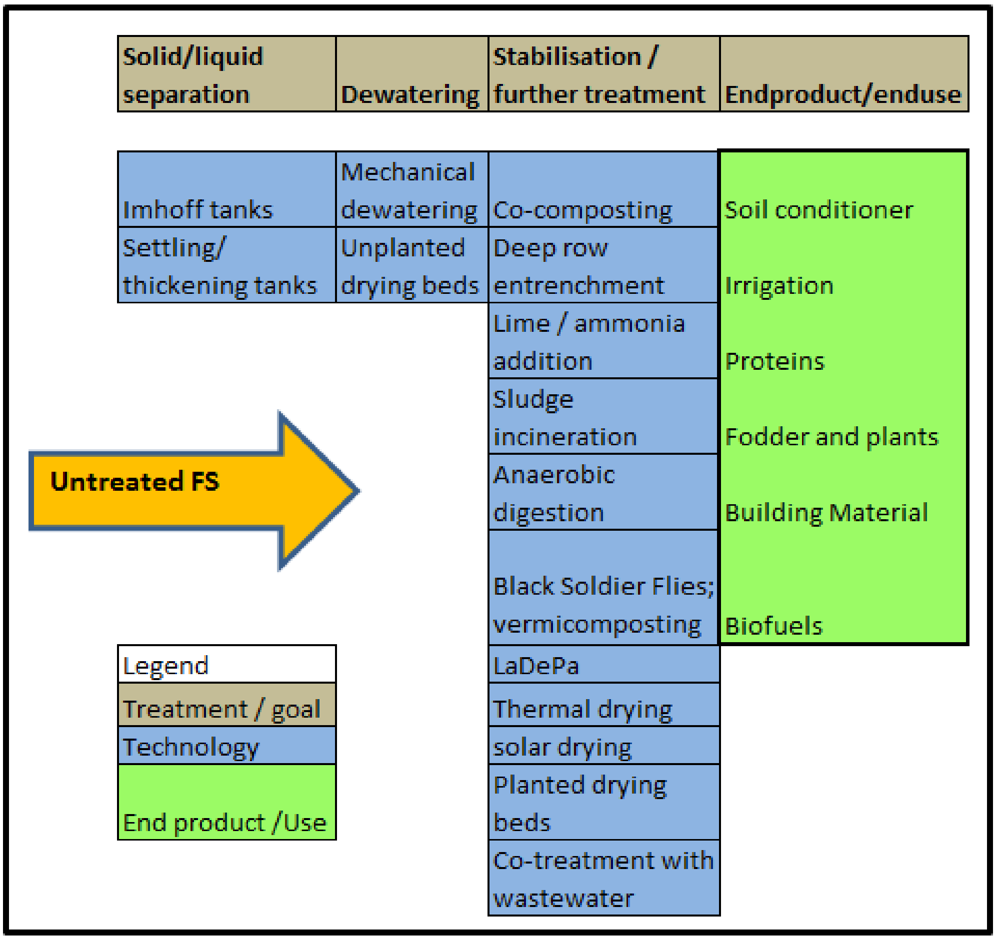


Figure 2.1 Overview of FSM (Strande et al., 2014)

2.4 Overview of Treatment Technologies

FS will be treated either physical/chemical/biologically. Physical treatment is a robust mechanism widely used for dewatering, drying or reducing the sludge volume. Biological mechanisms dramatically reduce the organic matter, nutrients and pathogens via microorganisms. Chemical additives are added to enhance the sedimentation and disinfection by optimizing the process in dewatering (Bassan, 2014a). Figure 2.2 shows the available technology currently applied in FSM.



Solid/liquid separation	Dewatering	Stabilisation / further treatment	Endproduct/enduse
Imhoff tanks	Mechanical dewatering	Co-composting	Soil conditioner
Settling/ thickening tanks	Unplanted drying beds	Deep row entrenchment	Irrigation
		Lime / ammonia addition	Proteins
		Sludge incineration	Fodder and plants
		Anaerobic digestion	Building Material
		Black Soldier Flies; vermicomposting	Biofuels
		LaDePa	
		Thermal drying	
		solar drying	
		Planted drying beds	
		Co-treatment with wastewater	

Figure 2.2 Overview - treatment technologies (Ronteltap et al., 2014)

2.4.1 Solid/liquid separation

Imhoff tanks or settling/thickening tanks are principally engaged to separate solid and liquid. It is often used as a primary settler. Partially digested sludge and settled sludge are the outcome from imhoff tanks and settler respectively (Cofie et al., 2006). The advantages and disadvantages are listed below in table. 2.2.

Table 2.2 Advantages and Disadvantages of Imhoff /Settling Tank

Technology	Advantages	Disadvantages
Imhoff tank	small foot-print single tank	complex infrastructure
	easy Operation and Maintenances (O&M)	high cost need skilled operator frequent removal of scum and sludge
Settling - Thickening tanks	efficient/ robust/ resilient,	lack of implementation in FS
	subsequent reduction of sludge volume	high concentration of organic matter with SS post treatment (e.g. drying beds) no removal of pathogens end-products cannot be used directly

2.4.2 Dewatering

Mechanical dewatering is employed to reduce the sludge volume significantly. Belt filter/frame filter/screw press, centrifuges are widely in practice. Implementation of these techniques in wastewater treatment is very effective, whereas needs a pilot-scale study for FS treatment (Ronteltap et al., 2014).

Unplanted drying bed is also equipped for dewatering via natural process. Approximately, 20-50% liquid evaporates and 50-80% liquid drains off as leachate (Heinss et al., 1998b). Climatic factors chiefly decide the effectiveness of drying bed. According to Dodane et al. (2014), using fresh FS in drying bed do not settle down well, which has low specific sludge resistance compared with settled sludge. Post treatment is necessary to dispose the sludge cake after drying. The pros and cons of dewatering technology are shown in table 2.3.

Table 2.3 Pros and Cons of Dewatering Technology

Technology	Advantages	Disadvantages
Mechanical dewatering	compactness and rapidness	high cost, skilled O&M flocculants addition need of electricity post treatment
Unplanted drying bed	easy to design and operation Low cost	large foot-print odour potential climatic problems post treatment

2.4.3 Stabilization and further treatment

2.4.3.1 Deep row entrenchment

It is a technology for treatment as well as end-use. The design follows the steps; digging of deep trenches, burying the sludge into the soil and planting the trees on top (Ronteltap et al., 2014). Employing FS in this technology might cause harmful pollutants and metals contaminate the ground water (Still et al., 2012). The major advantages and disadvantages are listed in Table 2.4 (Kengne et al., 2014).

2.4.3.2 Vermicomposting

In vermicomposting, worms convert FS into humic like substances. These worms largely breakdown the organic particles by stimulating the microbial activity. It stabilizes the sludge dramatically by removing volatile matter. Despite of 46% reduction of volatile suspended solids, this technology is incapable for pathogen removal (Zhao et al., 2010). Table 2.4 gives the overview of the advantages and disadvantages.

2.4.3.3 Black soldier flies

Larvae of black soldier flies are fed into the mixture FS with municipal organic waste. About 75% degradation of organic matter is achieved with removal of nitrogen and phosphorous (Diener et al., 2009). The end-product can be directly used as a soil conditioner or treated in anaerobic digestion. Summary of the potential benefits and drawbacks are shown in Table 2.4.

2.4.3.4 Co-composting

Co-composting refers the degradation of biological organic matter under controlled aerobic/thermophilic conditions by microorganisms (mainly bacteria and fungi). Different types of composting can be recommended depending on the availability of the resources and effluent quality (Tchobanoglous et al., 1993). Number of key factors influence on the entire system such as C/N ratio, moisture content, oxygen supply, aeration, size of particles, pH, temperature, degree of decomposition etc. The final end-product seems to be a stabilized material and can be used as soil conditioner-cum- fertilizer in agriculture (Koné et al., 2007). Benefits and limitations are shown in table 2.4.

2.4.3.5 Incineration

Generally, the treated sludge from WWTP is burnt at very high temperature 850°C - 900°C in incineration process (Kengne et al., 2014). Generally, it reduces sludge into ash (10% of its initial volume). Further applications of the products and the energy recovery are still under research. Pros and cons are displayed in table 2.4.

Table 2.4 Benefits and Limitations of Different Treatment Technologies

Technology	Benefits	Limitations
Deep Row entrenchment	low cost and less O&M no odour minimal exposure of pathogen afforestation/ soil erosion protection CO_2 fixation	hazardous pollutants/metals Importance of soil characteristics groundwater contamination
Vermi-composting	low capital cost soil conditioner	pathogen inactivation worms susceptible to toxic components

Technology	**Benefits**	**Limitations**
Black solider flies	low capital cost benefits for small entrepreneurs	limitation in large scale application
Co-composting	low CAPEX and O&M recycling the nutrients soil amendment controlling GHG emission	low market value for the product inadequate quality of feedstocks needs managerial skilled operators
Incineration	fertilizer/soil conditioner sludge volume reduction pathogen inactivation reuse of the product	high CAPEX emission of pollutants skilled operators, residual ashes

CAPEX - Capital expenditures

2.4.4 Anaerobic digestion

Anaerobic digester (AD) has been adopted to stabilize the sludge from activated sludge plant. The high concentration of organic matter in the sludge undergoes into different biochemical reactions and produces mixture of gases (Park et al., 2005). It principally works into 4 digestion process: hydrolysis, acidogenesis, acetogenesis and methanogenesis.

2.4.4.1 Fermentation

Degradation of organic matter into amino acids, sugars and some fatty acids is occurred at the acidogenesis stage. In this phase, volatile organic matter is fermented by acidogeneic bacteria (Metcalf and eddy, 2003). However, environmental conditions like temperature, pH and C/N ratio are played the vital roles that control the effectiveness of acetogen microbes (Park et al., 2005). At end of the fermentation process, acetate, hydrogen, CO_2 and propionate and butyrate will be produced as the principal components. These products further will be converted as acetate and CH4 at acetogenesis and methogenesis stage respectively (Roneltap, 2014). Additionally, according to Khanal (2008), the conversion rate of hydrogen and CO_2 into acetic acid is quiet low compared with acetate. This is one of the major drawbacks in AD systems, which fully controlled by the reactions of bacterial-microorganisms.

At the end of anaerobic digestion, approximately 50-70 % of methane will be yielded that will be used as biofuel (Table 2.5) (Kengne et al., 2014). Various parameters influence the biogas production effectively such as temperature, pH, moisture, nutrients and toxicity of the feedstock. In addition, organic loading rate, sludge retention time and biodegradability of the substrates are needed to consider (Chen et al., 2008). This technology is most popular since different biomass can be added. Co-digestion may also possible using mixture of organic wastes (Cao and Pawłowski, 2012). These complex processes will also digest the FS that contains high biodegradable matter. Number of studies have been revealed using sewage sludge and obtained good results of biogas (Tyagi and Lo, 2013). 100 -200Nm^3 of biogas was generated per ton of municipal organic wastes by using this technology (Claassen et al., 1999). Nevertheless, numbers of factors also limit this technology point out in Table 2.6.

Table 2.5 Biogas Yield from Different Substrates used in AD (Ronteltap 2014)

Different substrates	Yield of Biogas (m^3/kg TS)	Different substrates	Yield of Biogas (m^3/kg TS)
Animal barnyard manure	0.260 - 0.280	Liquid	1.44
Pig manure	0.561	Protein	0.98
Horse droppings	0.200 - 0.300	Water Hyacinth	0.16
Green grass	0.63	Alligator weed	0.2
Flax straw	0.359	Water Lettuces	0.2
Wheat straw	0.432	Cattle Dung	0.12
Leaves	0.210 - 0.294	Pig manure	0.22
Sludge	0.64	Human wastes	0.31
Brewery liquid waste	0.300 - 0.600	Dry grass	0.21
Carbohydrate	0.75	Rice straw	0.23

Table 2.6 Advantages and Disadvantages of AD

Advantages	Limitations
reducing sludge volume and odors	skilled O&M/high CAPEX
production of biogas	temperature depended / start-up problem
Controlling GHG emission	long retention time
widely used in industrial wastewater	hydrolysis process hindered by lingo-cellulosic biomass
	low removal ability of organic compounds
	not suitable for all biomass (e.g. lignocellulose)

2.4.5 Thermo-Chemical Processes

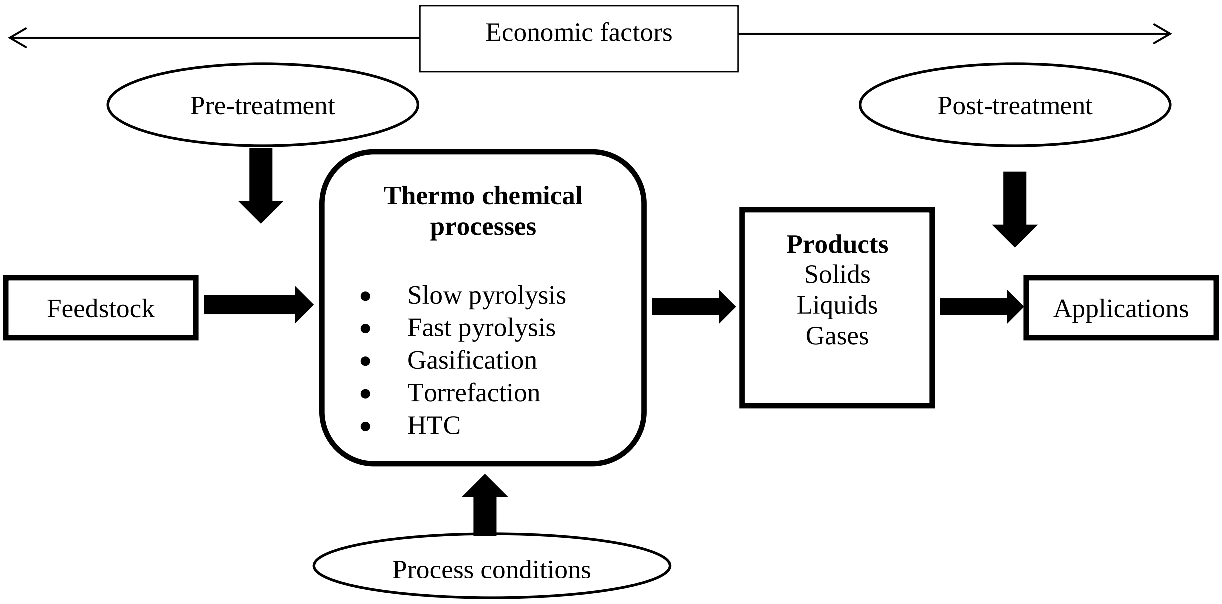


Figure 2.3 Types of Thermo-chemical processes (Child, 2014)

Terrestrial and aquatic plants balance the atmospheric CO_2 sequestration via respiration and photosynthesis naturally. Due to rapid industrialization, excessive carbon has been emitted into atmosphere, resulting an imbalance in carbon cycle. In order to control GHG emission and balance the CO_2 sequestration, pyrolysis and HTC were introduced to produce artificial carbon rich material within several minutes to hours (Lo 1991). Naturally the degraded plant materials are stored as solid sediments (e.g. peat) under certain pressure and temperature in the absence of oxygen converts into coal (Antal and Grønli, 2003) and it is called as coalification. These processes can be distinguished by its feedstock, temperature, reaction time and end-products (Figure 2.3) (Child 2014).

2.4.5.1 Slow pyrolysis

It is a traditional process (naturally occurred) that degrades the organic matter for thousands of years around 400°C. The solid end-product is called as “charcoal” also produces tar-like liquid substances with some amount of gases (Demirbas and Arin, 2002).

2.4.5.2 Fast pyrolysis

This is a rapid heating process, where the biomass is devolatilized at 500°C - 1000°C in the presence of little or no oxygen. Approximately, 75% tar-like liquid is yielded with few amounts of solid char (Libra et al., 2011).

2.4.5.3 Gasification

In contrast to pyrolysis, gasification is a continuous process with the presence of oxygen and yields 85% gaseous products (mixture of H_2, CO, CO_2 and CH_4) with very low solid. This process is carried out at 800°C for short residence time (Libra et al., 2011).

2.4.5.4 Torrefaction

This process is also called as “mild pyrolysis”. The solid recovered from this process is nearly 70% that produced at low temperature of 200°C - 300°C with longer residence time. However, it requires pre-heating, pre-drying, intermediate heating and post-drying (Child 2014).

2.5 Hydrothermal Carbonization (HTC)

HTC is an exothermic process, pioneered in 1913. This also works under thermo-chemical reactions. While dry pyrolysis is not suitable to the feed stock containing high moisture content (Robbiani 2013), HTC suits for all types of biomass, which transforms carbohydrates into a coal-like material at elevated temperature. Moreover, the required temperature range (180- 350°C) is relatively in low when compared with the other processes. Table 2.7 distinguishes the different processes based on the temperature used and product yielded.

Table 2.7 Comparison of Different Processes (Robbiani, 2013)

Process	Process conditions				Products yield (%)		
	Temp (°C)	Residence time	Pressure	medium	Char	Liquid	Gas
Slow pyrolysis	~ 400	hours to weeks	low	little no O_2	35	30	35
Fast Pyrolysis	~500	seconds	variable	little no O_2	12	75	13
Gasification	>800	10 – 20 s	variable	lightly reducing atmosphere	<10	5	>85
Torrefaction	200-300	several hours	atmospheric	little no O_2	70	0	30
HTC	180-350	minutes – hours	high autogenous	water	50-80	20-5	2-5

2.5.1 Advantages of HTC

- Low CAPEX and easy O&M (compared to conventional wastewater treatment)
- Short time requirement
- Suitable for all biomass (wet/humid/ dry)
- Carbon conversion efficiency reaches 100% and balances the CO_2 sequestration by CO_2 neutral/ CO_2 negative.
- Superior degradation of organic matter by different processes
- Complete disinfection
- Used either centralized/decentralized
- Minimizes the transportation costs
- Easy to store the char (end-product)
- Applicable for environmental, electrochemical and catalytic studies
- Hydrochar can also be used for combustion plants, combined heat and power plants, cement and steel factories (Robbiani 2013)
- Hydrochar can be utilized as a water- and ion binding component to improve soil quality
- Adsorbent in drinking water treatment

2.5.2 Constraints

- Supply of external energy (electricity) is important for HTC process
- Treatment of process water from HTC is a problematic issue
- The necessary materials to construct a reactor (stain stainless steel) or infrastructures (pressure vessel engineering) or qualified personal (welders) might not be available in all developing countries

2.5.3 Basic criteria for HTC process

Funke et al. (2010) listed out the important operational conditions for HTC experiments that yields the optimum results: HTC has to operate in subcritical conditions for reaction time 1-72 hours. The temperature must be above 100°C to initiate the reactions and minimum temperature of 180°C is required for hydrolysis process. Thorough out the process, the feedstock must be submerged into water and needs to maintain the saturated pressure approximately 20bar (Libra et al., 2011). In some cases, alkaline condition should be avoided by maintaining pH < 7. Based on these conditions, number of chemical reactions will be involved to convert the feedstock into valuable products. Feedstock, moisture conditions, temperature, residence time, pressure, solid load and pH are the parameters involved. These parameters are explained in detail.

2.5.4 Parameters involved in HTC

2.5.4.1 Feedstock

Any renewable/ biological material can be used directly and converted as biofuel is called as feedstock. It has significant energy content in nature. It is also known as natural precursors, which readily participates in the chemical reactions and produces byproducts (Titirici and Antonietti, 2010). Funke et al. (2010) stated that "HTC has a high flexibility on the choice of feedstock". Any kind of stabilized or non-stabilized biomass can be used as feedstock (e.g. agricultural residues, animal manures, algae, municipal organic waste). HTC also adopts fresh excrements, faecal sludge and sewage sludge. The unique characteristics of individual biomass conclude the quantity and quality of the output materials. In addition, chemical compositions (e.g. cellulose, hemicellulose, lignin), volatile and non-volatile matter, moisture content, particle size and the energy content principally determine the efficiency of the char production (Libra et al., 2011).

2.5.4.2 Moisture content

Water plays a crucial role in HTC mechanisms. It dissipates the heat among the medium and acts as a storage medium. Furthermore, the heated water acts as a good solvent and a catalyst. As a result, it helps to increase the rate of reactions. Moreover, thermo-chemical processes are controlled by water even at peak level of temperature and results exothermic reactions (Titirici et al., 2007). Therefore, keeping the feedstock suspension in water is mandatory where the transportation of molecules happen through this medium (Funke et al., 2010).

2.5.4.3 Temperature

Temperature is the ultimate parameter that significantly determines the energy content of produced hydrochar. Heating up the feedstock at higher temperatures encourages the reaction kinetics and significantly increases the severity of reactions. HTC mechanisms are prominently effective at 180°C-350°C (Funke et al., 2010). Both temperature and reaction time impact the rate of reactions. In some cases, the higher energy content of hydrochar will be obtained even at low temperature by increasing the reaction time or vice versa (Robbiani, 2013).

2.5.4.4 Residence time

HTC process is also depended on its residence time. HTC is comparably a slow reaction with fast pyrolysis, which is operated between 1 – 72 hours (Funke et al., 2010). Feedstocks, based on reaction time, produce hydrochar with different characteristics. Moreover, increasing the reaction time increases the recirculation of water within the processes. As a result, losses of organic matter might be suppressed that will be economically beneficial (Robbiani, 2013).

2.5.4.5 Pressure

High autogenous pressure (20bar) is required for the entire HTC mechanisms. Pressure plays a vital role, which maintains the equilibrium in a closed system. When temperature is increased in the reactor, automatically the pressure will start to increase. At critical temperature, water attains the saturated pressure and initiates the evaporation. It keeps the water in liquid state throughout the process. At this stage, the evaporated water will begin to condense and assists to maintain the same amount of liquid. However, experiments at higher temperatures increase the pressure drastically that needed to be controlled by cost-effective equipment (Funke et al., 2010).

2.5.4.6 Solid load

The ratio of biomass to moisture content is called as solid ratio. A high solid ratio helps to lower the residence time and yields higher solid recovery (Funke et al., 2010). However, He, et al. (2013) investigated the energy content of hydrochar produced from sewage sludge. The energy content increased along increment of the solid content. 25 – 35% of total solid, yields higher solid recovery.

2.6 HTC Mechanisms

In HTC, the chemical reactions between carbohydrates and hydrocarbon atoms yield carbon rich nanostructured materials (Funke et al., 2010; Titirici and Antonietti, 2010). Hydrolysis, dehydration, decarboxylation, aromatization polymerization and condensation are the fundamental processes. The overview mechanisms are depicted in Figure 2.4 (Kruse et al., 2013).

2.6.1 Hydrolysis

Cellulose, hemicellulose and lignin are the carbohydrates abundantly available in biomass. Decomposition of these in hydrothermal technology is challenging and produces numerous new components via complex set of chemical reactions (Minowa et al., 1998). Generally, hydrolysis initiates the HTC mechanisms. Breaking of complex polysaccharides into monomers with the presence of water molecule is the general perception. However, hemicelluloses are quickly hydrolyzed into its respective monomeric sugar derivatives, whereas the molecules are weakly bonded with lower degree of polymerization (Gupta and Demirbas, 2010). At this stage, five-carbon (e.g. pentose) atoms are predominantly produced due to the cleavages of ester and ether bonds (Kruse et al., 2013). Moreover, hemicelluloses are not crystalline and so the energy required for hydrolysis is quiet low. Normally, at temperature 180 - 200°C, hydrolysis of hemicellulose occurs (Funke et al., 2010). Obviously, 95% of hemicellulose degrades at 200 - 230°C within few minutes. Furthermore, the monomeric sugars converted from hemicellulose undergoes into dehydration process (Mok et al. (1992)). On the other hand, cellulose is the major component found in plants’ cell wall. Hydrothermal degradation of cellulose is a heterogeneous reaction usually happens at >220°C (He et al., 2013). At this temperature range, it is broken into smaller oligomer groups (e.g. hexose) with low molecular weight. These oligomers are easily dissolved into water and further splits into glucose. Glucose is a water-soluble sugar that rapidly obtains the higher degree of degradation at elevated temperature (Gupta and Demirbas, 2010). Hence the degraded atoms are readily involved in dehydration or other processes (Kruse et al., 2013).

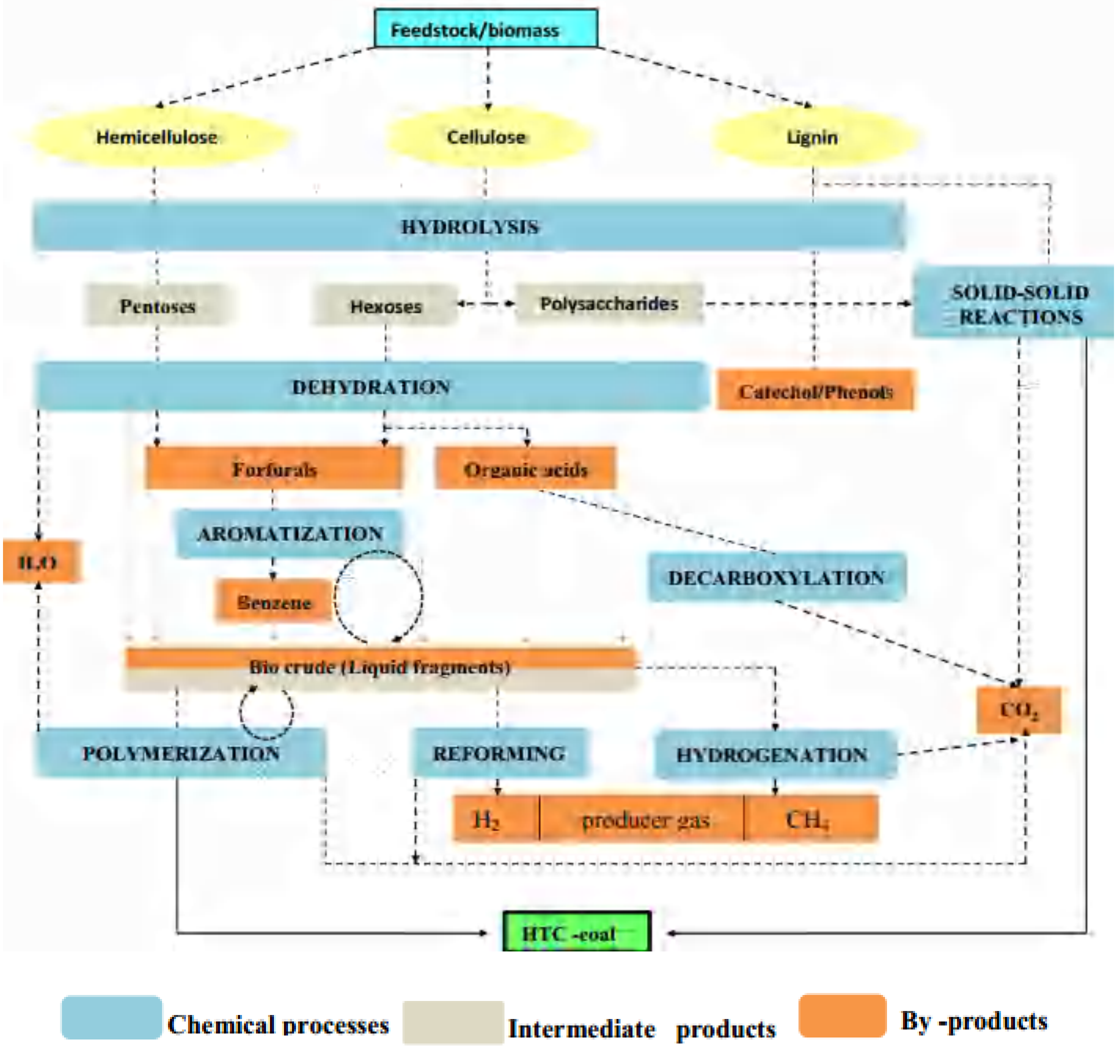


Figure 2.4 Overview of HTC mechanisms (Kruse et al., 2013)

Simultaneously, lignin starts to involve in hydrolysis. Naturally, lignin has complex characteristics, where the atoms are mostly bounded by phenyl-propane derivatives. These derivatives usually have higher molecular weight. At <200°C, part of the lignin starts to solubilize like hemicellulose. However, it mainly depends on the density of the medium. Despite of its hydrolysis at low temperature, it will recondense again by cross-linking bondage and form the high molecular products consequently. This is due to its higher reactivity and this process might be called as solid-solid reactions. The products are generally hydrophobic (Gupta and Demirbas, 2010).

In conclusion, reaction rate of hydrolysis is governed and limited by diffusion/transport phenomena between the molecules, in biomass matrix (Funke et al., 2010). The groups of fragments and their amounts are influenced mainly by the characteristics of feedstock. Moreover, pH, temperature and reaction time are also contributed. Monosaccharaides from cellulose, phenolic fragments from lignin are the pre-dominant end-products from hydrolysis. These products undergo into further reactions or else remain as by-products in trace amounts (Kruse et al., 2013).

2.6.2 Dehydration

After hydrolysis, elimination of hydroxyl groups initiates due to the increase of temperature. Sugar derivatives from hydrolysis degrade into furfural and other compounds by losing its water molecules (Gupta and Demirbas, 2010). Additionally, glucose derivatives from cellulose hydrolysis further epimerizes into fructose or decompose into other compounds. Fructose readily dehydrates into hydroxyl methyl furfural (HMF) compounds (Funke et al., 2010). Organic acids, aldehydes and alcohols are the major products after dehydration (Kruse, Funke and Titirici, 2013).

2.6.3 Decarboxylation

Decarboxylation normally takes place after the significant amount of water removal due to dehydration. Comparatively, the rate of dehydration is always higher than decarboxylation (Kruse et al., 2013). However, the ratio of decarboxylation to dehydration is largely depended on temperature at subcritical level. It usually begins at 150°C and releases CO_2 significantly. During dehydration, derivatives of cellulose produce organic acids with high amount of formic acid. This formic acid undergoes into decarboxylation process and primarily yields CO_2 and H_2O. Other sources of CO_2 are due to destruction of oxidizing agent, condensation reaction also due to hydrogenation (Funke et al., 2010).

2.6.4 Aromatization

Conversion of aliphatic or alicyclic compounds into aromatic structures due to its cross-linking condensation reactions is called as aromatization. These aromatic rings are highly stable compounds in HTC process is considered as a building block for hydrochar. This is mostly influenced by temperature and residence time. In addition, alkalinity environment helps to enhance the formation of aromatic compounds (Funke et al., 2010).

2.6.5 Polymerization condensation

At this stage, most of the fragments from the liquid are being polymerized. The rate of reaction between the fragments is determined by their origin and degree of conversion. Unsaturated compounds are easily polymerized by eliminating the hydroxyl and carboxyl groups. Temperature and pressure are very effective to produce the hydrochar from polymerization condensation. In some cases, formation of gases suppress the condensation reactions that results low yield of hydrochar (Funke et al., 2010).

2.6.6 Other mechanisms

Apart from the discussed reactions, demethanation, pyrolytic reaction, Fischer-Trospsch-type reactions are also involved in HTC process. Furthermore, some components are not involved in many reactions and remain as it is in the final products (Funke et al., 2010).

2.7 HTC Products

HTC processes yield the products as solid, liquid and gas. Compositions of the yielded products are varied for different temperature and reaction time (Child, 2014). Figure 2.5 roughly depicts the quantity of products from HTC (Funke et al., 2010).

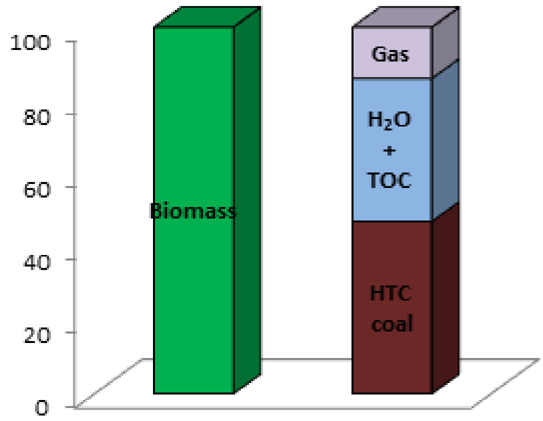


Figure 2.5 HTC products (Funke et al., 2010)

2.7.1 Solid products

Hydrochar is the main solid product of HTC, which depicts the efficiency of HTC technology. Similar to natural coal formation, HTC also produces the hydrochar by agglomeration of different chemical substances from different reactions (Libra et al., 2011). The production of the solid is totally influenced by the process conditions. Elimination of hydroxyl and carboxyl groups will be very effective to increase the solid recovery via polymerization/re-polymerization reactions (Xiao et al., 2012).

Table 2.8 Solid Recovery from Different Biomass (Child, 2014)

Solid yield (%)	Biomass
50 - 80	Biomass, waste materials
20 - 50	Municipal/ paper/ food waste
75 - 80	Variety of organic waste materials
36 - 66	Cellulose, peat, wood
30 - 50	Cellulose
50 - 69	Jeffery pine and white fir mix
63 - 83	loblolly pine

Moderately, 50% solid yield will be observed, whereas the characteristics of the feedstock really influence the amount of products (Figure 2.4). Table 2.8 shows the quantity of solid recovered by using different biomass. HTC changes the input cellulosic material into mono-dispersed colloidal carbonaceous spheres (Hu et al., 2010). These nanoparticles normally exhibit the size of 1-3µm. Due to the breaking of cellulose matters as well as recombination of carbon materials after decarboxylation, nanostructure will be resulted (Xiao et al., 2012). These carbon rich material is highly dispersed in water with less hydrophobicity (Funke et al., 2010). The elemental compositions (C, H and O) of hydrochar will be compared with the lignite or sub-bituminous coal. Many researches have already reported about the coalification characteristics of hydrochar from various biomass (Ramke et al., 2009). Moreover, the produced hydrochar are highly versatile and easy to do pelletizing either soft, hard templating. Based on the morphological properties, hydrochar will be involved in the field of electrochemistry (e.g. batteries and super capacitors). Still research is done in order to compare the hydrochar with activated carbon (Titirici, 2013). In conclusion, the applications of hydrochar is widening in different field of study. This helps to prove its sustainability with CO_2 sequestration. The detail about its energy and carbon content are discussed later in detail.

2.7.1.1 Characterization of hydrochar

Energy recovery from the biomass is the core objective of HTC technology (He et al., 2013). The characteristics of produce hydrochar will be determined by using ultimate analyzer, to measure the carbon and hydrogen content. The mol ratio H/C to O/C will be helpful to analyze their appropriate position in coalification diagram (Ramke et al., 2009).

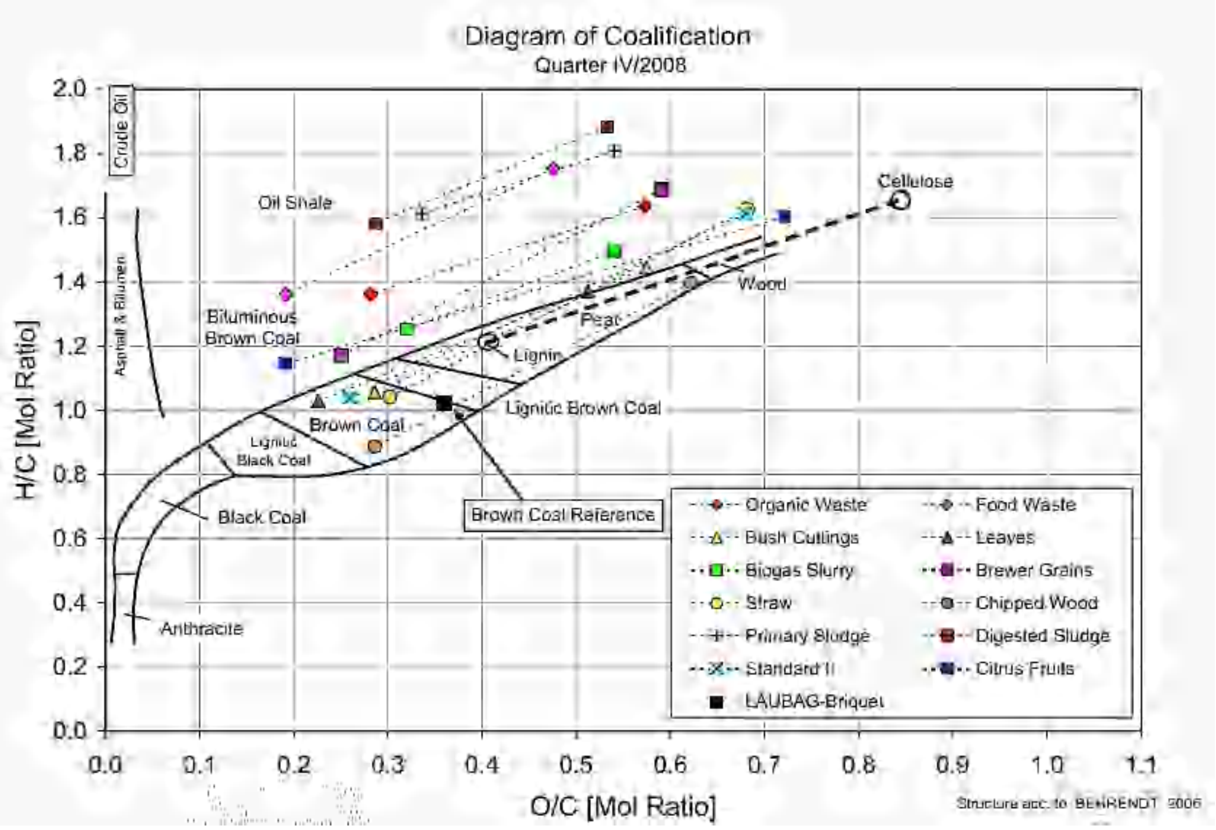


Figure 2.6 Coalification diagram of different biomass (Ramke et al., 2009)

Figure 2.6 clearly illustrates the decrease in the atomic ratios after HTC processes from upper right to lower left. Almost hydrochar obtained from biomass like straw, leaves, bush cuttings and chipped wood has the brown coal characteristics. This explains the efficiency of the HTC processes, where the biomass will be converted as coal within few hours. On the other hand, digested sludge, food waste, primary sludge and organic wastes have not fully achieved the properties as brown coal. Their atomic ratios are higher than the values of brown coal. However, their values are extremely decreased from its original values.

The explanations of different mechanisms in HTC could be proved by plotting "van Krevelen" diagram. Moreover, the paths of the reactions that are actively involved in HTC mechanisms such as dehydration, decarboxylation and demethanation can also be defined with the help of this diagram. Overall, Decarboxylation is significantly increased and results a carbon rich material. Also, dehydration and demethanation are reduced and produces a less condensed hydrochar (Xiao et al., 2012). In conclusion, it indicates that HTC has efficiency to produce hydrochar with low atomic ratios by removing the oxygen and hydrogen functional groups, results greater energy densification with higher heating value (HHV) (Berge et al., 2011; Sevilla and Fuertes, 2009).

2.7.2 Liquid products

The amount of liquid filtered after HTC is about 40% of the output (Funke et al., 2010). Generally, the amount of water used will be retrieved with hydrochar. Approximately, 10-20% of by-products will be obtained with water. The filtrate or the process water is normally in acidic conditions. This is due to the presence of H^+ ion throughout the processes.

Table 2.9 Compounds Observed from Process Water Extracted in Ethyl Acetate

Sugar derived compounds	Lignin derived compounds
Acetic acid	Vanillin, Ethanone
Furfural	Benzoic acid
2-Furancarboxaldehyde	Acetophenone
5-hydoxymethyl furan	Ethanone
2,5 - Hexanedione	1,2,3, trimethoxy-5-methyl
2(3H)-Furanone	2-propanone
5-ethyldihydro	1-(4-hydroxy-3-methoxyphenly)-
2-Cyclopenten	Dimethyl-(isotrophyl)-silyloxybenzene
2-Acetonylcyclopentanone	Benzaldehyde
Lignin derived compounds	Ethenone
Ethylbenzene	4-Ethoxy,2,5-dimethoxybenzaldehyde
p-xylene	Phthalic acid
Phenol	isohexyl ispopyl ester
Silane	1,2,-Benzenedicarboxylic acid
trimethylphenoxy	butyl 2-methylproplyl ester
1,2, Benzenediol	Other compounds
Benzene	Ethyl acetate
Hydroquinone	Tetracosane

The filtrate generally has COD/TOC ratio of 2.30 and BOD is in the range of 10 – 40 g/l. The high concentration of COD will be treated in anaerobic digestion for further applications (Ramke et al., 2009). Additionally, the high organic content process water can be used for recirculation, whereas the acidity and the warm conditions help to speed up the new process (Berge et al., 2011). The derivatives from the process water are analyzed by extracting the liquid in ethyl acetate solution. It represents the number of compounds particularly as sugar-derived, lignin derived and other compounds (Funke et al., 2010).

These are also varied based on the type of biomass used in HTC. Table 2.9 shows the different types of compounds extracted from corn stalk and Tamarix ramosissima (plant biomass) used in HTC (Xiao et al., 2012). Acidic acid, furfural, 2-ethyl, 5-hydroxy methyl-furan derivatives are largely extracted as sugar derived compounds, which are resulted from hemicellulose and cellulose decompositions. Moreover, phenolic compounds are largely presented. It is evidently resulted the degradation of lignin from the raw materials. In conclusion, compounds obtained from the filtrate are rich with phenolic compounds and furan derivatives. This helps to confirm more about the dehydration, decarboxylation and demethanation chemical reactions. The applications of these by-products are widely researched in many fields.

2.7.3 Gaseous products

Compared with the solid and liquid products, the amount of gases produced are very less. The yield of gases and their compositions are largely deepened on the substrate and their reactivity (Ramke et al., 2009). CO_2 predominantly occupies 70 – 90% in gas compositions, followed by CO, CH_4, and H2. Lesser amounts of hydrocarbon gaseous products are noticed in the range of 1-4% to >10%. These are called as volatile organic compounds (VOC) is shown in Table 2.10. The main reason for the CO_2 release is from the decarboxylation process. However, decarboxylation is a heat sensitive process, whereas it increases its rate of reactions with increasing temperature (Funke et al., 2010). Approximately 3- 6% of input carbon is converted as gaseous products that differ for different feedstocks (Ramke et al., 2009). The purpose to determine the carbon atoms from the gaseous products will help to do carbon balance later.

Table 2.10 Compositions of VOC

Volatile organic compounds	
Acetone	Toluene
Benzene	Trichloroethylene
2-Butanone	1,1,1-Trichloroethane
n-Butyl acetate	Xylene
Carbon tetrachloride	Hexane
Chloroform	Methylene chloride
Cyclohexanone	Methyl isobutyl ketone
Diethyl ether	Styrene
Ethylene dichloride	Tetrachloroethylene
Ethyl benzene , Ethyl acetate	Pentane

2.8 Hydrothermal Carbonization of Lignocellulosic Biomass

Biomass resources that include all plant and plant derived (organic) materials are excessively available to produce bio energy and biofuels. Renewable energy or by-products from biomass are sustainable (Wright et al., 2006). HTC also uses different types of biomass from different sources (Xiao et al., 2012). Agricultural waste, animal manures, harvested residues, food waste, paper waste etc., produces the hydrochar with higher heating values. It is largely comparable with LAUBAG-Briquette coal (Berge et al., 2011, Oliveira, et al., 2013; Ramke et al., 2009). Numbers of studies have been revealed the characteristics of hydrochar produced from biomass. It is evidently proven that the energy content of raw materials remarkably increased. However, the process parameters are very sensitive for various biomasses. Figure 2.7 represents the energy content of different biomass obtained from different process conditions. Moreover, it also depicts the carbon content of respective hydrochar. Hence, involving biomass in HTC yields the hydrochar with higher energy content, which also aids to solve the solid waste management effectively.

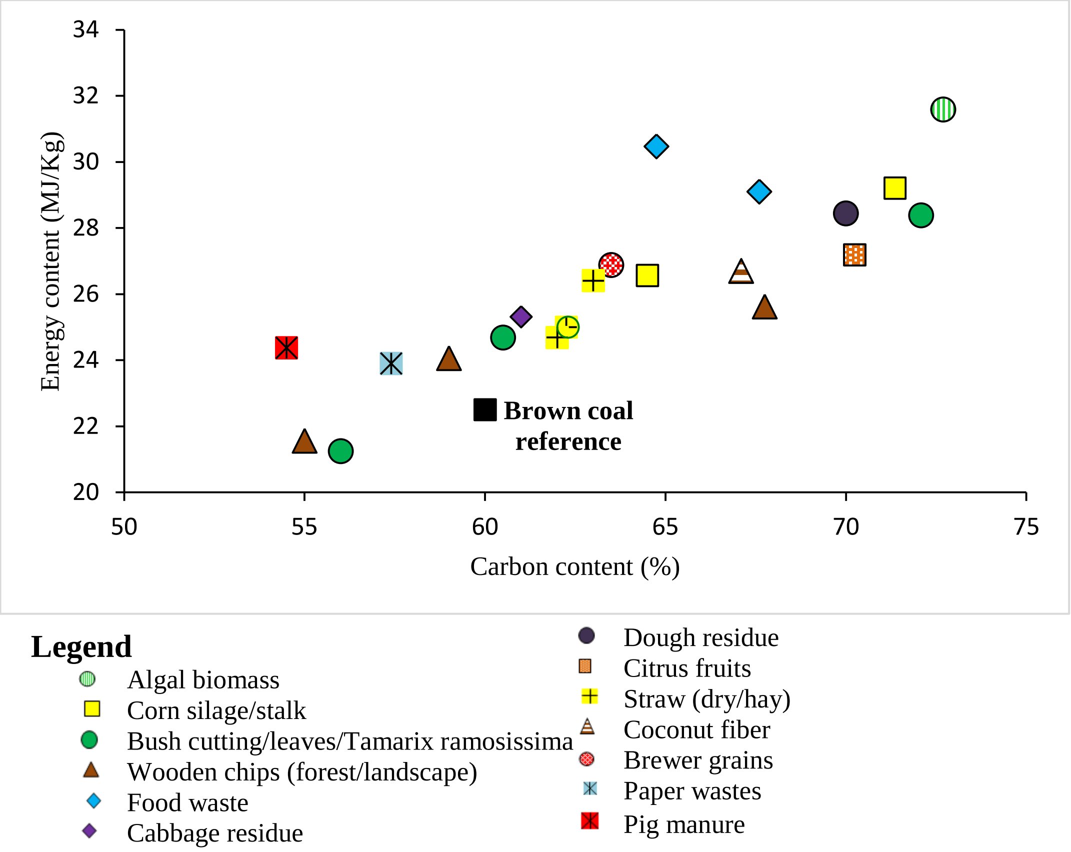


Figure 2.7 Energy & carbon contents of different biomass hydrochar
(Berge et al., 2011; Heilmann et al., 2010; Liu et al., 2013; Oliveira et al., 2013; Ramke et al., 2009; Xiao et al., 2012)

2.9 Hydrothermal Carbonization of Different Types of Sludge

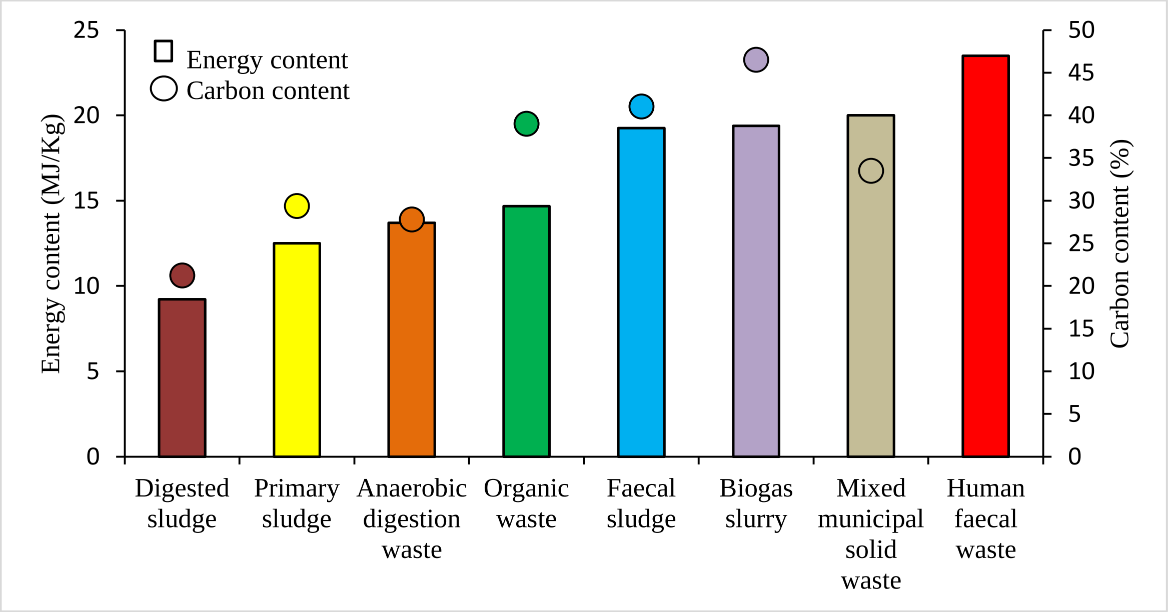


Figure 2.8 Energy & carbon contents of different types of sludge hydrochar
(Berge et al., 2011; Oliveira et al., 2013, Ramke et al., 2009)

HTC is a sustainable technology that also treats the human waste including faecal sludge and converts into useful end products (Afolabi and Wheatley, 2014). Furthermore, treating municipal wastewater by conventional treatment produces large quantity of sludge. Excessive sewage sludge remains as a waste without proper solution (Rulkens, 2007). HTC aids to solve this problem and yields a sterilized product, which can be used as a renewable energy. Many researches have been done to produce carbonaceous material by using primary sewage sludge, municipal organic waste, digested sludge, anaerobic digested sludge etc. The carbon content is highly enhanced from the raw materials through HTC. Based on the temperature, reaction time, source of collection, the obtained energy content will be varied (Figure 2.8).

2.10 Hydrothermal Carbonization of Addition of Chemical Catalysts

Enhancing the energy content of produced hydrochar or increase the reaction rate, pretreatment with catalyst is also an option in HTC. Numbers of studies have been revealed using different type catalysts (e.g. acetic acid, zeolite, borate, citric acid etc.) (Xu et al., 2009).Yan et al., (2009) investigated the effects of catalysts in HTC and resulted increment of HHV from 21.12 MJ/kg to 22.09 MJ/kg at 200°C and to 26.55 MJ/kg at 230°C. However, the amount of catalyst loading varies and enhancing the HHV is significantly depended on the characteristics of feedstock and process parameters mainly. According to Lynam et al. (2011), addition of 0.4g acetic acid per gram of loblolly pine is increased the energy densification ratio from 1.06 to 1.12 for without and with acetic acid respectively.

2.11 Research Gaps

Literature studies review the overall concept of FSM. It also explains about different technologies presently used for FS treatment. Moreover, advantages and disadvantages of each technology were briefly described. While comparing the available treatment technologies, anaerobic digestion is the most effective one that provides the renewable energy until now. Although, it produces biogas effectively, disposal of sludge as landfilling or reuse in agriculture as fertilizer are still not acceptable due to its high organic matter and presence of pathogen. Hence, seeking a technology which overcomes the drawbacks and provides a sustainable sanitation is essential. Now days, HTC is blooming technology that satisfies the requirement.

FS alone in HTC process produces hydrochar with low energy content. On the other hand, HTC is very effective for the plant biomass and produce hydrochar similar to the characteristics of brown coal. Therefore, in order to enhance the energy content of hydrochar produced, addition of different biomass with FS were used as feedstock. Biomass from different sources was mixed with FS for different mixing ratio. From these results, the effective biomass in terms of its energy content was preferred. In order to seek the optimum process parameters, the effective biomass further was carried on and analyzed with thesis characteristics. Furthermore, addition of acetic acid as a catalyst aids to increase the reaction rate. Therefore, in order to produce acetic acid from acetogenesis stage, fermentation was carried out by using co-digestion of FS with effective biomass. Hydrochar will be produced from digested sludge using HTC. The results from both without fermentation and with fermentation will be compared via energy contents. In conclusion, this research supports to compare both technologies AD and HTC from its efficiency to produce renewable energy.

Chapter 3

Methodology

3.1 Outline of the Study

The experimental studies of HTC were conducted at ambient laboratory of the EEM, AIT in Thailand. The research was divided into three different phases. Figure 3.1 illustrates the outline of the research and the descriptions are explained as follows.

3.2 Materials and Apparatus

3.2.1 Faecal sludge

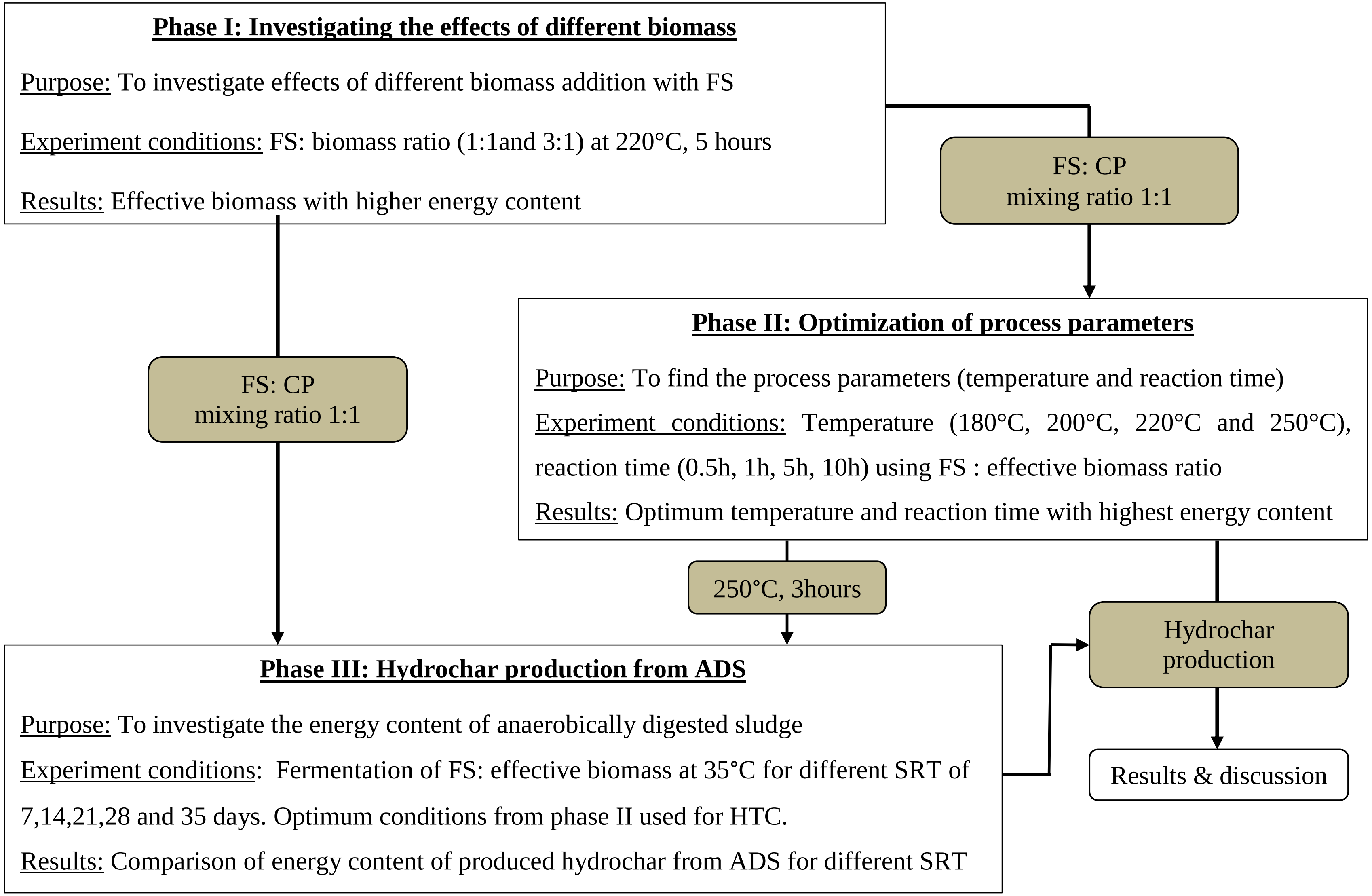
FS collected from the municipality of Pathumthani and Nonthaburi provinces were emptied into a reservation tank located in AIT. It was allowed for a couple of days to allow the sludge to stabilize. The FS from the tank was periodically collected for the HTC experiments. FS is dark in color due to its high degree of biodegradability. Removal of foreign materials like sanitary napkins, bits of plastic paper, pebbles, chilly seeds, watermelon etc., were done by manually. Samples was collected and stored inside 5°C room (Appendix A).

3.2.2 Biomass

Various types of biomass such as cassava pulp (CP), dried leaves/grass cuttings (DL), pig manure (PM) and rice husk (RH) were collected from different sources (Table 3.1). Preliminary works like shredding/chopping/grinding were carried out separately and stored in 5°C room (Appendix A).

Table 3.1 Source of Different Biomass

Biomass		Source	Category
Cassava pulp	(CP)	Chao Khun Agro Products Company Ltd., Saraburi province	Industrial waste
Dried leaves/grass cuttings	(DL)	AIT environment	Municipal solid waste
Pig manure	(PM)	Local farm in Klongluang region, Pathumthani province	Agricultural waste
Rice husk	(RH)	Local farm in Klongluang region, Pathumthani province	Agricultural waste



Phase I: Investigating the effects of different biomass

Purpose: To investigate effects of different biomass addition with FS

Experiment conditions: FS: biomass ratio (1:1and 3:1) at 220°C, 5 hours

Results: Effective biomass with higher energy content

Phase II: Optimization of process parameters

Purpose: To find the process parameters (temperature and reaction time)

Experiment conditions: Temperature (180°C, 200°C, 220°C and 250°C), reaction time (0.5h, 1h, 5h, 10h) using FS : effective biomass ratio

Results: Optimum temperature and reaction time with highest energy content

Phase III: Hydrochar production from ADS

Purpose: To investigate the energy content of anaerobically digested sludge

Experiment conditions: Fermentation of FS: effective biomass at 35°C for different SRT of 7,14,21,28 and 35 days. Optimum conditions from phase II used for HTC.

Results: Comparison of energy content of produced hydrochar from ADS for different SRT

Figure 3.1 Research outline

3.2.2.1 Cassava pulp

Cassava is a woody perennial shrub crop that grows in tropical and sub-tropical regions, which is mostly used for food. In Thailand, 20 – 25 million tons per annum of cassava is produced. Approximately, 40% from the yield is used to produce cassava starch, since rich in carbohydrates. The produced starch extract will be used in food processing, pharmaceutical and chemical industries. Moreover, it is used as an additive in paper and plywood production. During the starch extraction process, 86% of cassava pulp is generated as waste. The pulp contains significant amount of residual starch and moisture. This residue is being used as animal feed in a small amount and the rest is left as waste into the environment. Due to its higher biodegradability, disposal of this waste will create environmental problems by contaminating the natural resources. Now days, cassava pulp is widely used as a co-digestion substrate in AD, resulting good yield in biogas production (Panichnumsin et al., 2010). It looks ivory color and holds the squeezable amount of water within it (Appendix A).

3.2.2.2 Dried leaves/grass cuttings

Dried leaves fallen from the trees and grass cuttings due to trimming generate a huge amount of organic waste daily. This waste is dumped as a solid waste and used for composting. The composted material is rich in organic carbon content and used as a soil fertilizer. While composting will be successful in summer and tropical climatic conditions, rainy or winter seasons, natural composting will pose a tedious process. For this study, samples were collected from the AIT environment. In order to remove the excessive moisture, samples were kept at 105°C for overnight, which also helps to shred them easily. It looks like greenish brown color with homogenous size (Appendix A).

3.2.2.3 Pig manure

Pig manure also called as swine manure is a mixture of pig’s feces (60%) and urine (40%). The characteristics of pig manure are varied based on its diet. Corn and sorghum are the basic feed, which is rich in carbohydrates and fats. Due to its high moisture and nitrogen content of the pig manure, it is widely applicable in biogas production (Møller et al., 2004). The pig manure looks like greenish yellow color and it is in semi-solid state. It was collected from the farm land (Appendix A).

3.2.2.4 Rice husk

Rice husk acts as a protecting cover for the rice grains. It is bright yellow in color and has a hard surface. It is widely used as fertilizer, building and insulation material. Moreover, bio-char produced from rice husk/hulls are widely applied in the field of green energy (Olivier, 2012) (Appendix A).

3.2.3 HTC reactor

HTC batch experiments were conducted by using 1 L reactor (Figure 3.2). The reactor is broadly divided into three different parts namely reactor tube, heating jacket and cooling bucket. Table 3.2 gives the description of the different components of the reactor. Reactor tube is the main body of the system, where the feed stocks are fed. The reactor tube is enclosed by the heat jacket. The heat jacket dissipates heat around the reactor tube and also helps to prevent from overheating. Temperature of the heat jacket is controlled by a control panel, which constantly maintains the desired temperature. The reaction time can also be set at the control panel. After completion of the operation, the reactor tube is quenched inside a cooling bucket, in order to stop furthermore reaction of feedstocks. The cooling bucket is constantly supplied with flow of water, this decreases the temperature drastically. After cooling, the pressure is released from the pressure gauge present at the head of the reactor. Finally, HTC produces coal-slurry end-product which has to be involved in further processes (Appendix A).

Figure 3.2 Laboratory setup of HTC reactor

Table 3.2 Components of HTC Reactor

No.	Components	Description
1	Control panel	Temperature and operation time control
2	Tube head	Pressure gauge, thermocouple, gas collection port
3	Heating jacket	Electrical heater 2000 Watts
4	Reactor tube	Material : Stainless steel ; Total volume : 1000 cm^3 (1 L) Inner diameter, depth : 10.16 & 13.72 cm
5	Cooling bucket	cooling by water flow

3.2.4 HTC procedure

The overall procedures for HTC were carried out by four major steps (Figure 3.3) and followed though out the experiments. Firstly, the experiment was started by feeding the substrates into HTC reactor and followed by filtration and drying. Finally, the solid recovery from the experiments was employed for further analysis (Appendix A).

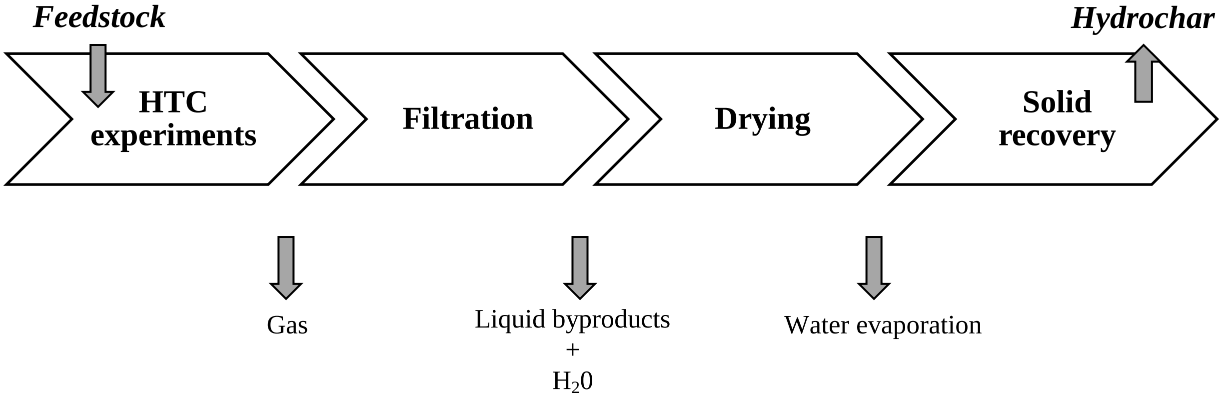


Figure 3.3 Overall HTC procedures

3.2.4.1 HTC experiments

HTC processes are mainly controlled by temperature and pressure. Therefore, temperature and pressure along the consumption of electricity were noted down for each experiment. Primarily, temperature and pressure are gradually started to increase, which predominantly depends on the initial temperature of the feedstock as well as its characteristics. It requires approximately 30 minutes reaching temperature from 10 - 180°C and pressure 0 - 20 bar.

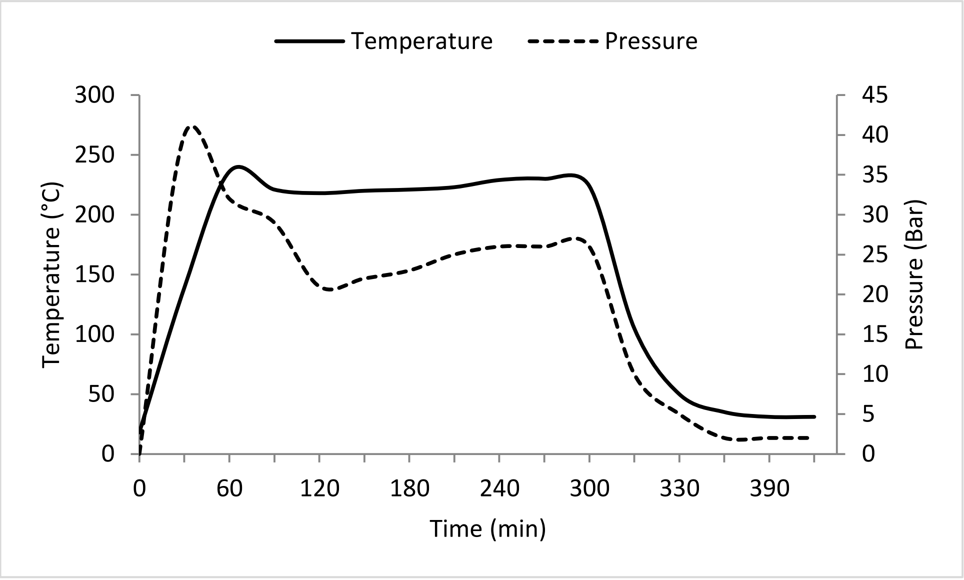


Figure 3.4 Temperature & pressure profile (recorded on 31.10.2014)

Thus, the heating rate of the reactor was calculated as ≈ 6°C/min that also includes the fluctuation of heat within the system. It might differ for different reactors. After reaching the desired temperature zone, the control panel begins the operation for assigned reaction time. Moreover, the efficiency of the reactor is calculated from the supply of ,external energy. Total power consumption for one batch experiment includes the heat loss from the body of the reactor. For this reactor, 90% of the supplied heat losses and radiates from the reactor body via conduction and convection. This is mainly dependent on the material and design construction of the reactor. Calculating the heat loss is important that will be helpful for energy balance. Finally, the reactor has to be cooled down drastically with the help of a cooling bucket, which is filled by constant flow of water. The cooling rate was observed as 45 - 50°C/min (Appendix B). Figure 3.4 and 3.5 represents the profile of temperature, pressure with consumption of electricity. It was observed at 220°C, 5hours. For this case, ±5°C fluctuation of temperature from the prerequisite temperature was noticed. Also the pressure was ranged between 25 – 30 bar. Approximately, 3.60 – 3.93 kWh, electricity was supplied to operate the reactor continuously.

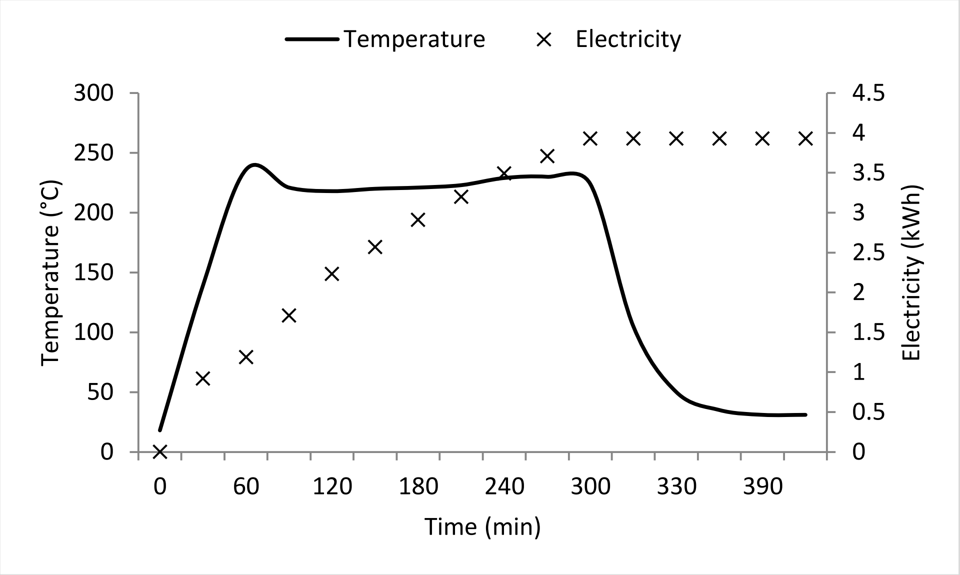


Figure 3.5 Temperature & electricity (recorded on 31.10.2014)

3.4.2.2 Mechanical dewatering

After HTC processes the end-product needs to be mechanically dewatered (Figure 3.6). The coal-slurry product was filtered through 1.2µm (pore size) Whatmann filter paper by using a vacuum filter. The capillary suction time (CST) was recorded. However, it is dependent on the characteristics of the end-product. Based on the hydrophobicity of produced hydrochar, CST varied and ranges between 5- 10 minutes to remove 60 – 80% of moisture. The filtrate was preceded for analysis.

3.4.2.3 Thermal drying

The filtered hydrochar was dried at 105°C overnight to remove excessive moisture content. The weights of the hydrochar before and after drying were measured (Figure 3.6). However, dried end-product is essential to measure their energy content as well as its proximate analysis.

3.4.2.4 Solid recovery

The dried hydrochar was powdered using a blender (Figure 3.6). The powdered hydrochar is used for further analysis. The solid recovery is fully dependent on the characteristics of the feedstock. In addition, it also varies by varying the solid content in feedstock (Appendix B).

Coal-slurry (After HTC) **Vacuum filtration** **Filtrate**

Filtered hydrochar **Weighing** **Dried hydrochar**

Figure 3.6 Different stages of separating hydrochar

3.2.5 Fermentation setup - lab scale

In order to investigate the effects on the energy content of hydrochar by using anaerobically digested sludge, wet fermentation process was carried out for the mixture of FS: CP. Firstly, the mixture was adjusted to approximately 12 -15% of solid content, in order to maintain the wet fermentation. One liter capacity of reagent bottles with the sample of 700ml was setup for lab-scale. In order to maintain the anaerobic condition, nitrogen gas was introduced that purges the excessive oxygen from inside the bottle. Afterwards, the bottles were sealed and kept inside an incubator chamber as shown in figure 3.7. Mesophilic range of 35°C was maintained inside the incubator for total SRT 35 days. Gas compositions, pH, TS and volatile fatty acids (VFA) were measured every 7days of SRT. This digested sludge was fed into HTC reactor and produced the hydrochar. Finally, energy contents of dried hydrochar were measured.

Figure 3.7 Experimental set-up for fermentation process

3.3 Methodology

3.3.1 Phase I - Investigations the effects of different biomass

Feedstock, mixture of FS with biomass was prepared separately for different mixing ratio. Mixing ratio of 1:1 and 3:1 were adopted for FS: biomass. Approximately 79 - 81% of moisture content in 350ml of feedstock were maintained for each experiment. The required volume of each biomass is varied and depended on its solid content. Moreover, the quantities of each biomass were weighed individually before mixing. Table 3.3 represents their individual weight for mixing. Finally, the mixture was fed into the HTC reactor. (Appendix B).

Table 3.3 Amount of Feedstock for Different Mixing Ratio – Phase I

Experiment no.	Mixing ratio	Feedstock (FS: biomass)	Sample volume (350g) (TS ≈ 20%)	
			*Weight of FS (g)	*Weight of biomass (g)
1	-	FS (only)	70	0
2	-	CP (only)	0	70
3	1:1	FS:CP	35	35
4	3:1	FS:CP	52.5	17.5
5	-	DL (only)	0	70
6	1:1	FS:DL	35	35
7	3:1	FS:DL	52.5	17.5
8	-	PM (only)	0	70
9	1:1	FS:PM	35	35
10	3:1	FS:PM	52.5	17.5
11	-	RH (only)	0	70
12	1:1	FS:RH	35	35
13	3:1	FS:RH	52.5	17.5

** measured on the dry basis and varied based on the total amount*

3.3.1.2 HTC conditions – phase I

The temperature and the operation time for phase I were selected from the literature studies as 220°C, 5hours. By assigning the uniform conditions for all mixing ratio, helps to compare the results effectively. Initially, HTC experiments were conducted FS and biomass alone. This helps to understand own capabilities of biomass in HTC. Moreover, hydrochar was produced from different mixing ratio of 1:1 and 3:1. The characteristics of hydrochar were determined from each batch. Totally three batches of experiments were conducted in this phase. Average values were considered for the results and analysis and calculated with its standard deviations (Appendix B).

3.3.2 Phase II - Optimization of process parameters

3.3.2.1 HTC conditions – phase II

In this phase, the optimized process parameters in terms of temperature and operation time were perceived. HTC experiments were conducted for effective biomass from phase I. The temperature was varied from 180°C, 200°C, 220°C and 250° for the respective operation times of 0.5h, 1h, 3h, 5h and 10h C (Table 3.4). Optimized temperature and operation time from this phase were moved to the phase III experiments. Moreover, the characteristics of the products obtained from this phase were analyzed. Experiments were conducted into two batches and average values were considered for the analysis with its standard deviations (Appendix B).

Table 3.4 HTC Experimental Conditions – Phase II

Temperature (°C)	Operation time (h)	*Total solids in feedstock (FS:CP = 1:1) (g)
180	0.5	70.5
180	1	70.5
180	3	70.5
180	5	70.5
180	10	70.5
200	0.5	70.6
200	1	70.6
200	3	70.6
200	5	70.6
200	10	70.6
220	0.5	70.5
220	1	70.5
220	3	70.5
220	5	70.5
220	10	70.5
250	0.5	70.6
250	1	70.6
250	3	70.6
250	5	70.6
250	10	70.6

*measured approximately on dry basis

3.3.3 Phase III – Hydrochar production from fermented sludge

3.3.3.1 Conditions for fermentation process

The amount of wet feedstock per fermentation bottle was weighed before conducting the experiments. Moreover, the total solid presented were determined on dry basis (Table 3.5). Basic parameters like pH, TS were measured from standard method (APHA, 2005).

Table 3.5 Fermentation Conditions

SRT (Day)	#Amount of feedstock (g)	*Total solids (g)
7	703.3	102.3
14	706.4	105.3
21	705.4	109.8
28	704.8	104.6
35	705.9	107.2

wet feedstock, *dry basis

Additionally, total volatile fatty acids (VFA) were measured for the sample by extracting the liquid part in centrifugation. The standard distillation method was followed, where all volatile organic acids was measured in terms of acetic acid (Appendix B). Two bottles were adopted per SRT in terms of duplicates and average results were considered for the results analysis.

3.3.3.2 HTC conditions – phase III

After fermentation, HTC experiments were conducted for every 7days at 250°C for 3 hours. Normally, 350g of digested sludge as feedstock and their respective TS content were measured for every batch of experiments (Table 3.6). After HTC experiments, pH in the filtrate, weight of dried solids with their energy contents were also measured (Appendix B).

Table 3.6 HTC Conditions – Phase III

SRT (Day)	Temperature (°C)	Operation time (h)	*Total solids in fermented sludge (g)
0	250	3	53.9
7	250	3	51.8
14	250	3	48.4
21	250	3	47.4
28	250	3	48.1
35	250	3	44.8

* weighed on dry basis

3.4 Analytical Method

3.4.1 Characteristics of solids

The initial characteristics such as total solids (TS), moisture content (MC), total volatile solids (TVS) of raw materials were determined by standard method (APHA, 2005) (Table 3.7). Energy contents and volatile matter (VM), fixed carbon (FC), ash, moisture contents were measured by using bomb calorific meter and thermo gravimetric analyzer respectively (Appendix B).

3.4.1.1 Bomb calorimeter

The energy contents of the samples were measured by AC-500 Isoperibol calorimeter (Leco, USA). The heat of combustion (energy content) of a sample is defined as the number of heat units liberated by a unit mass of a sample. The sample is burned with oxygen in an enclosure of constant volume. As a result, all carbon and hydrogen from the sample will be burned with oxygen and liberated as CO_2 and water. In addition, oxidation of other elements such as sulfur will also be resulted due to combustion. The energy content is measured as calorie per gram. (Appendix A).

3.4.1.2 Thermo gravimetric analyzer

TGA – 701 ((Leco, USA) was equipped to analyze the proximate characteristics of the samples. The instrument consists of 19 furnace carousels, which is connected with a computer. High degree of temperature is applied into a controlled environment that incinerates the sample. As a result, total moisture, ash, volatile matter content from various organic, inorganic and synthetic materials are measured in terms of its weight loss after heating. Results are determined in percentage. (Appendix A).

Table 3.7 Characteristics of Feedstocks

*Characteristics	FS	CP	DL	PM	RH
Moisture content (MC)	79.8	80.9	10.1	74.5	3.2
Total solids (TS)	20.2	19.2	89.9	25.5	96.8
Total Volatile solids (TVS)	60.6	98.3	85.2	55.1	84.8

** measured in % for dry basis;*

3.4.1.3 Elemental compositions

The ultimate analysis such as carbon (C), hydrogen (H) and nitrogen (N) and sulfur (S) for the feedstocks and produced hydrochar were measured by using CHNS analyzer (Truspec, Leco, USA). Finally, oxygen (O) (%) was calculated as 100 – (C+ N+ H+ S+ Ash). (Appendix B).

3.4.2 Liquid characteristics

After filtration, the process water was analyzed. The basic characteristics such as total organic carbon (TOC), chemical oxygen demand (COD), total nitrogen (TN) and total phosphorous (TP) were determined based on the standard method (APHA, 2005). (Appendix B).

3.4.3 Gas compositions

Agilent 7890A Gas Chromatograph was equipped to determine the compositions of produced gas. Principally, it works at 150°C with the help of Helium or nitrogen as carrier gas. The sample is injected into the instrument and it travels through a column as a gas stream. The column separates the samples into different components. As a result, a graph was generated with corresponding area of peaks with respect to the retention time. The results are compared with the standard sample peak. Finally, different compositions of CO_2, O_2, N_2, CH_4 etc. are obtained as percentage. (Appendix B).

Chapter 4

Results and Discussion

This chapter explains about the results obtained from the study with relevant discussions. All the results are delivered from its average values. Results sections are divided into three phases based on the objectives. In the first phase, the effects of different biomass addition with FS will be illustrated with its results. Secondly, the effects of the process parameters of biomass addition will be discussed from the experimental studies with the help of its characteristics. Based on these results, mass balance, carbon balance and energy balance were done and discussed their importance in this study. Third phase reveals the results obtained from the fermentation process and verified their effectiveness on HTC. Also, a case study were attempted to compare the HTC with anaerobic digester process.

4.1 Phase I: Effects of Different Biomass

Different biomass such as CP, DL, PM and RH were mixed with FS for the mixing ratio of 1:1 and 3:1. The results were analyzed based on their solid recovery, energy content, proximate analyzer. Moreover, the energy contents were compared with each other and the effective biomass was selected, in order to study their effects on process parameters in detail.

4.1.1 Solid recovery

Solid recovery also called as mass yield was calculated as a ratio for the measured dried weight solid hydrochar to the input solid weight of feedstock (figure 4.1) (Li et al., 2013). The amount of solid obtained from the HTC is fully based on the characteristics of feedstock including its porosity and bulk density. The yield ranges from 54 – 77%. The data is comparable with the previous studies that yielded 35 – 80% from different biomass (Child, 2014). (Appendix B).

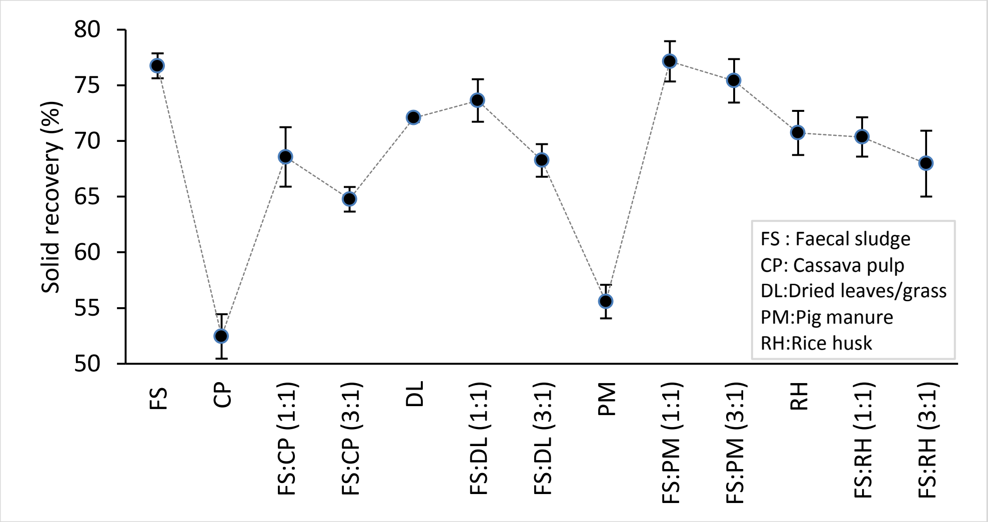


Figure 4.1 Solid recovery

Biomass alone yields hydrochar as 76, 54, 72, 57 and 72% for FS, CP, DL, PM and RH respectively. Comparatively, FS produces higher amount of hydrochar, this might be due to the presence of high inorganic substances. In contrast, CP and PM yields lower than other biomass, due to its higher volatile organic matter. Moreover, 72% solid gained from both DL and RH. By addition of FS with biomass for mixing ratio of 1:1, helps to increase the mass yield as 15, 2 and 20% for CP, PM and DL respectively. This was not achieved for the mixing ratio of 3:1. Moreover, the weight of obtained hydrochar is significantly lower than the input total solid and moderately decreased as 28% and 31% for 1:1 and 3:1 mixing ratio. It is evident that HTC undergoes into the solid decomposition to produce hydrochar (Libra et al., 2011). Additionally, the rate of decomposition is responsible for the end-products (Xiao et al., 2012).

4.1.2 Energy content

Figure 4.2 compares the energy contents for different mixing ratio. 19.5, 29.13, 26.33, 25.63 and 25.14MJ/kg were obtained only for biomass alone respectively for FS, CP, DL, PM and RH. The energy contents of FS were significantly increased from 3 – 16% by addition of biomass. For the mixing ratio of 1:1, the energy contents of FS were enhanced to 16, 9, 8 and 3% by adding CP, DL, PM and RH respectively. On the other hand, the energy contents were gained for 3:1 ratio as 10, 12, 12 and 8% for CP, DL, PM and RH respectively. These results are proven that the addition of biomass really aids to increase the energy content of FS. (Appendix B).

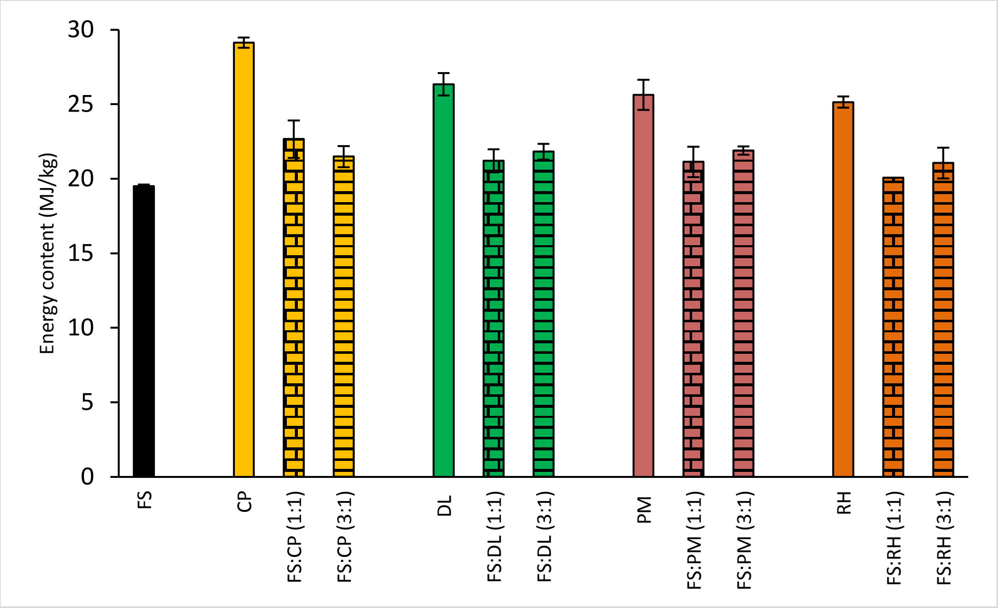


Figure 4.2 Energy content

Although the energy content of hydrochar was increased from both mixing ratio, the values of 3:1 ratio is quiet lower than 1:1. The possible reason is that while mixing both FS and biomass equally, it effectively mixed and involved into the process and aided to increase the energy content. However, for mixing ratio 3:1, more FS was added with biomass and the characteristics of FS might be dominated and declined the energy content.

4.1.3 Volatile matter and fixed carbon content

Apart from energy content, fixed carbon (FC) and volatile matter (VM) were plotted with its respective ash and moisture content (Figure 4.3). Overall, decrement of VM from its original value was found. For the possible reason is that most of the hydrocarbon and aromatic carbons might be converted as gas during HTC process (Funke et al., 2010). As a result, the converted VM might be involved in liquid byproducts. Moreover, the percentage of VM in hydrochar had tremendously increased by addition of biomass. It is increased up to 7% from both mixing ratio compared with hydrochar produced from FS alone. Additionally, the ash content was significantly decreased by using mixture of FS and biomass (Mumme et al., 2011). As a result, biomass addition helps to increase the coal characteristics in hydrochar. (Appendix B).

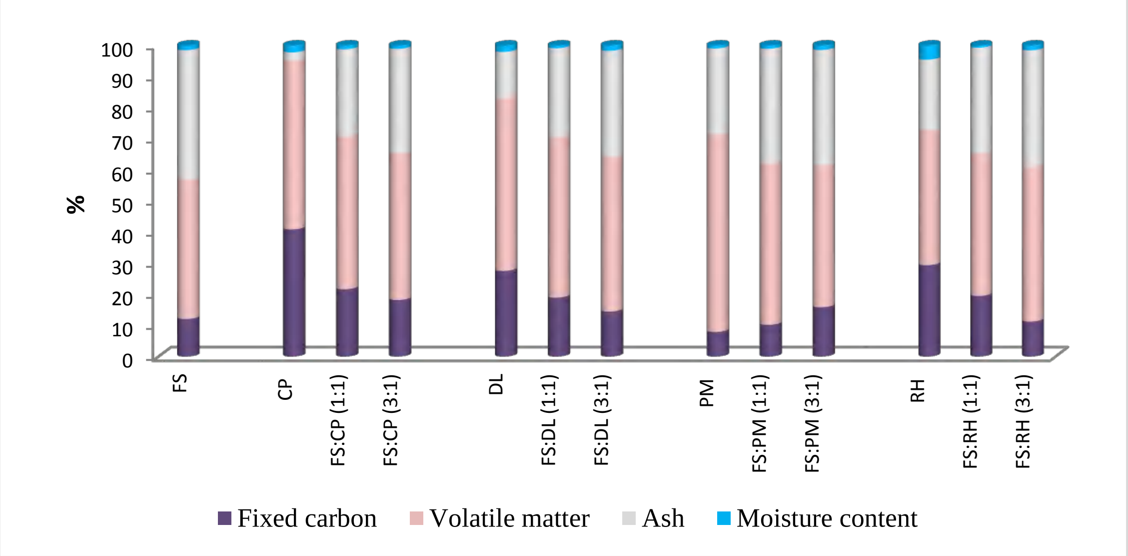


Figure 4.3 FC, VM, ash and MC of hydrochar

While comparing the FC from the initial feedstock values, it is noticeable that the FC content was increased from its raw feedstock (Figure 4.4). More than 100% increment on FC was found for CP and RH. From these results, the carbonization of HTC is proven. Additionally, it also helps to explain about the effectiveness of HTC process in carbon sequestration (Titirici, 2013).

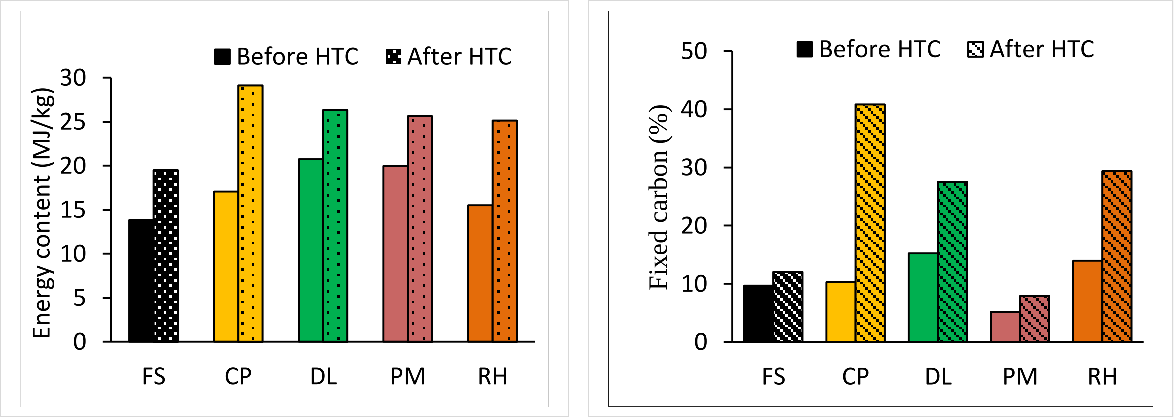


Figure 4.4 (a) & (b) Energy content and fixed carbon of feedstocks (before and after HTC)

4.1.4 Effective biomass

Effective biomass was analyzed based on its obtained energy content (Figure 4.5). While analyzing the effect of biomass addition, CP with FS of 1:1 yields higher energy content followed by FS: DL and FS: PM with the ratio of 3:1. On the contrary, FS with RH produces hydrochar with lower energy content. A possible explanation is that cellulosic biomass with lower woody formation is called as “soft biomass” that provides higher processing efficiency (RIKEN, 2001). Moreover, biomass which falls under soft biomass category are readily undergoes into hydrolysis phases in HTC mechanisms (Titirici and Antonietti, 2010). In this study, CP and PM looked like smooth textured nature with higher moisture content might be involved in the HTC processes cursorily and yielded higher energy content. On other hand, DL and RH might not be effective on the desired temperature and operation time. It may yield higher energy content for increasing temperature and operation time (Appendix B).

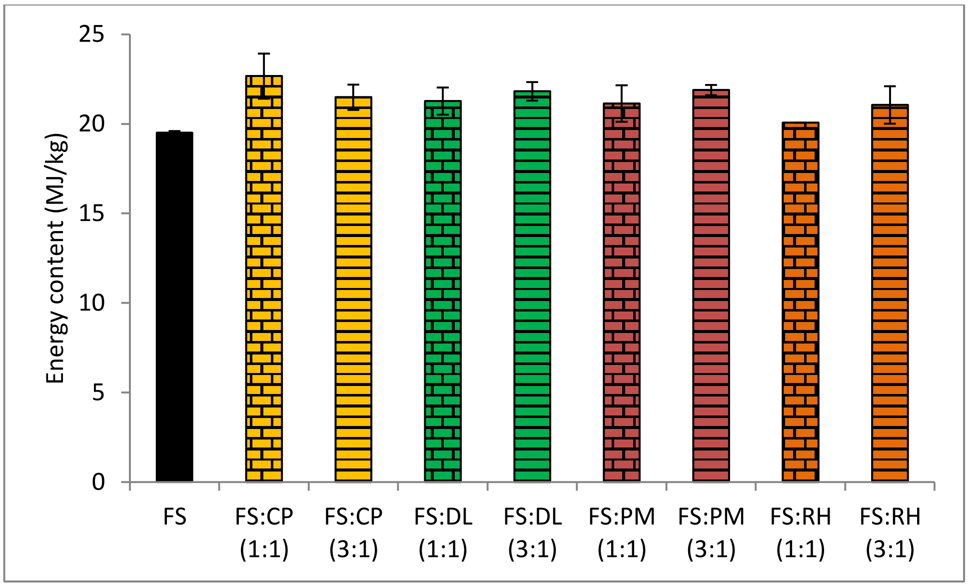


Figure 4.5 Effective biomass based on energy content

4.1.5 Comparative studies – phase I

Finally, FS: CP with mixing ratio of 1:1 effectively gains higher energy content of 22.66 MJ/kg along with FC content. This is evident to show the effectiveness of HTC process for carbon fixation (Titirici et al., 2007). Furthermore, figure 4.6 compares the results of with other studies (Oliveria et al., 2013). It is proven that FS with CP comparable with other biomass mixtures. Moreover, the obtained result is slightly higher than LAUBAG-Briquette. In conclusion, combination of different biomass improves the carbonization of produced hydrochar with higher energy content (Oliveria et al., 2013).

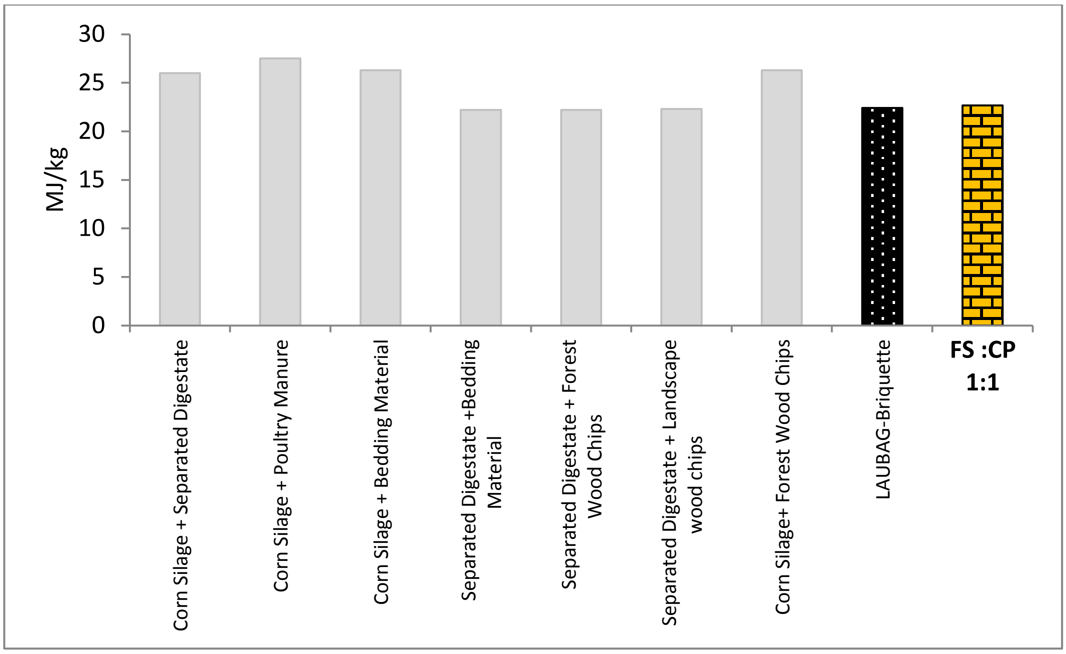


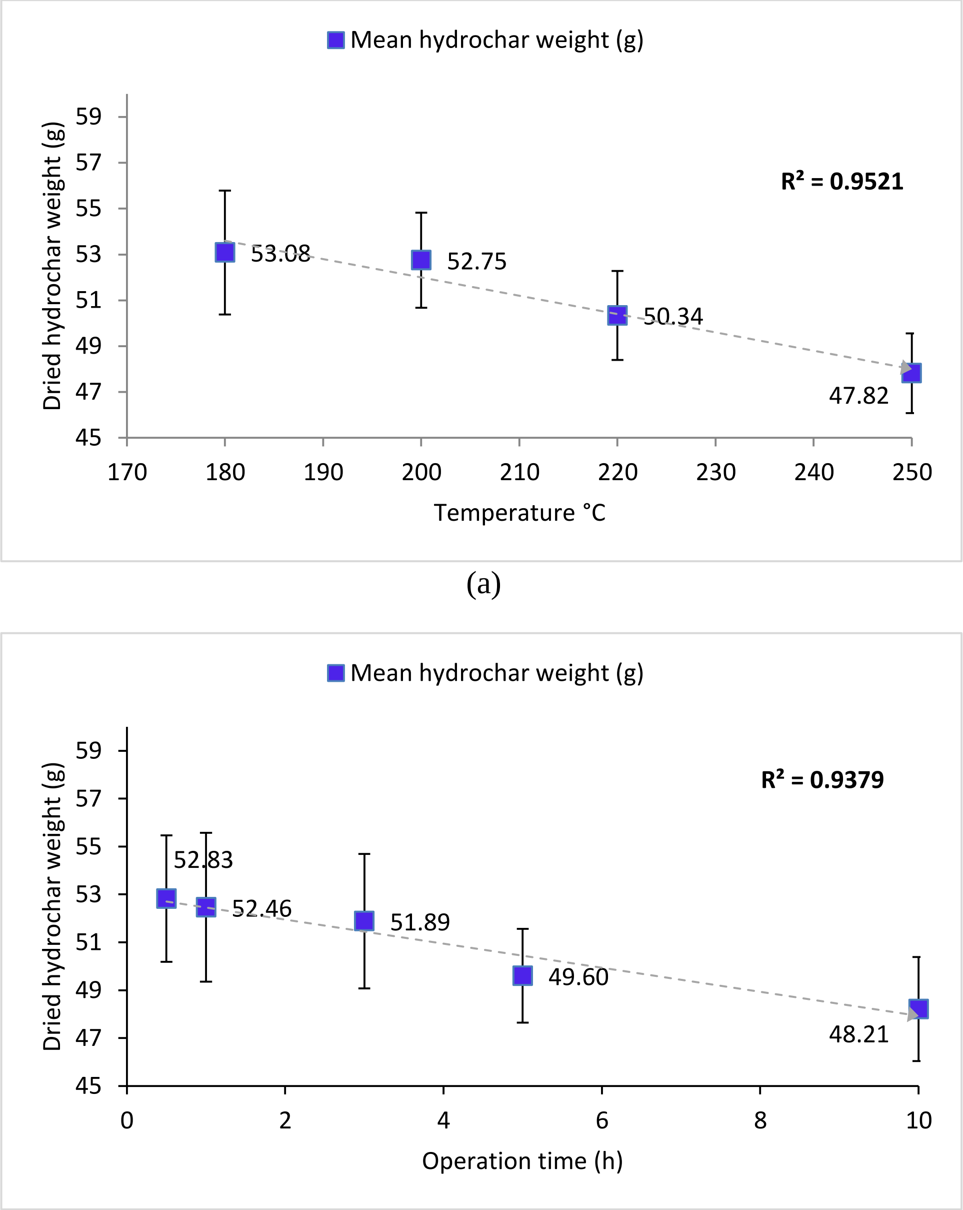
Figure 4.6 Comparative studies – phase I (Oliveria et al., 2013)

4.2 Phase II: Effects of Process Parameters

The yielded higher energy content of hydrochar from the combination of FS and CP with the mixing ratio of 1:1 was used as the effective biomass in this phase. By varying temperature with operation time, the characteristics of the produced hydrochar were analyzed and resulted. Finally, optimized temperature and operation time were found from the highest energy content. Furthermore, elemental compositions of the produced hydrochar were measured. Based on the end-products, mass balance, carbon balance and energy balance were done for the optimum conditions.

4.2.1 Hydrochar recovery

Figure 4.7(a) and (b) were plotted and compared for different temperature and operation time against the dried hydrochar weight. It shows that the amount of hydrochar drastically decreasing along with temperature and operation time (Xiao et al., 2012). At low temperature and operation time, the produced hydrochar is quiet high while comparing with increased temperature and time and it is shown by linear regression line. Overall, the solid recovery was moderately gained as 72.8%. It is decreased from 79 – 64% from 180 - 250°C at 0.5 – 10h respectively. Child (2014) found that 50% solid recovery by using different biomass as average. Moreover, the decrement in the solid recovery along with process conditions proves the elimination of hydroxyl and carboxyl groups effective for increasing temperature and time (Xiao et al., 2012). The characteristics of the hydrochar will be discussed later sections. (Appendix B).



(a)

(b)

Figure 4.7 (a) and (b) shows the hydrochar weight vs temperature and operation time

4.2.2 Process water

Process water obtained after the dewatering process is also called as filtrate. Figure 4.8 illustrates the increment of process water (ml) along with temperature and operation time with regression fit. This is contradictory to the solid recovery. The amount of process water was varying from 125 - 250 ml from 180 - 250°C at 0.5 – 10h respectively. These data aids to prove the effectiveness of dehydration process from the input solid molecules along with temperature and operation time (Libra et al., 2011). The characteristics of the liquid will be discussed in detail. (Appendix B).

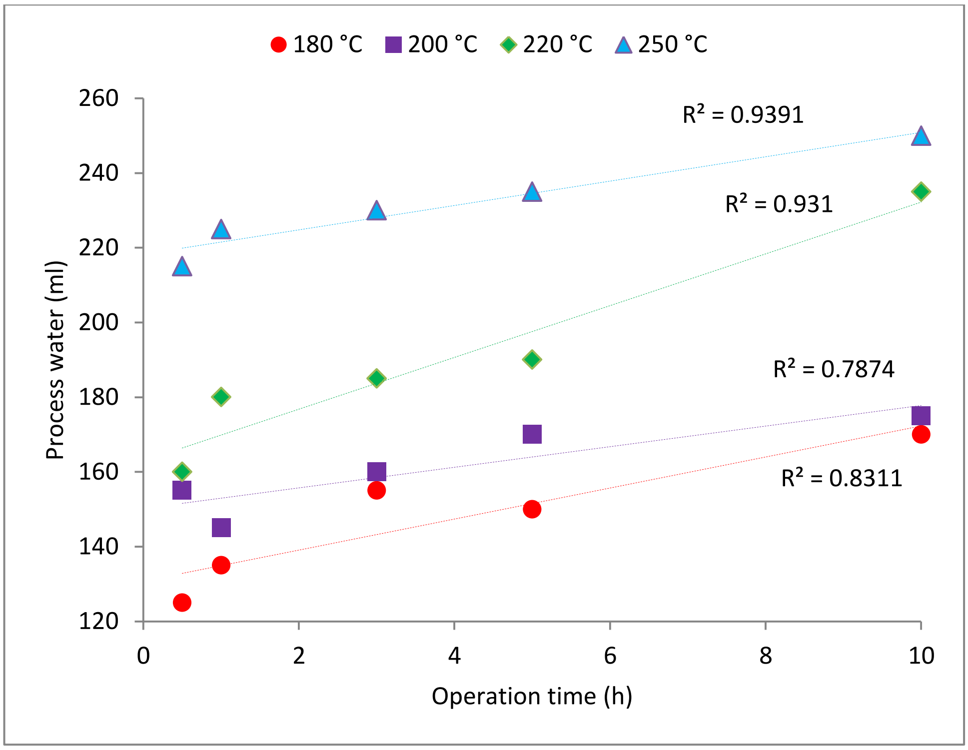


Figure 4.8 Process water

4.2.3 Energy content

Figure 4.9 shows that the energy content for different temperature with their respective operation time. The results are following the trend same as process water.

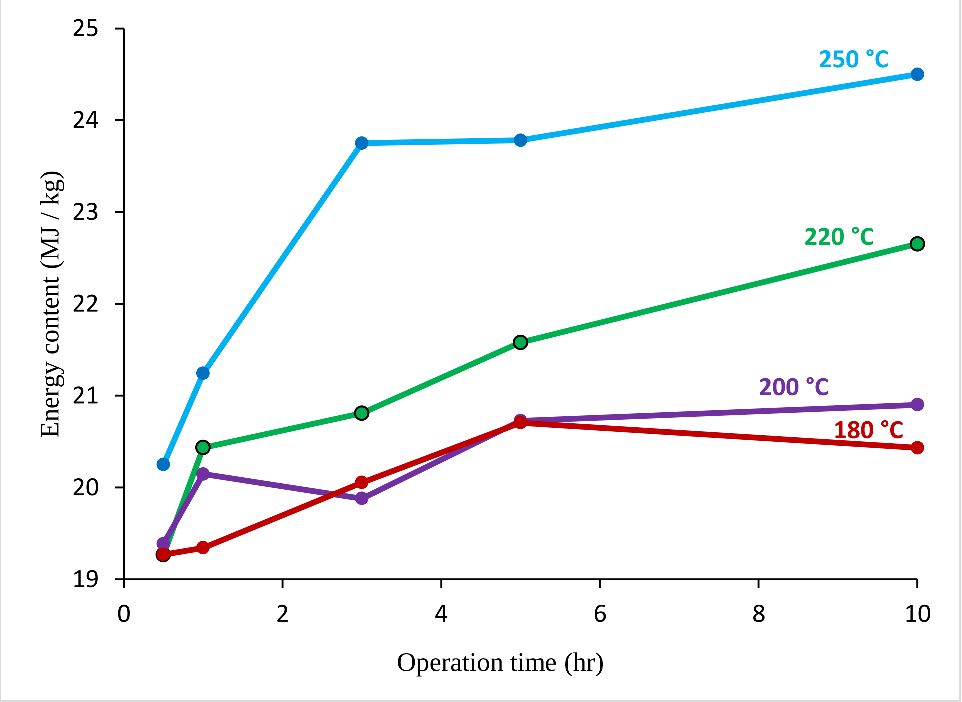


Figure 4.9 Energy content of hydrochar

While temperature and reaction time increases energy content is also increased. Minimum of 19.27 MJ/kg and the maximum value of 24.49 MJ/kg were obtained for 180 - 250°C at 0.5–10h respectively. Energy recovery from different biomass is the core objective of HTC technology that achieved from the study (He et al., 2013). Moreover, the results explain about the efficiency of HTC process where the wet biomass is converted as hydrochar within few hours (Fühner C., 2012). Additionally, it also proves about the chemical reactions which yield hydrochar with higher energy content. The effectiveness for the higher energy content will be discussed later sections. (Appendix B).

4.2.4 Volatile matter and fixed carbon

FC and VM by varying temperature and operation time were measured using proximate analyzer. Figure 4.10 shows the results of VM and FC as a separated plot for temeprature and time. VM decreases for both temperature and operation time (Mumme et al., 2011). While comparing both, gentle reduction is seen against time and steep reduction for tempertaure is noticed. Totally, 45% of reduction of VM is found from the initial feedstock to final hydrochar at 250°C, 10h.

On the other hand, FC is increasing along with temperature and operation time. While comparing both parameters, at 180°C for 0.5 h, the values of the FC is very low. From the results, it is clearly viewed that HTC mechanisms require a minimum time to start its processes (Child, 2014). The values are varied from 18.08 – 23.92%. Moreover, maximum increment of FC was noticed from 10.45 – 23.92 % from input feedstock to the output hydrochar (Figure 4.10). (Appendix B).

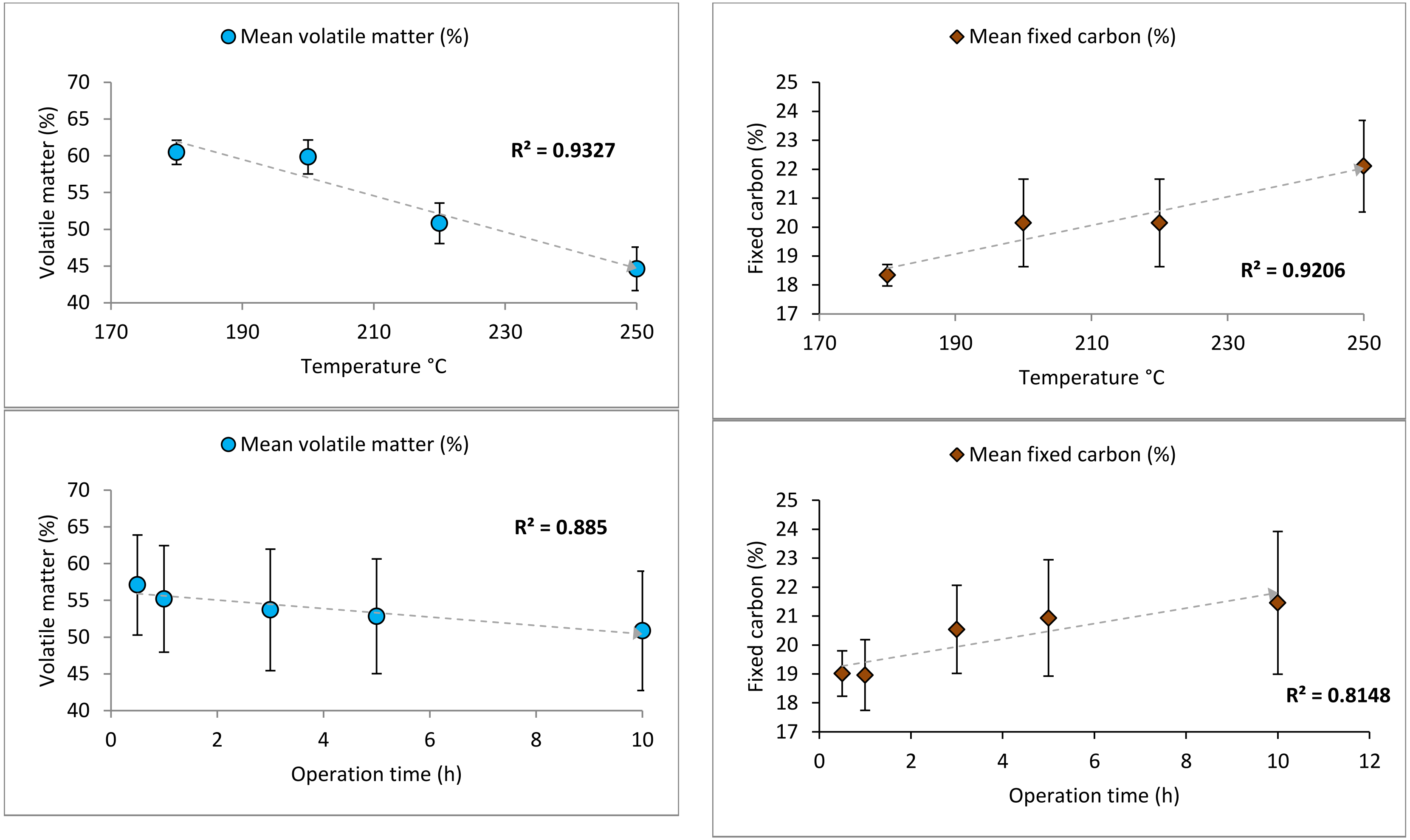


Figure 4.10 VM and FC for different temperature and operation time

4.2.4.1 Volatile matter conversion rate

By analysing the VM, it decreases thorught out the process along with temperature and time. It concludes that presence of organic volatile matter also assists in HTC mechnaisms. This may help to study about the reaction kinectics. Furthermore, previous studies confirmed that the solid decompositions in terms of hydrochar recovery follows the first order kinetics (Danso-Boateng, et al., 2013 ; Reza et al., 2014). It was followed for the volatile matter degradation in this study. Most of the points did not exactly fit into the first order kinectics, it might be due to the limitations of data. Another possible reason for that addition of biomass might double the concentration of VM and not able to follow the first order reaction. Therefore, conversion of VM studied and plotted in figure 4.11. (Appendix B).

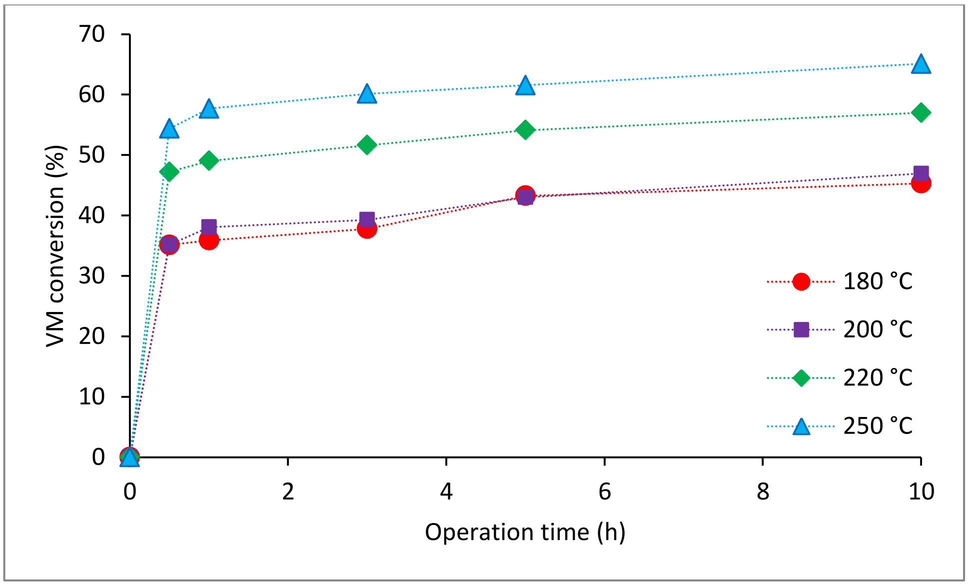


Figure 4.11 Volatile matter conversion

From the results, the higher conversion rate of VM was noticed within 1hour. This may be the highly reactive time in HTC mechanisms. Whereas, the conversion rate steeply increased up to 45, 47, 57 and 65% at 180°C, 200°C, 220°C and 250°C respectively. Interestingly, the conversion rate is significantly increased to 35, 35, 47 and 54% from 0 - 0.5h at 180°C, 200°C, 220°C and 250°C respectively. Whereas it was approximately increased up to 9.8 – 11.78% from 0.5 – 10h at all temperature level. In conclusion, the temperature is highly significant for the VM conversion. This may also result to increase the energy content of produced hydrochar.

4.2.5 Effects of temperature and operation time on HTC

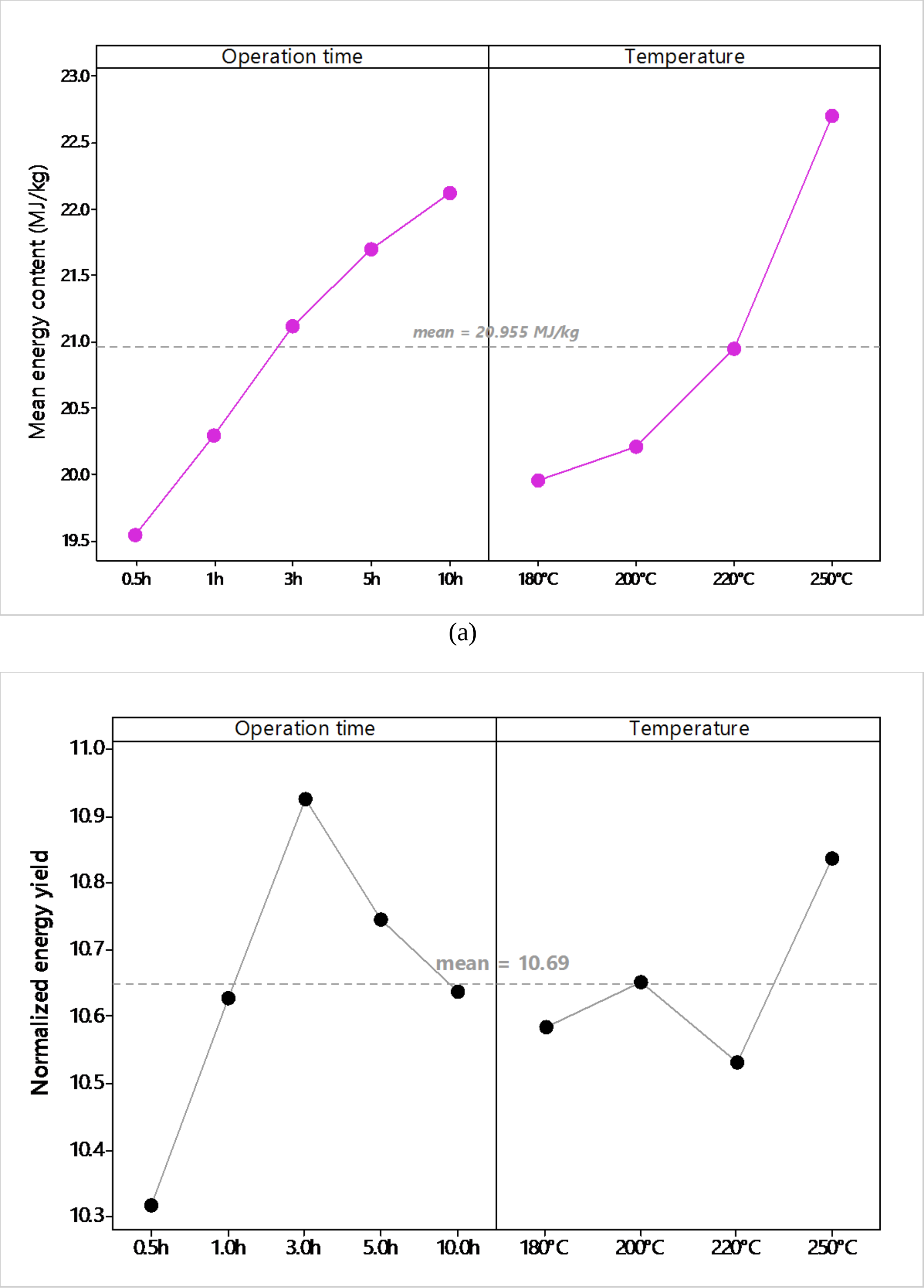
The characteristics of different parameters such as hydrochar weight, process water, VM, FC also for the energy content from HTC process were analyzed using one-way ANOVA. Table 4.1 shows their appropriate p-value for both temperature and time. The weight of dried hydrochar, process water and energy content are fully depended on operated temperature. In contrast, VM degradation is following the operating time. For FC, both temperature and operation time are influencing the increasing rate. Furthermore, it is clearly able to explain that solid decomposition by eliminating the hydroxyl and carboxyl groups influenced by temperature also for dehydration process. The degree of degradation of volatile organic matter and the fixation of carbon materials are very effective on the reaction time. This analysis helps to decide the coal characteristics of the hydrochar. (Appendix B).

Table 4.1 p-value for different parameters (ANOVA)

Parameters	p -value	
	Temperature	Time
Hydrochar weight	0.004	0.095
Process water	0.000	0.560
Energy content	0.010	0.109
Fixed carbon	0.000	0.000
Volatile matter	0.068	0.001

4.2.6 Optimum process parameters

The second objective of this study is to find out the optimum process parameters such as temperature and operation time based on the energy content and energy yield (Reza et al., 2014). The mean energy content was calculated as the ratio between the energy content of produced hydrochar to its initial energy content by multiplying with their respective solid yield. The main effects of temperature and reaction time were analyzed and resulted in figure 4.12(a) and (b). The graphs were plotted for the mean energy yield against operation time and temperature. From the graph, the moderate energy content was calculated as 20.955MJ/kg at 220 - 250°C for 1 – 3h. Therefore, the optimized processing parameters are situated in between. The energy contents were obtained as 21.24MJ/kg and 23.75MJ/kg at 250°C for 1 and 3 hours respectively. Drastic increment on energy content is observed from 1h to 3h at 250°C. However, the energy content is further increased only 3% from 3h to 10h. By considering the economic feasibility, it required 2 fold input energy to operate the reactor from 3 to 10hours. In conclusion, the optimum temperature and operation time were selected as 250°C and 3h for FS: CP of mixing ratio 1:1. This result is also confirmed by plotting the respective normalized energy yield and checked their effects on process parameters (Figure 4.12b). Moreover, finding effective process parameters are feasible to study about the unique characteristics of the products. Also, directs to calculate mass, carbon and energy balance. (Appendix B).



(a)

(b)

Figure 4.12(a) and (b) Optimum conditions from mean energy content and normalized energy yield

4.2.7 Comparative studies – phase II

In order to validate the results obtained from FS: CP at 250°C for 3 hours, data collected from previous studies and presented in figure 4.13. Appropriate data were collected that has to be relevant for the conditions used in this study. From the graph, it is clearly viewed that hydrochar produced from CP alone gained higher energy.

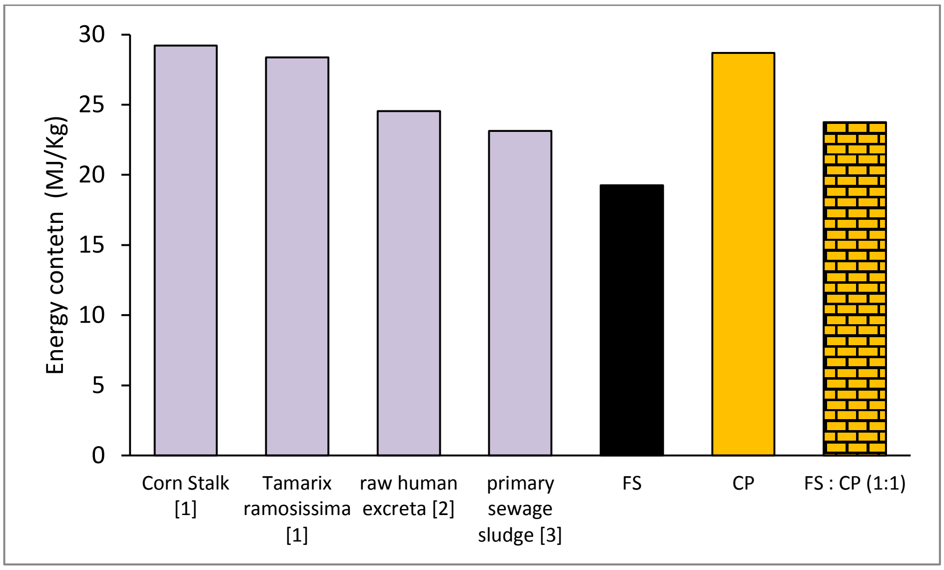


Figure 4.13 Comparative studies – phase II

[1] - (Xiao et al., 2012, [2] - (Afolabi and Wheatley, 2014), [3] - (Danso-Boateng et al., 2013)

The results are comparable and validated with the hydrochar produced from corn stalk and Tamarix ramosissima grass (Xiao et al., 2012). On the other hand, FS alone shows lower value, while it is mixing of CP is quiet higher than the hydrochar produced from primary sewage sludge (Danso-Boateng et al., 2013) and comparable with hydrochar produced from raw human excreta (Afolabi and Wheatley, 2014). However, the energy content of hydrochar is basically depended on the characteristics of feedstock used in HTC (Funke et al., 2010).

4.2.8 Characteristics

HTC separates its products as solid, liquid and gas phases. However, the compositions and amount of the products are varied from its feedstock characteristics also depends on the process parameters (Funke et al., 2010). After HTC, the end products look like a coal-slurry product and 97.8% of input feedstock was retrieved. It contains high moisture content with oily based texture. Smell of the products after HTC is fully depended on the characteristics of feedstocks (Afolabi and Wheatley, 2014). Generally, HTC vanishes the foul odours of FS while treated and produces the smell of mixture of roasted coffee and oil.

4.2.8.1 Solid – Hydrochar

Solid is the main product and looks like dark coal-like colour that confirms the carbonization of input feedstock (Xiao et al., 2012). In order to separate the solid from the slurry part, dewatering was done by using vacuum pump. While comparing with the feedstocks, the filtration of the slurry is quiet easy that occurs a sharp interface between the solid and liquid (Ramke et al., 2009). Additionally, the hydrophicity of the hydrochar also makes filtration easier. However, the rate of dewaterability is depended and increased with increasing time and temperature (Afolabi and Wheatley, 2014). For this study, it took approximately 4 -5 min to complete the filtration, which depends on the efficiency of the vacuum pump used. After filtration, the hydrochar still holds 60% of moisture within it and so thermal drying was carried out to evaporate the excessive moisture. (Appendix B).

4.2.8.2 Liquid

Aqueous phase was measured from the filtrate obtained from mechanical dewatering. Approximately, 65% of liquid was filtered from the feedstock that looks like bright straw colour. The amount of liquid produced is evident to prove the effectiveness of HTC that converts feedstocks into coal within suspension of water. Moreover, the amount of filtrate is 5- 6% larger than the input moisture content. From these results, the higher degree of dehydration is proved also evident the chance of producing liquid by-products. Approximately, 93 – 95% of water occupies in the filtrate.

The process water shows pH in the range of 4.6 – 4.8. This aids to prove the acidic nature due to the organic acids formation after dehydration process. Table 4.2 shows the biological characteristics of the filtrate measured from this study. The obtained ratio of COD/TOC = 2.59 and it is comparable with the previous studies. Ramke et al.,(2009) found the ratio COD to TOC is 2.30 and proved 85 % of organic COD degradation from anaerobic decomposition tests. Furthermore, the process water will be treated either by anaerobic digestion or will be used as a process water in HTC processes that helps to increase the reaction rate (Berge et al., 2011). Additionally, Xiao et al., (2012) mainly identified phenolic compounds along with furan derivatives by extracting the liquid by-products from corn stalk and Tamarix ramosissima biomass using ethyl acetate and confirmed the decarboxylation, demethanation processes. Additionally, the liquid products are highly rich with furfural and hydroxymethyl-furan derivatives that will be widely used in different field of studies (Libra et al., 2011). (Appendix B).

Table 4.2 Characteristics of Liquid

Parameter*	unit	Value
Volume of filtrate	ml	220 - 225
COD	mg/L	46400 - 48000
TOC	mg/L	17020 - 19305
TN	mg/L	2440 - 19016
TP	mg/L	63 - 125

*measured only at optimum condition

4.2.8.3 Gas

Gas is generally produced in HTC, where the hydrochar produced in a closed system at high temperature and high autogenoues pressure. The productivity of gaseous phase is also depended on the characteristics of the feedstocks and the process parameters. While comparing with the solid and liquid products, the amount of gas produced is very less. Approximately, 2 - 3 % of total amount gas from the input feedstock was produced which is comparable with 3 – 6% from other studies (Ramke et al., 2009). Table 4.3 represents the compositions of gas produced at optimum condition. Decarboxylation is responsible for the production of CO_2 that increases with increasing rate of temperature (Funke et al., 2010).

Table 4.3 Gas Compositions

Elements	Units*	Compositions
CO_2	%*v*	63.0
CH_4	%*v*	n.d
N_2	%*v*	31.3
O_2	%*v*	5.7

*% from the measured volume
n.d - not detected

4.2.8.4 Characteristics of hydrochar

After thermal drying, the wet hydrochar changed into sandy brown color hydrochar with high hydrophicity. The size of the particle is significantly reduced while comparing with the dried input material also gained smooth texture due to the breaking of cellulose matters as well as recombination of carbon materials (Xiao et al., 2012). Moreover, the dried hydrochar is easily blended and compactable that significantly reduces the storage area. Additionally, the friable nature of the solid makes easier for pelletizing (Titirici, 2013). (Appendix B).

Table 4.4 Characteristics of Hydrochar

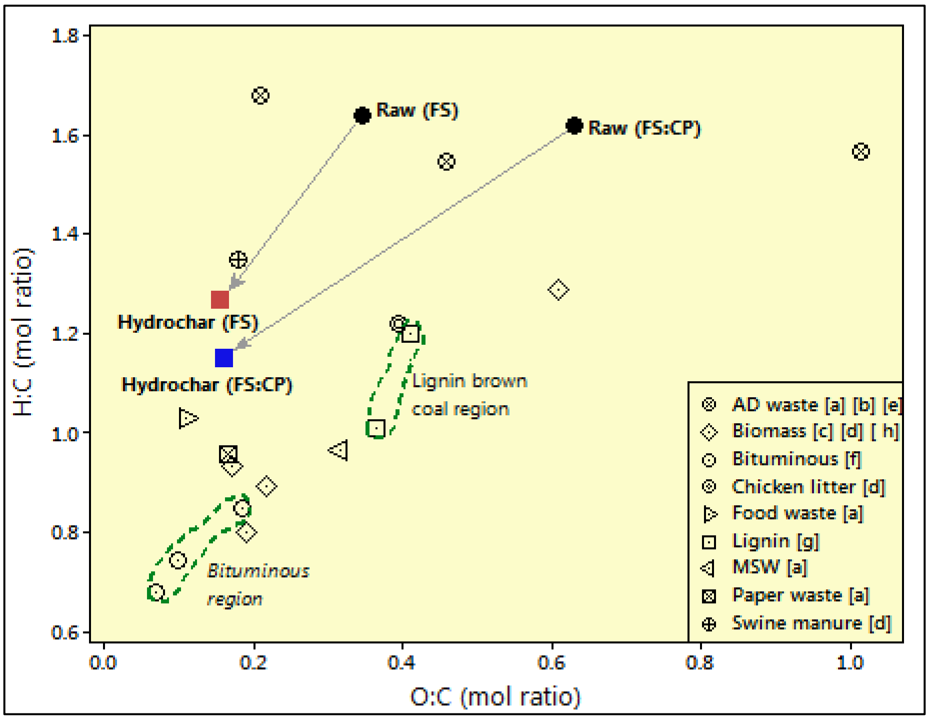
Parameter*	unit	Raw (before HTC)		Hydrochar (after HTC)	
		FS	FS:CP	FS	FS:CP
Proximate analysis					
MC	%wt	3.20	2.2	1.9	0.1
VM	%wt	53.5	75.2	42.6	44.0
Ash	%wt	33.1	20.6	42.9	33.2
FC$^{\#}$	%wt	10.2	11.4	12.6	22.6
Ultimate analysis					
Carbon (C)	%wt	38.5	38.6	41.0	48.3
Hydrogen (H)	%wt	5.3	5.20	4.3	4.6
Nitrogen (N)	%wt	3.8	1.9	1.9	2.2
Sulfur (S)	%wt	1.6	1.2	1.3	1.4
Oxygen (O)$^{'''}$	%wt	17.8	32.5	8.5	10.3
H:C		1.6	1.6	1.3	1.2
O:C		0.4	0.6	0.16	0.2
Energy content	MJ/kg	13.8	15.5	19.3	23.8

*measured on dry basis, $^{\#}$FC= 100 – (MC+ VM+ ash), $'''$O = 100 – (C% + H% + N% + S% - ash)

The fuel characteristics of produced hydrochar were determined from both proximate and ultimate analysis. Elemental compositions of C, H, N, and S were analyzed for raw feedstock and the produced hydrochar and resulted in table 4.4. Moreover, it also compares the obtained results with the characteristics of hydrochar produced from FS alone. The importance of ultimate analysis leads to plot the coalification diagram and verifies with the coal region. It is clearly viewed that the elemental composition of carbon (C) is significantly increased ≈10% that confirms the carbonization of HTC process. Simultaneously, the oxygen content is extremely reduced to 22% from the feedstock. Decrement of oxygen and hydrogen elements indicates the less condensation of hydrochar that contains higher H:C and O:C mol ratio (Xiao et al., 2012).

4.2.8.5 Coalification diagram

A plot against H/C and O/C mol ratio validates the characteristics of hydrochar from other studies (Figure 4.14). The H/C mol ratio is declined from 1.27 to 1.15 by addition of biomass with FS. The decrement of elements of H and O help to explain about the decreasing of rate of decarboxylation, dehydration along with demethanation in Van Krevelen diagram (Berge et al., 2011). Additionally, the place in coalification of hydrochar obtained from the optimum condition lies besides to the lignin coal region. Moreover, the obtained result is significantly higher while comparing the values of anaerobic digestate and swine manure from the diagram.



References
[a] - (Berge et al., 2011)
[b] - (Danso-Boateng, et al., 2013)
[c] - (Funke et al., 2010)
[d] - (Libra et al., 2011)
[e] - (Mumme, et al., 2011)
[f] - (Park and Jang, 2011, Ronteltap et al., 2014)
[g] - (Ramke, et al., 2009)
[h] - (Ingallinella et al., 2002; Xiao, et al., 2012

Figure 4.14 Coalification diagram

4.2.9 Mass balance

Figure 4.15 illustrates a simple process diagram throughout the process. It guides to calculate how much solid is converted as hydrochar, liquid and gas products. It is following the order from feedstock to hydrochar production through filtration and drying processes (Zhao et al., 2014). Moreover, attempting mass balance makes easier to calculate carbon and energy balance further. In order to make easier in calculation, spillage of solids and unaccounted release of gases did not consider that much. Based on the calculated data, 100% mass balance was expected.

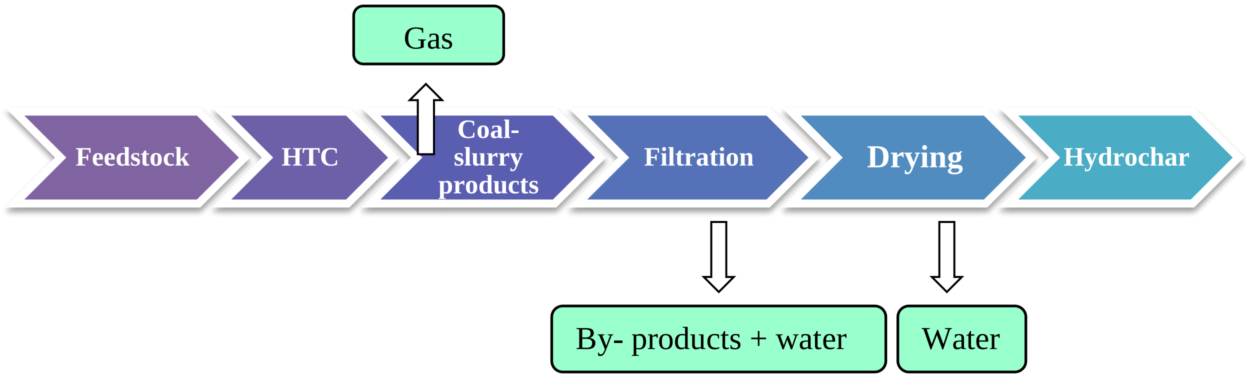


Figure 4.15 Mass balance

From the optimum conditions, 79.82 % MC with 20.18% TS were measured from the total feedstock volume of 350g. After HTC, amount of filtrate and amount of water evaporating via drying was accounted for liquid balance. Weights of hydrochar before and after drying were weighed for solid phase. The amount of gas produced was slightly adjusted, in order to try 100% mass balance. Figure 4.17 shows the overall mass balance that helps to interpret the conversion of solid from input material into different phases.

4.2.9.1 Solid balance

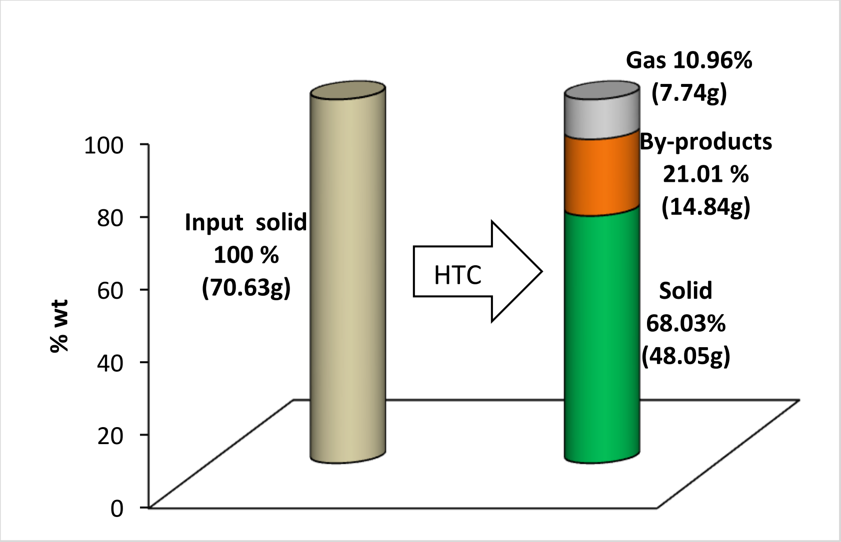


Figure 4.16 Solid balance

The main product of HTC is the solid hydrochar. From this study, it is identified that moderately 68.03% of solid converted as dried hydrochar and is validated with other studies (Figure 4.16). 50% of average solid yield was achieved by using different biomass in HTC (Child, 2014).

Approximately, 21.01% of solubilized liquid by-products were found it is comparable with previous studies of 10 – 20% (Ramke et al., 2009). Apart from those measured values, remaining 10.96% were assumed to convert into gas that produced due to the conversion of hydrocarbons and compared with the past studies of 1 – 4% to <10% (Funke et al., 2010). (Appendix B).

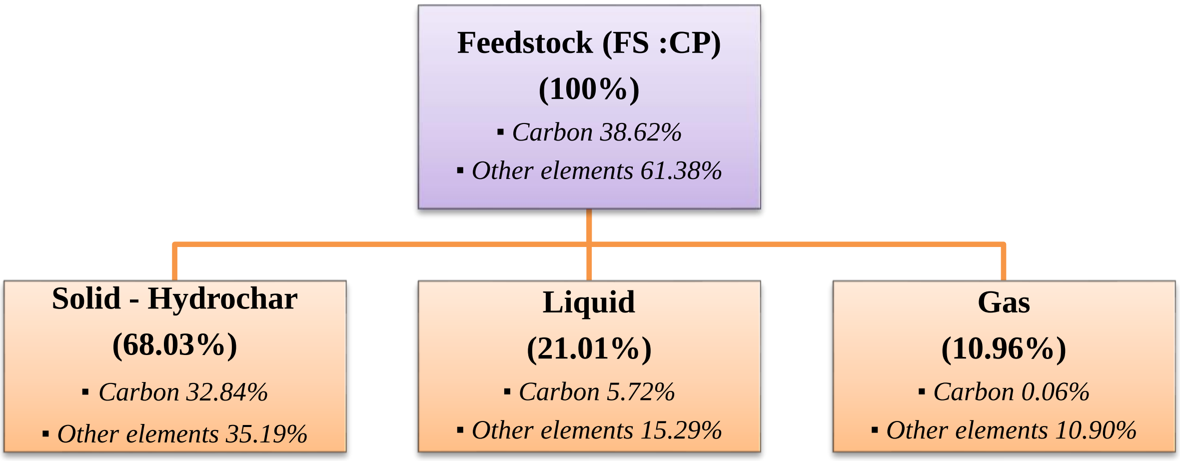


Figure 4.17 Overall mass and carbon balance

4.2.10 Carbon balance

Carbon balance is absolutely helped to estimate the carbon distribution throughout the process. These data significantly argues about the carbon sequestration by comparing with other technologies (Figure 4.18).

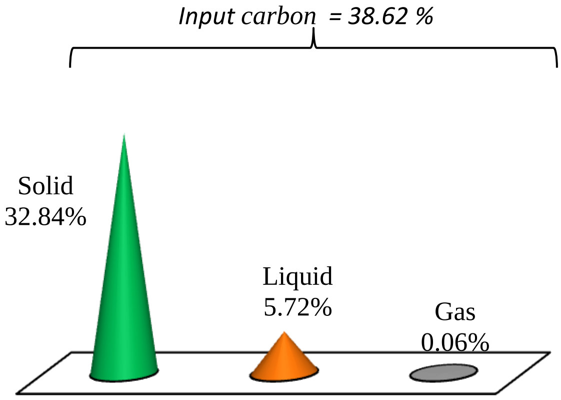


Figure 4.18 Carbon distribution

The input and output carbon were measured and followed by TOC in total filtrate and CO_2 from gaseous products. The distribution of carbon content is fully depended on the feedstock characteristics and influenced by temperature and operation time. Figure 5.6 shows the carbon distribution among solid, liquid and gas products. Approximately 85% and 14.8% input carbon is converted as solid and liquid and rest is converted into $CO_{2.}$ From this study, < 1% of carbon converted as gas is found. This result is validated by comparing with other studies that produces 2 -11% CO_2 from the total carbon from different biomass (Berge et al., 2011).

Furthermore, carbon balance also aids to calculate the wastage of carbon via CO_2 emission from different solid waste technologies. Figure 4.19 compares the emission of CO_2 from different studies (Mata-Alvarez et al., 2000). CO_2 emission declines from 1.97 - 1.19 from landfill to the combination of different techniques. It is recommended that handling the SW in different technologies controls the CO_2 emission. If the results are compared with HTC technology, relatively 95% CO_2 reduction is found from this study. In conclusion, HTC significantly stores more carbon in solid material and extremely reduces the mitigating carbon emission by comparing with the landfill technology (Berge et al., 2011).

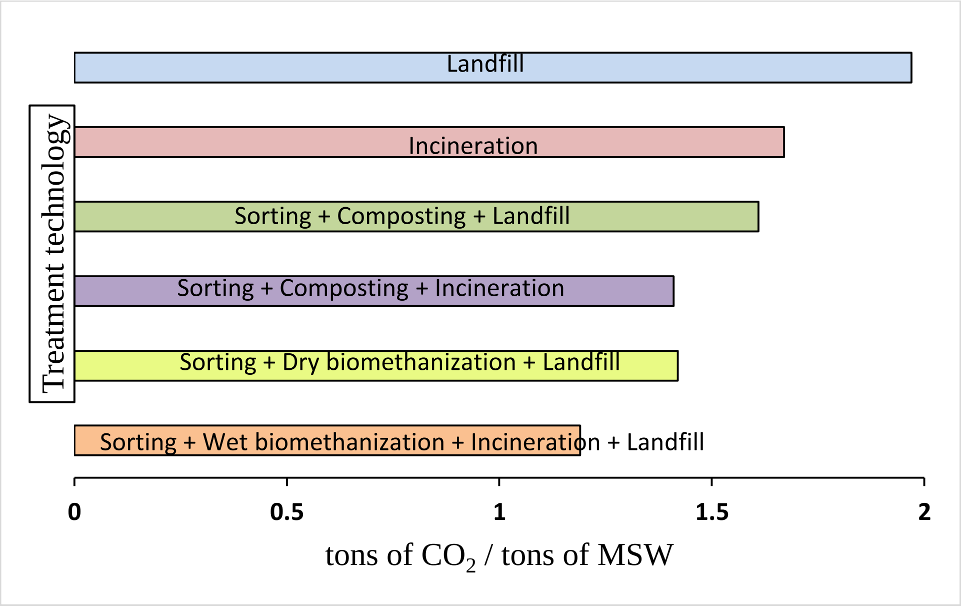


Figure 4.19 Emission of CO_2 from different MSW technologies

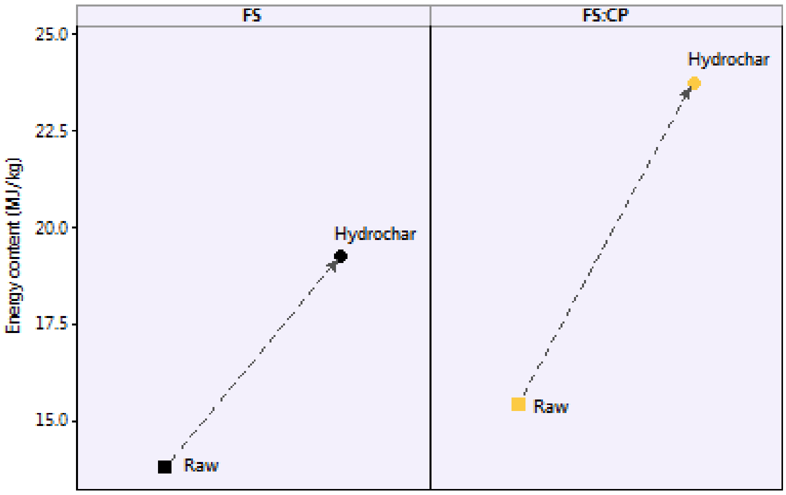
4.2.11 Comparison with FS – effects of biomass addition

The core objective of this study is to assay the effective on HTC by addition of biomass with FS. In order to validate the results, the characteristics of the produced hydrochar from FS: CP is compared with the results obtained from FS only. Figure 4.20(a) and (b) compare the energy content and carbon content of hydrochar produced from FS and FS: CP respectively. Approximately 54% increment of energy content and 7.23% increment on carbon content were found by addition of biomass. Manifesting the increasing the severity of reaction by combination of biomass is also resulted (Olivier, 2012).

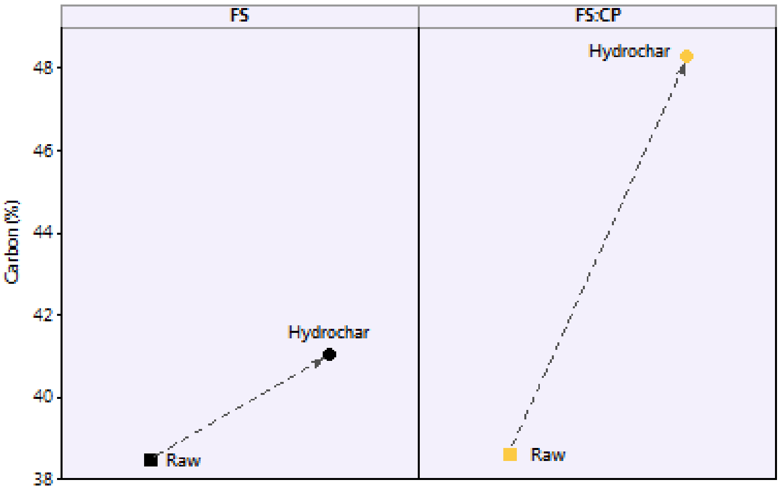
Table 4.5 Properties of Carbon and Energy Comparisons

Parameter*	Formula	FS	FS:CP
Energy retention efficiency	$\frac{energy\ content\ of\ recovered\ solids}{energy\ content\ of\ feedstock} * solid\ recovery$	94.88	104.61
Energy densification	$\frac{measured\ energy\ content\ of\ hydrochar}{measured\ energy\ content\ of\ feedstock}$	139.46	153.77
Carbon fraction (solid)	$\frac{mass\ carbon\ in\ solid, liquid\ or\ gas\ phase}{mass\ of\ carbon\ in\ inital\ feedstock}$	77.01	85.03
Carbon fraction (liquid)		18.62	14.82
Carbon fraction (gas)		4.37	0.15
Carbon densification	$\frac{\%\ carbon\ in\ the\ recovered\ solids\ (hydrochar)}{\%\ carbon\ in\ the\ initial\ feedstock}$	106.74	124.98

*calculated as %



(a)



(b)

Figure 4.20 (a) and (b) Comparisons on energy and carbon content

Previous studies were done finding the effectiveness of HTC processes in terms of its energy retention efficiency, energy densification, carbon fraction and carbon densification by increasing temperature and operation time of HTC (Lu et al., 2013). Therefore, it was adapted to the present study in order to compare the effectiveness of biomass addition. As a result, approximately 9.73%, 14.31%, 8% and 18.24% increment on efficiency of energy retention, energy densification, solid carbon fraction and carbon densification respectively were found (Table 4.5). It might be due to the increment of reaction rate by combining biomass with FS.

4.2.12 Energy balance

Energy balance is a tool, which determines and calculates the economic efficiency and its cost-effectiveness. Moreover, it also aids to find out the optimum operation parameters that economically satisfied from the raw material to hydrochar production (Zhao et al., 2010). For this study, HTC mechanisms are divided into three important zones such as heating up the reactor, operating the reactor for desired temperature and time and cooling. Moreover, mechanical dewatering and drying are also added to calculate the energy efficiency (Figure

4.21). Among these, external energy in terms of electricity was supplied to run HTC, to operate vacuum pump and to heat up the oven.

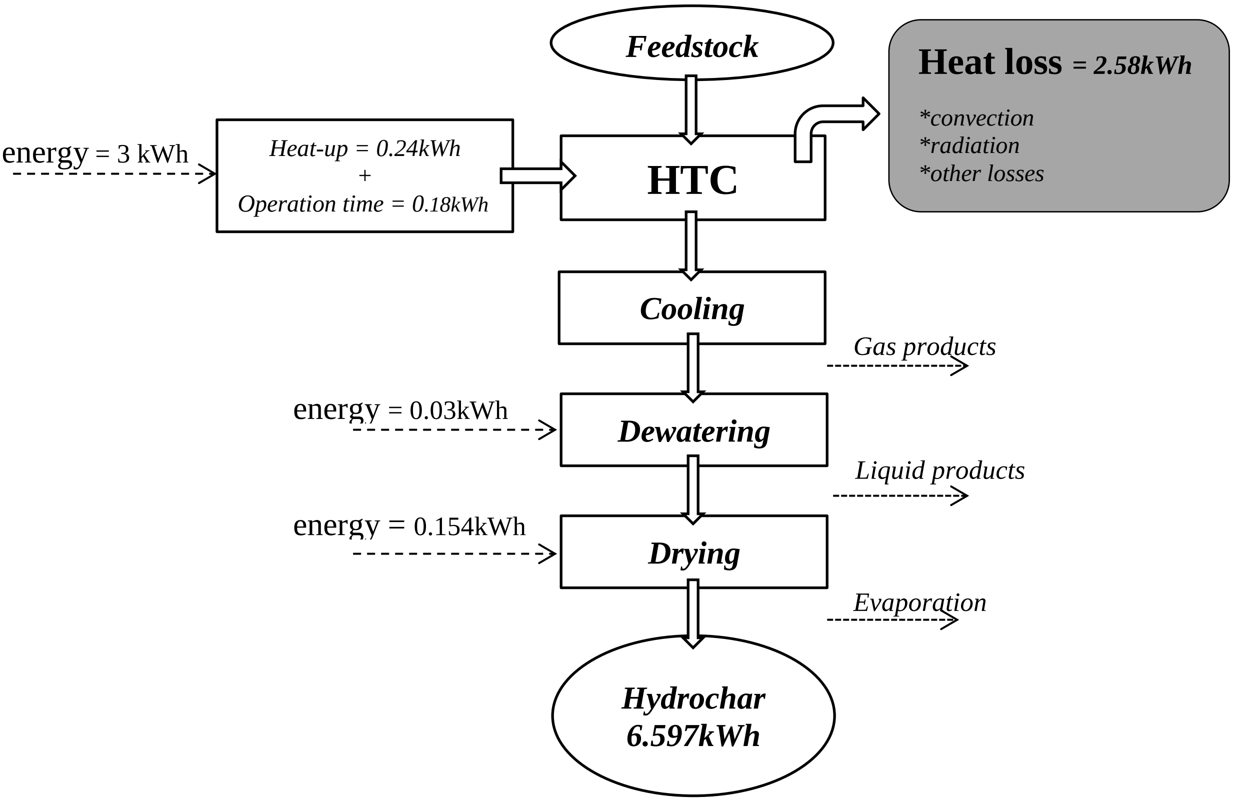


Figure 4.21 Overview of energy balance

Moreover, the total energy supplied to operate the HTC was lost mainly due to convection, radiation from the heat jacket. In order to compare the supplied energy to the output produced hydrochar energy, it was tried from both scenarios of with heat loss and without heat loss. Table 4.6 gives the important variables considered for the energy balance.

In order to follow the standardization in the calculation, energy balance was determined for 1kg wet feedstock (FS: CP) with 20% TS. Moreover, the optimum parameters such as 3h as the operation time at 250°C were considered. The data resulted from the mass balances were used as the optimum yield for this study. (Appendix B).

Table 4.6 Variables used for Energy Balance

Variables	Value	Unit
Mass of the reactor	3.5	kg
Side length of the reactor	0.12	m
Diameter of the reactor (bottom)	0.06	m
No. of ceramic plates inside the heating jacket	4	
Plate temperature of the reactor (T_p)	722	°C
Air temperature (T_a)	30	°C
Moisture content	79.8	%
Total solids (dry basis)	20.2	%
Initial temperature of feedstock (T_i)	15	°C

Variables	Value	Unit
Desired operation temperature	250	°C
Heating up the reactor (15 - 250°C)	35	min
Desired operating time (t)	180	min
Total electricity supplied	3	kwh
coal-slurry after HTC	97.8	%
Duration for dewatering (by using vacuum pump)($t_{dewater}$)	5	min
Filtrate (water + byproducts)	65	%
wet hydrochar (water + dry solids)	35	%
Drying temperature	105	°C
Hydrochar yield (dry basis)	68	%

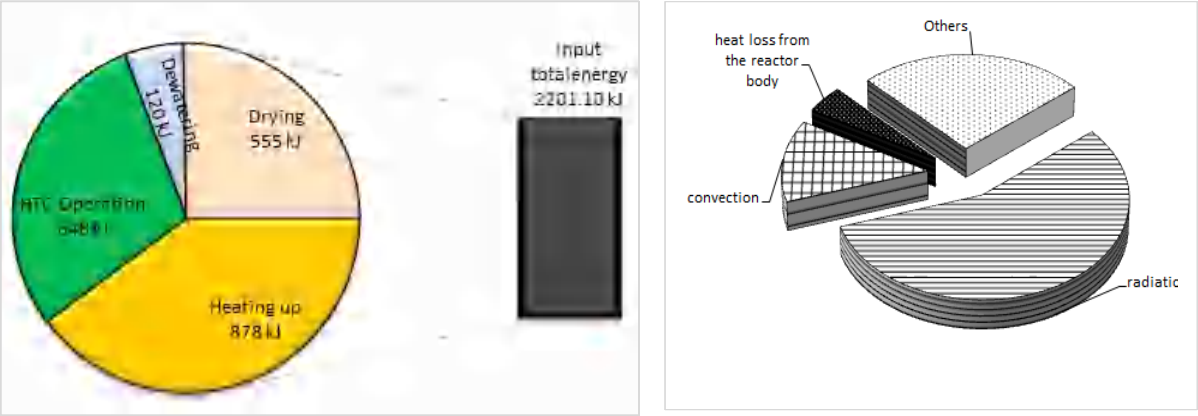
4.2.12.1 Energy efficiency – without heat loss

The total energy needed to supply to the reactor for heating up the reactor from the initial to the desired temperature (15 - 250°C) and operating time (0 – 3h) were theoretically calculated as 0.24 kWh and 0.18 kWh by using equation (1) (Xu and Lancaster, 2008). But, the actual supplied energy was 1.1kWh and 1.9kWh for heating up and operating the reactor respectively. The efficiency of the reactor was estimated approximately as 8 – 10 %. Therefore, the remaining ≈ 90% of the supplied energy might be wasted as heat loss. Additionally, the energy required for mechanical dewatering was calculated by using equation (2), where P and $t_{dewater}$ are the energy of the vacuum pump and time to dewater respectively. The value obtained for filtration was 0.03kWh. Finally, electricity to dry the wet hydrochar into dried hydrochar was calculated as 0.154kWh by using equation (3) (Kim and Parker, 2008). The results are shown in figure 4.22. (Appendix B).

Energy required for HTC $\approx [m_{water} * C_{p\ water} * (T_p - T_i)] + [m_{FS} * C_{p\ FS} * (T_p - T_i)]$ ------------ (1)

Energy required for dewatering $\approx P * t_{dewater}$ -- (2)

Energy required for drying $\approx [(m_{water})(C_{pwater})(\Delta T) + (m_{water})(L)] + [(m_{hydrochar})(C_{p,solid})(\Delta T)]$------ (3)



(a) (b)

Figure 4.22 (a) and (b) Energy distributions and its losses

4.2.12.2 Energy efficiency – with heat loss

Heat loss is the massive while comparing with the actual energy used by the reactor. Convection and radiation were caused as major losses that were approximately calculated by using thermo-dynamical equations (4) and (5). (Roncati, 2013). (Appendix B).

Heat transfer coefficient by convection, $Q_{convection} = h_c * A* (T_p - T_a)$ ------- (4)

Heat transfer coefficient by radiation, $Q_{radiation} = \sigma * \varepsilon * A * (T_p - T_a)$ ------- (5)

Figure 4.22(a) and (b) represent the estimated heat loss due to convection, radiation and other losses. It seems that approximately 48%, 11% and 22% losses occurred due to radiation, convection and other losses respectively. Heat loss from the reactor body itself was calculated as 4%. Totally, 80 – 90% of supplied energy was lost due to the heat losses. In conclusion, figure 4.23 compares the energy efficiency of the produced hydrochar with the supplied energy. However, the produced hydrochar energy content gained 148% higher than the input supplied energy. Therefore, the energy consumption calculation is evident to prove the efficiency of the HTC processes.

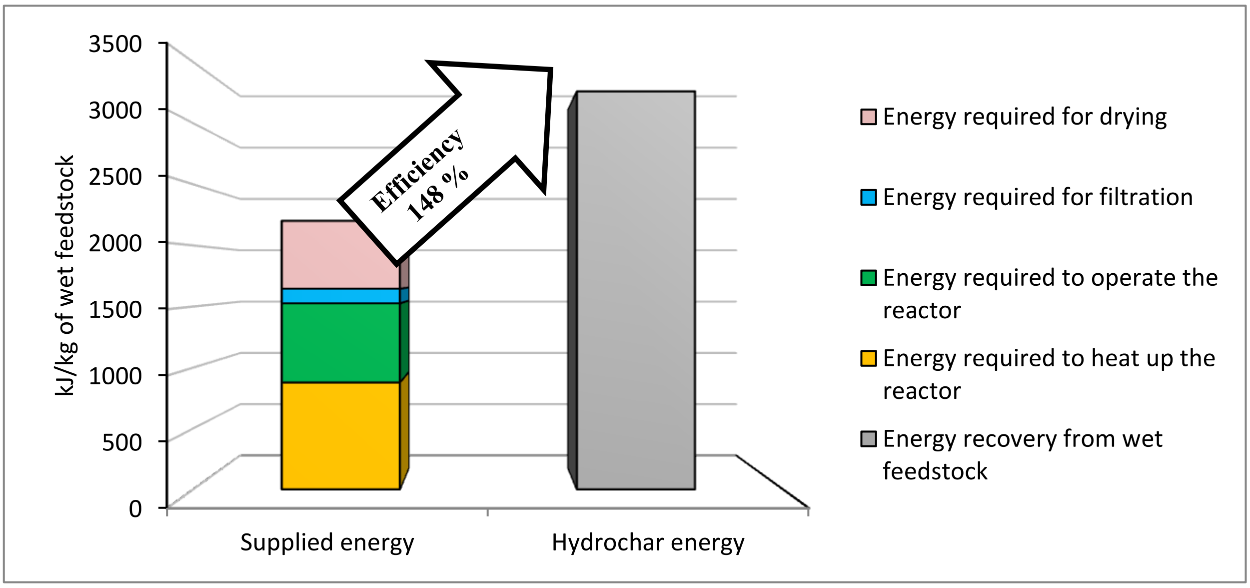


Figure 4.23 Energy efficiency

4.3 Phase III - Effects of Fermentation

Production of acetic acid was examined in this phase III with the help of fermentation processes. Firstly, the basic parameters that observed from the fermentation process such as pH, VFA and TS were measured and resulted in figure 4.24. pH moderately drops from 5.62 to 4.41 from 0 to 35 days of SRT. The obtained data confirms the acidic nature due to its declining pH and might be due to the production of VFA (Macias-Corral, et al., 2008). VFA production was drastically increased from day 7 to 14 as 47.58% and afterwards it had been slightly started to decline. A possible reason is that the produced VFA might be utilized by methanogenic bacteria to produce CH_4 gas (Macias-Corral et al., 2008). This can be validated from the biogas measurement (Figure 4.25). (Appendix B).

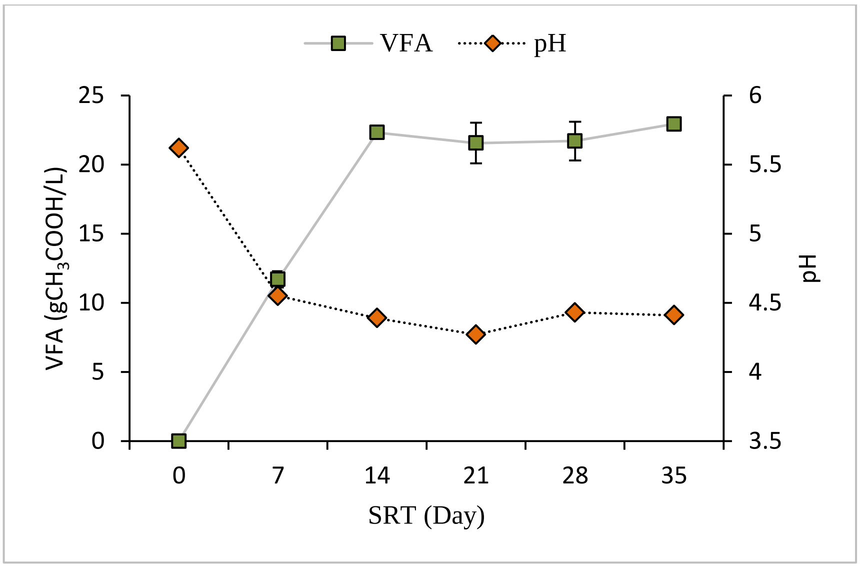


Figure 4.24 Parameters during fermentation

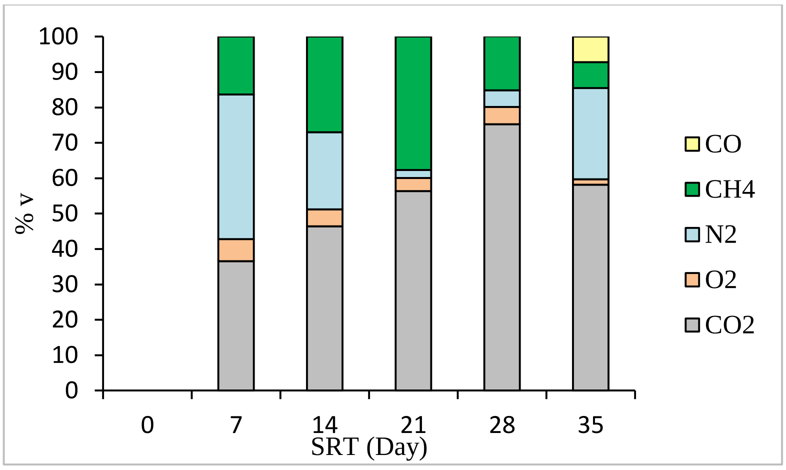


Figure 4.25 Biogas compositions during fermentation

Clisso, (2000) stated that acidogenesis is the most important stage also called as fermentation stage, where VFA are formed along with CO_2 and H_2. CO_2 production started from approximately 36% and increased up to 45, 56 and 75% from SRT 0 to 28 days and gradually decreased on day 35. Moreover, higher methane production of 38%was found on day 21. A possible reason for this, in AD system, the SRT is to be maintained in between 10 – 20 days for mesophilic temperature (Lee et al., 2011). However, increasing SRT more than 20 days will not be able to produce impressive production of biogas (Cao and Pawłowski, 2012). Finally, the sludge after fermentation was used as feedstock in HTC. But, production of trances amount of CO was also observed on SRT 35 days. According to Hickey and Switzenbaum (1990), traces amount of CO production in anaerobic digestion is common due to the disturbance in fermentation process either organic loading rate or acetate production. Also, decrease head space level is responsible for CO production.

4.3.1 HTC results using digestate sludge

HTC experiments were conducted and resulted in figure 4.26. pH were measured after HTC, it ranges 4.67 – 4.3 from SRT 0 – 35 days. Hence, it is confirmed that HTC is also effective to use digested sludge as feedstock. (Appendix B). Moreover, the energy content is decreased from 22.29 MJ/kg to 18.35, 19.67, 21, 18.37 and 18.21 MJ/kg from day 0 to 7, 14, 21, 28 and 35 respectively. The results were compared with the previous studies that obtained energy content as 9.22 MJ/kg and 13.7 MJ/kg (Berge et al., 2011; Ramke et al., 2009). Additionally, average solid recovery was obtained as 59% and it is lower than the non-fermented sludge. In conclusion, it is stated that the energy contents produced from the fermented sludge are not effective while comparing with the energy content without fermentation. A possible reason for that, during fermentation most of the carbon was wasted as CO_2 and CH_4 and traces of CO. Moreover, the AD waste is insignificant to the initial hydrolysis process and be largely influenced by decarboxylation (Berge et al., 2011).

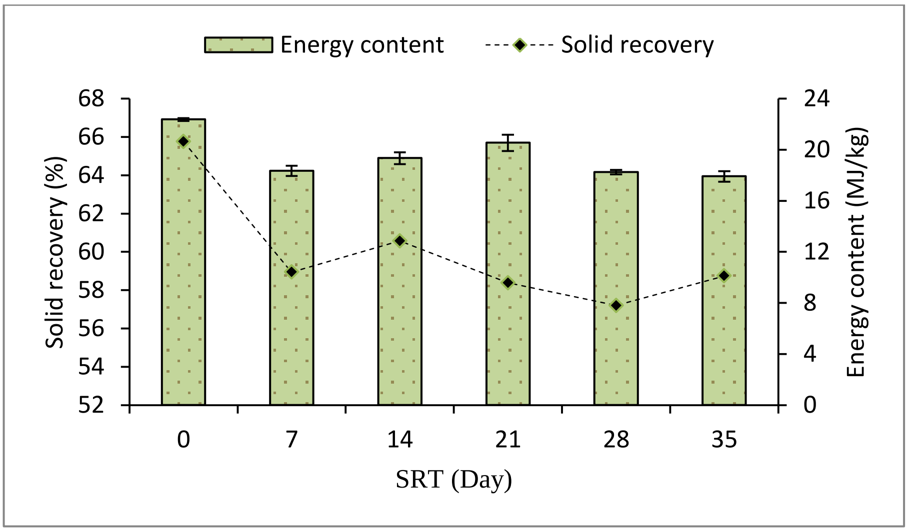


Figure 4.26 Energy content and solid recoveries from digested sludge

Additionally, the amount of acetic acid production may not be sufficient to increase the rate of reaction in HTC process. According to (Lynam et al., (2011), 0.4 g acetic acid / g of feedstock is required to increase the energy densification of hydrochar. But, only 0.02 g of acetic acid per g of feedstock was noticed at their maximum level from the fermentation process. Another possible reason to explain about the low energy content may be due to process parameters used in HTC process such as temperature and operation time.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The effects of different biomass addition on the energy content of the hydrochar produced from faecal sludge (FS) were examined in this study. Biomass were effectively involved in HTC and helped to enhance the energy up to 3 -16% content with FS. Cassava pulp (CP) favorably increased the energy content of hydrochar from 19.5 MJ/kg to 22.66 MJ/kg. Additionally, the effective mixing ratio of 1:1 was resulted from the phase I. The results were validated that the obtained energy content of hydrochar produced from FS: CP is in par with LAUBAG-Briquette (22.4 MJ/kg). In conclusion, the effects of HTC were examined that converts wet biomass into coal like hydrochar within few hours. Secondly, the effective process parameters were analyzed by varying temperature and operation time. From the results, it is concluded that HTC is effect for temperature rather than operation time. Moreover, the characteristics of the products were examined with its mass, carbon and energy balance. From the results, HTC is proven as one of the effective technologies in terms of its economic beneficial. Finally, investigations the effects on the energy content of hydrochar by using digested sludge via fermentation process were studied. The expected results could not be achieved. In conclusion, biomass addition with FS not only aided to increase the energy content also to enhance the characteristics of the hydrochar in terms of its quality.

5.2 Recommendations

For further research, biomass which quietly yields good renewable energy either on pyrolysis or gasification process will also be investigated in HTC along with FS. For an example, sawdust, switch grass, corn husks, pine needles, paper pulp, food wastes etc., can be used. Additionally, combinations of biomass for different mixing ratio may also be helpful to enhance the energy content. Recirculation of the process water, usage of solar energy for drying the wet hydrochar are chiefly recommended that may result cost-effectiveness.

The optimum process parameters such as temperature and operation time could be examined for all types of biomass that might compare the HTC mechanisms. Moreover, the coal characteristics of the hydrochar produced will be investigated in detail such as cellulose and lignin content. The kinetic modeling study of each parameter which are responsible to increase the energy content of hydrochar will be extended in depth and this may help for further research to choose the best biomass.

It is also suggested that the effects of accumulated sludge from any decentralized treatment (e.g. septic tanks, cess-to-fit, urine diversion toilet, pond systems, anaerobic digester etc.) might be investigated in HTC. It may result to extend the research for the combination of different technologies.

According to the characteristics of the liquid that produced during HTC is mandatory needed to be analyzed. It may help to study about the liquid by products in different field of studies. Although literature studies have been revealed about the good bio-degradability of the liquid products, it is recommended to check its toxicity for the least case. Otherwise, the efficiency of HTC processes will not be proven.

Applications of Hydrochar in real field that were not carried out from this study, is highly recommended. The produced hydrochar has to be tested in its further applicable field of studies (e.g. Activated carbon, cosmetics, electrodes etc.). Additionally, more research is still needed to extend the applications of hydrochar as soil-amendment too.

Importantly, environmental impact assessment (EIA), life cycle assessment (LCA) and sustainability management on HTC studies are encouraging that results a holistic approach on the basis of environmental, economic and health aspects.

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Appendices

Appendix A – Photographs

a. Raw materials Collections / Feedstock Preparations

Plate A1. Faecal sludge and Biomass collection

Plate A2. Separation of foreign materials

Plate A3. Preparation of samples (cutting/chopping/sieving/grinding)

b. Instruments used for analytical method

Plate A4. Bomb calorimeter and Thermo gravimetric analyzer (Leco, USA)

Plate A5. Gas chromatograph

c. HTC operations

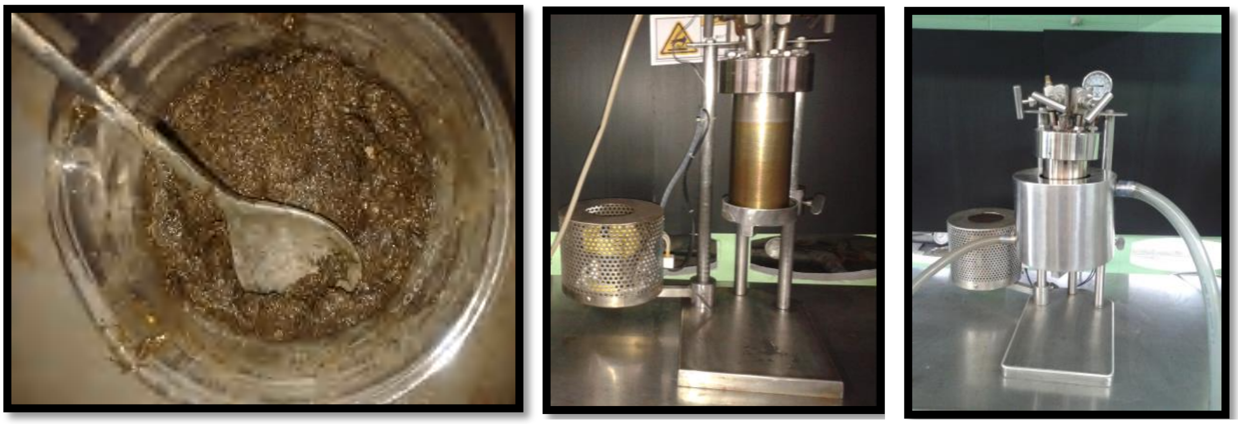


Plate A6. Different stages in HTC operation

d. Filtration / drying

Plate A7. Coal slurry product /Vacuum filtration

Plate A8. Process water / Weighing

e. Solid recovery

Plate A9. Wet hydrochar / dry hydrochar

Appendix B - Tables and Calculations

Table B1. TS and TVS Calculations

Date	Sample (S)	No.	Cup (g) (W1)	Cup + S (g) (W2)	Cup + S (g) (105°C) (W3)	Cup + S (g) (550°C) (W4)	Sample Weight (SW)(g)	%wt solid	% TVS (dry wt)	Average %TVS	Average %TS
10/9/2014	Faecal sludge (FS)	1	75.69	79.21	76.34	75.98	3.51	18.45	55.41		
		2	77.77	81.58	78.51	78.00	3.81	19.52	68.94		
		3	77.47	80.80	78.22	77.73	3.32	22.40	64.84		
		4	78.50	81.91	79.28	78.84	3.41	22.87	56.13		
		5	90.66	94.37	91.31	90.94	3.71	17.63	57.49	60.56	20.18
10/9/2014	cassava pulp (CP)	1	64.85	68.72	65.48	64.86	3.86	16.27	97.98		
		2	75.66	78.50	76.21	75.67	2.84	19.51	98.22		
		3	85.01	89.11	85.81	85.03	4.10	19.57	98.22		
		4	87.00	90.56	87.72	87.01	3.56	20.31	98.38		
		5	74.77	78.74	75.53	74.78	3.97	19.05	98.23	98.20	18.94
16/10/2014	Dried leaves/grass (DL)	1	92.86	93.69	93.58	92.95	0.83	87.24	86.63		
		2	72.54	73.49	73.38	72.67	0.95	88.42	83.64		
		3	64.85	65.84	65.75	64.98	0.99	91.24	86.09		
		4	78.28	79.77	79.67	78.50	1.50	93.18	84.14		
		5	77.77	78.96	78.84	77.93	1.19	89.34	85.31	85.16	89.88
10/9/2014	Pig manure (PM)	1	70.58	74.87	71.63	70.97	4.29	24.56	62.82		
		2	77.62	82.71	78.96	78.34	5.08	26.29	46.67		
		3	74.66	80.68	76.19	75.53	6.02	25.41	43.16		
		4	96.31	102.03	97.72	96.94	5.71	24.58	55.25		
		5	82.14	87.11	83.48	82.58	4.97	26.88	67.42	55.06	25.55
16/10/2014	Rice Husk (RH)	1	94.02	99.11	98.88	94.83	5.09	95.36	83.42		
		2	94.40	99.78	99.66	95.19	5.38	97.71	85.00		
		3	64.85	69.36	69.21	65.52	4.51	96.80	84.62		
		4	84.27	88.16	88.07	84.77	3.89	97.82	86.80		
		5	46.48	48.53	48.45	46.80	2.05	96.10	83.90	84.75	96.76

Calculations

Example:

W1 = 92.8578 g, W2 = 93.6883 g, W3 = 93.5823 g, W4 = 92.9547 g,
SW = (W2-W1) = (93.6883 - 92.8578) = 0.8305g

$$\mathrm{TS}\ (\%) = \frac{(\mathrm{W3} - \mathrm{W1}) * 100}{\mathrm{SW}}$$

TS (%) = ((93.5823 – 92.857) /0.8305) *100 = 87.32%

Moisture (%) = 100 – TS (%) = 100 – 87.32 = 12.68 %

$$\mathrm{TVS}\ (\%) = \frac{(\mathrm{W3} - \mathrm{W4}) * 100}{(\mathrm{W3} - \mathrm{W1})}$$

TVS = (93.5823 - 92.9547)*100 / (93.5823 - 92.8578) =86.63 %.

HTC Data

Table B2. *Recorded Data during HTC Operation

Time (min)	Temperature ° C	Pressure Bar	Electricity (KWh)
0	15	0	0
30	139	40	0.92
60	236	32	1.19
90	221	29	1.71
120	218	21	2.23
150	220	22	2.57
180	221	23	2.91
210	223	25	3.2
240	229	26	3.49
270	230	26	3.71
300	224	26	3.93
315	105	10	3.93
330	50	5	3.93
360	35	2	3.93
390	31	2	3.93
420	31	2	3.93

*(Recorded on 31.10.2014)

Phase I - Investigation the effects of different biomass

Table B3. Measured Input Feedstock and Output Hydrochar

Feedstock	Mixing ratio	*Input solids (g)	*Hydrochar weight (g)			*Solid recovery (%)				Std. deviation
			Batch I	Batch II	Batch III	Batch I	Batch II	Batch III	Average	
FS		68.60	52.46	53.48	51.98	76.47	77.96	75.77	76.73	1.12
CP		66.50	36.17	34.96	33.51	54.39	52.57	50.39	52.45	2.00
FS:CP	1:1	70.00	47.99	46.12	49.86	68.56	65.89	71.23	68.56	2.67
FS:CP	3:1	72.10	46.77	47.46	45.86	64.87	65.83	63.61	64.77	1.11
DL		70.00	50.73	50.21	50.41	72.47	71.73	72.01	72.07	0.37
FS:DL	1:1	73.50	54.11	55.52	52.71	73.62	75.54	71.71	73.62	1.91
FS:DL	3:1	71.40	48.73	49.78	47.69	68.25	69.72	66.79	68.25	1.46
PM		70.00	40.03	38.76	37.92	57.19	55.37	54.17	55.58	1.52
FS:PM	1:1	70.00	54.00	55.27	52.73	77.14	78.96	75.33	77.14	1.81
FS:PM	3:1	70.00	52.78	51.42	54.15	75.40	73.46	77.36	75.40	1.95
RH		70.00	50.72	49.81	47.99	72.46	71.16	68.56	70.72	1.99
FS:RH	1:1	70.00	49.25	48.02	50.48	70.36	68.60	72.11	70.36	1.76
FS:RH	3:1	70.00	49.95	46.28	46.49	71.36	66.11	66.41	67.96	2.94

*measured on dry basis

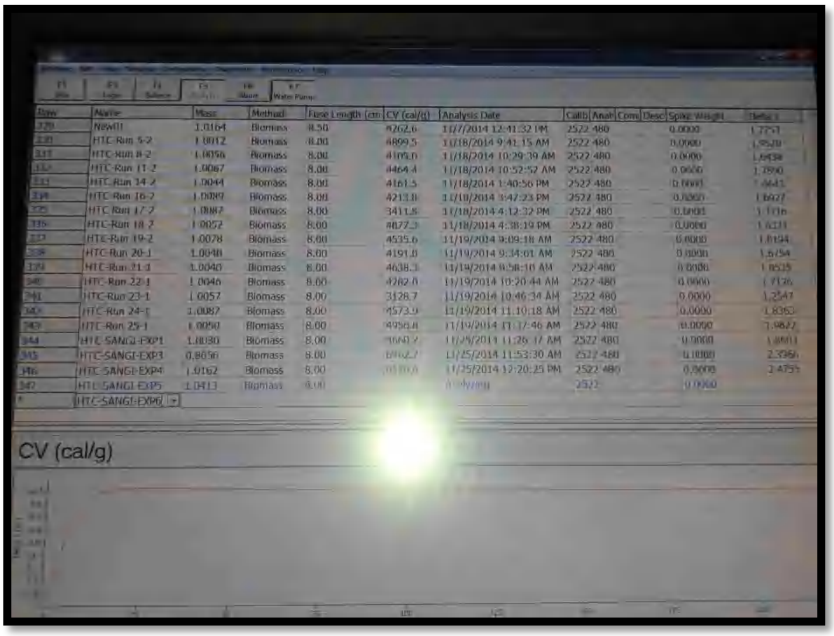
$$\text{Solid recovery (\%)} = \frac{\text{Output hydrochar weight}}{\text{Input feedstock weight}} * 100$$

Example:

Input solid weight = 71.40 g, Output produced hydrochar weight = 48.73g

$$\text{Solid recovery (\%)} = \frac{48.73}{71.40} * 100 = 68.25\ \%$$

Data Measured from Bomb Calorimeter



Row	Name	Mass	Method	Fuse Length (cm)	CV (cal/g)	Analysis Date	Calib	Anal	Com	Desc	Spike Weight	Delta T
[illegible]	New111	1.0164	Biomass	8.50	4262.6	11/7/2014 12:41:32 PM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 5-2	1.0012	Biomass	8.00	4899.5	11/18/2014 9:41:15 AM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 8-2	1.0056	Biomass	8.00	4105.0	11/18/2014 10:29:39 AM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 11-2	1.0067	Biomass	8.00	4464.4	11/18/2014 10:52:52 AM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 14-2	1.0044	Biomass	8.00	4161.5	11/18/2014 1:40:56 PM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 16-2	1.0089	Biomass	8.00	4213.8	11/18/2014 3:47:23 PM	2522.480				0.0000	1.6927
[illegible]	HTC-Run 17-2	1.0087	Biomass	8.00	3411.8	11/18/2014 4:12:32 PM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 18-2	1.0052	Biomass	8.00	[illegible]	11/18/2014 4:38:19 PM	2522.480				0.0000	[illegible]
[illegible]	HTC-Run 19-2	1.0078	Biomass	8.00	4535.6	11/19/2014 9:09:18 AM	2522.480				0.0000	1.8194
338	HTC-Run 20-1	1.0048	Biomass	8.00	4191.0	11/19/2014 9:34:01 AM	2522.480				0.0000	1.6754
339	HTC-Run 21-1	1.0040	Biomass	8.00	4638.3	11/19/2014 9:58:10 AM	2522.480				0.0000	1.8535
340	HTC-Run 22-1	1.0046	Biomass	8.00	4282.0	11/19/2014 10:20:44 AM	2522.480				0.0000	1.7136
341	HTC-Run 23-1	1.0057	Biomass	8.00	3128.7	11/19/2014 10:46:34 AM	2522.480				0.0000	1.2547
342	HTC-Run 24-1	1.0087	Biomass	8.00	4573.9	11/19/2014 11:10:18 AM	2522.480				0.0000	1.8363
343	HTC-Run 25-1	1.0050	Biomass	8.00	4956.8	11/19/2014 11:37:46 AM	2522.480				0.0000	1.9827
344	HTC-SANGI-EXP1	1.0030	Biomass	8.00	[illegible]	11/25/2014 11:26:17 AM	2522.480				0.0000	[illegible]
345	HTC-SANGI-EXP3	0.8656	Biomass	8.00	[illegible]	11/25/2014 11:53:30 AM	2522.480				0.0000	2.3966
346	HTC-SANGI-EXP4	1.0162	Biomass	8.00	[illegible]	11/25/2014 12:20:25 PM	2522.480				0.0000	2.4755
347	HTC-SANGI-EXP5	1.0413	Biomass	8.00		Analyzing	2522				0.0000	
*	HTC-SANGI-EXP6											

Bomb calorimeter data (25.11.2014)

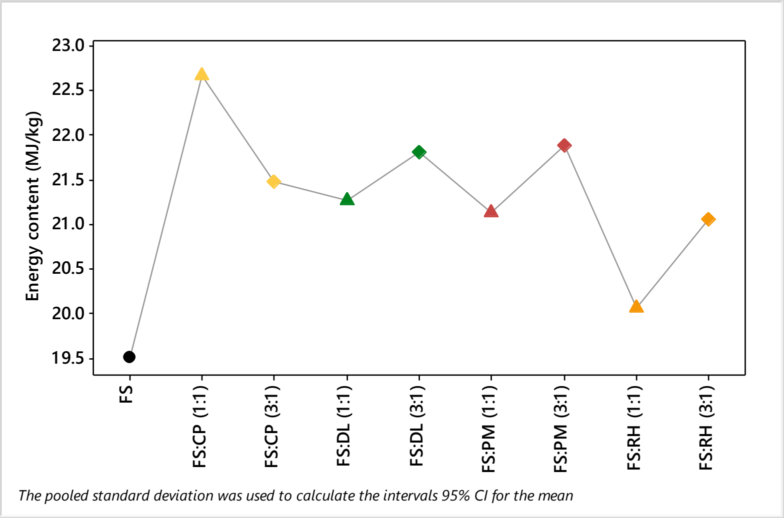
Table B4. Calorific Values from Bomb calorimeter

Feedstock	Mixing ratio	*Calorific value $^{\#}$(calorie /g)			
		Batch I	Batch II	Batch III	Std .deviation
FS		4634.32	4667.78	4682.12	0.10
CP		7043.50	6878.59	6964.63	0.35
FS:CP	1:1	5759.59	5293.42	5198.62	1.26
FS:CP	3:1	5136.23	4966.54	5303.54	0.71
DL		6242.83	6144.84	6493.79	0.75
FS:DL	1:1	5043.15	4923.77	5283.19	0.77
FS:DL	3:1	5341.78	5093.21	5207.93	0.52
PM		6398.18	6034.89	5941.68	1.01
FS:PM	1:1	4922.55	4897.89	5330.06	1.02
FS:PM	3:1	5200.76	5308.32	5184.03	0.28
RH		4909.18	5069.31	5052.58	0.37
FS:RH	1:1	4796.98	4793.94	4794.99	0.01
FS:RH	3:1	5066.92	5260.52	4768.16	1.04

*measured on dry basis

$^{\#}$conversion base : 1 calorie = 4.1868E-6 MJ (https://www.unitjuggler.com/convert-energy-from-cal-to-MJ.html)

One-way ANOVA: Energy content versus Mixing ratio



```
Method

Null hypothesis          All means are equal
Alternative hypothesis   At least one mean is different
Significance level       α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor         Levels  Values
Mixing ratio        9  FS, FS:CP (1:1), FS:CP (3:1), FS:DL (1:1), FS:DL (3:1),
FS:PM (1:1),
                       FS:PM (3:1), FS:RH (1:1), FS:RH (3:1)


Analysis of Variance

Source         DF  Adj SS  Adj MS  F-Value  P-Value
Mixing ratio    8   21.85  2.7310     4.79    0.003
Error          18   10.26  0.5702
Total          26   32.11


Model Summary

       S    R-sq  R-sq(adj)  R-sq(pred)
0.755092  68.04%     53.83%      28.09%


Means

Mixing ratio  N     Mean   StDev        95% CI
FS            3  19.5033  0.1026  (18.5874, 20.4192)
FS:CP (1:1)   3   22.666   1.256  ( 21.750,  23.582)
FS:CP (3:1)   3   21.487   0.705  ( 20.571,  22.403)
FS:DL (1:1)   3   21.269   0.766  ( 20.353,  22.185)
FS:DL (3:1)   3   21.817   0.521  ( 20.901,  22.733)
FS:PM (1:1)   3   21.130   1.015  ( 20.214,  22.046)
FS:PM (3:1)   3   21.887   0.282  ( 20.971,  22.803)
FS:RH (1:1)   3  20.0635  0.0065  (19.1476, 20.9795)
FS:RH (3:1)   3   21.053   1.038  ( 20.137,  21.969)

Pooled StDev = 0.755092
```

Thermo Gravimetric Analyzer

Table B5. Raw Data Resulted from Proximate Analyzer (22.12.2014)

Name	Analysis Date-Time	Initial Mass	Moisture Mass	Volatile Mass	Ash Mass	Moisture (%)	Volatile (%)	Ash (%)
1	12/22/2014 14:46	1.0831	1.0692	0.5648	0.31	1.28	46.57	28.62
2	12/22/2014 14:46	1.0381	1.021	0.5167	0.2874	1.65	48.58	27.69
3	12/22/2014 14:46	1.1237	1.1139	0.5713	0.3151	0.87	48.29	28.04
4	12/22/2014 14:46	1.0598	1.0469	0.5242	0.2958	1.22	49.32	27.91
5	12/22/2014 14:46	1.0104	0.9984	0.5369	0.3362	1.19	45.67	33.27
6	12/22/2014 14:46	1.0242	1.0117	0.5357	0.3503	1.22	46.48	34.2
7	12/22/2014 14:46	1.0446	1.0316	0.5485	0.3687	1.24	46.25	35.3
8	12/22/2014 14:46	1.0382	1.0266	0.4938	0.2894	1.12	51.32	27.88
9	12/22/2014 14:46	1.2027	1.1958	0.5628	0.3368	0.57	52.63	28
10	12/22/2014 14:46	1.1751	1.1628	0.5626	0.4354	1.05	51.08	37.05
11	12/22/2014 14:46	1.1651	1.1501	0.5575	0.4416	1.29	50.86	37.9
12	12/22/2014 14:46	1.0872	1.0814	0.6079	0.486	0.53	43.55	44.7
13	12/22/2014 14:46	1.0802	1.0671	0.6003	0.484	1.21	43.21	44.81
14	12/22/2014 14:46	1.1468	1.1212	0.635	0.505	2.23	42.4	44.04
15	12/22/2014 14:46	1.1318	1.1209	0.6056	0.459	0.96	45.53	40.55
16	12/22/2014 14:46	1.0323	1.0219	0.5321	0.4095	1.01	47.45	39.67
17	12/22/2014 14:46	1.0197	1.0093	0.5172	0.3844	1.02	48.26	37.7
18	12/22/2014 14:46	1.0454	1.0346	0.5476	0.4096	1.03	46.59	39.18
19	12/22/2014 14:46	1.0637	1.0534	0.5458	0.4132	0.97	47.72	38.85

Table B6. # Processed data Resulted from Proximate Analyzer

Feedstock	Mixing ratio	*Fixed carbon FC (%)	Volatile matter VM (%)	Ash (%)	Moisture (%)
FS		12.05	44.74	41.70	1.51
CP		40.85	54.25	2.67	2.23
FS:CP	1:1	21.64	49.17	27.96	1.24
FS:CP	3:1	18.16	47.02	33.71	1.11
DL		27.54	55.57	14.81	2.08
FS:DL	1:1	18.95	51.67	28.48	0.90
FS:DL	3:1	14.45	49.64	34.18	1.73
PM		7.91	63.36	27.76	0.97
FS:PM	1:1	10.20	51.84	36.88	1.08
FS:PM	3:1	15.85	45.42	37.27	1.46
RH		29.36	43.22	22.86	4.56
FS:RH	1:1	19.46	45.83	34.01	0.71
FS:RH	3:1	11.24	49.72	37.47	1.57

measured on dry basis *FC (%) = 100 – (VM+ ash +MC)

Phase II - Optimization of process parameters

Table B7. Volume of Process Water

Temperature	Operation Time	Process water (ml)		
(°C)	(h)	Batch I	Batch II	Average
180	0.5	120	130	125
180	1	130	140	135
180	3	160	150	155
180	5	145	155	150
180	10	160	180	170
200	0.5	160	150	155
200	1	135	155	145
200	3	150	170	160
200	5	155	185	170
200	10	190	160	175
220	0.5	180	140	160
220	1	160	200	180
220	3	175	195	185
220	5	190	190	190
220	10	240	230	235
250	0.5	225	205	215
250	1	230	220	225
250	3	220	240	230
250	5	215	255	235
250	10	255	245	250

Table B8. Measured Weight of Hydrochar

Temperature	Operation Time	Hydrochar weight (g)		
(°C)	(h)	Batch I	Batch II	Average
180	0.5	59.68	50.3	54.99
180	1	53.76	57.18	55.47
180	3	52.89	56.41	54.65
180	5	49.68	51.34	50.51
180	10	50.67	48.93	49.8
200	0.5	53.98	56.3	55.14
200	1	52.97	54.85	53.91
200	3	51.43	54.69	53.06
200	5	50.65	53.19	51.92
200	10	48	51.4	49.7
220	0.5	50.76	51.66	51.21
220	1	51.34	53.1	52.22
220	3	53.84	49.72	51.78
220	5	44.31	52.23	48.27
220	10	46.9	49.54	48.22
250	0.5	51.28	48.64	49.96

250	1	49.56	46.92	48.24
250	3	49.08	47.02	48.05
250	5	46.99	48.43	47.71
250	10	44.22	46.04	45.13

Table B9. Measured Calorific Value

Temperature	Operation Time	*Calorific value (calorie/g)		
(°C)	(h)	Batch I	Batch II	Average
180	0.5	4603.25	4608.03	4605.64
180	1	4956.98	4660.61	4622.37
180	3	4586.52	4629.54	4792.07
180	5	4968.93	4928.30	4947.42
180	10	4873.33	4892.45	4882.89
200	0.5	4359.46	4906.79	4634.32
200	1	4870.94	4758.60	4815.97
200	3	4784.89	4717.97	4751.43
200	5	4894.84	5011.95	4954.59
200	10	4847.04	5143.40	4995.22
220	0.5	4622.37	4586.52	4605.64
220	1	4878.11	4890.06	4882.89
220	3	4966.54	4978.49	4973.71
220	5	5167.30	4980.88	5074.09
220	10	5394.36	5434.99	5413.48
250	0.5	4679.73	4643.88	4663.00
250	1	4722.75	4768.16	4746.65
250	3	5222.28	5377.63	5301.15
250	5	5475.62	5382.41	5427.82
250	10	5516.25	5834.13	5676.39

*measured on dry basis

One-way ANOVA: Calorific Value versus Operation Time

```
Method

Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor  Levels  Values
Time_1       5  0.5, 1.0, 3.0, 5.0, 10.0


Analysis of Variance

Source  DF  Adj SS  Adj MS  F-Value  P-Value
Time_1   4   17.50   4.375     2.28    0.109
Error   15   28.76   1.918
Total   19   46.26
```

```
Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
1.38477  37.82%     21.24%       0.00%


Means

Time_1  N    Mean  StDev       95% CI
0.5     4  19.542  0.474  (18.067, 21.018)
1.0     4  20.291  0.784  (18.815, 21.767)
3.0     4  21.123  1.797  (19.647, 22.599)
5.0     4  21.698  1.447  (20.222, 23.173)
10.0    4  22.121  1.851  (20.645, 23.597)

Pooled StDev = 1.38477
```

One-way ANOVA: Calorific Value versus Temperature

```
Method

Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor         Levels  Values
Temperature_1       4  180, 200, 220, 250


Analysis of Variance

Source         DF  Adj SS  Adj MS  F-Value  P-Value
Temperature_1   3   23.03   7.676     5.29    0.010
Error          16   23.23   1.452
Total          19   46.26


Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
1.20505  49.78%     40.36%      21.53%


Means

Temperature_1  N    Mean  StDev       95% CI
180            5  19.961  0.641  (18.818, 21.103)
200            5  20.208  0.620  (19.065, 21.350)
220            5  20.948  1.266  (19.805, 22.090)
250            5  22.704  1.847  (21.561, 23.846)

Pooled StDev = 1.20505
```

Table B10. Data from Proximate Analysis

Temperature (°C)	Operation time	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Moisture (%)
180	0.5	62.65	18.43	18.53	0.39
180	1	61.36	18.08	20.06	0.50
180	3	60.44	18.95	19.90	0.71
180	5	59.67	18.20	22.00	0.13
180	10	58.31	18.03	23.66	0.00
200	0.5	62.45	18.73	18.76	0.06
200	1	61.01	18.50	20.25	0.24
200	3	60.76	20.30	18.38	0.56
200	5	58.31	21.24	19.78	0.67
200	10	56.69	21.94	21.37	0.00
220	0.5	54.76	18.06	27.15	0.03
220	1	51.85	19.12	28.85	0.18
220	3	49.62	20.80	29.04	0.54
220	5	50.5	22.47	26.62	0.41
220	10	47.35	23.66	28.99	0.00
250	0.5	48.51	20.17	31.27	0.05
250	1	46.58	20.77	32.53	0.12
250	3	44.04	22.61	33.31	0.04
250	5	42.81	23.05	34.09	0.05
250	10	41.08	23.92	34.98	0.02

Table B11. Volatile Matter Conversion

Temp (°C)	Reaction time (h)	Volatile matter in Feedstock (%)	Initial weight (g)	Initial concentration (g)	Volatile matter in Hydrochar (%)	Hydrochar weight (g)	Hydrochar concentration (g)	Volatile matter conversion(%)
180 °C	0	75.18	70.63	53.10	75.18	70.63	53.10	0.00
180 °C	0.5	75.18	70.63	53.10	62.65	54.99	34.45	35.12
180 °C	1	75.18	70.63	53.10	61.36	55.47	34.04	35.90
180 °C	3	75.18	70.63	53.10	60.44	54.65	33.03	37.80
180 °C	5	75.18	70.63	53.10	59.67	50.51	30.14	43.24
180 °C	10	75.18	70.63	53.10	58.31	49.8	29.04	45.31
200 °C	0	75.18	70.63	53.10	75.18	70.63	53.10	0.00
200 °C	0.5	75.18	70.63	53.10	62.45	55.14	34.43	35.15
200 °C	1	75.18	70.63	53.10	61.01	53.91	32.89	38.06
200 °C	3	75.18	70.63	53.10	60.76	53.06	32.24	39.29
200 °C	5	75.18	70.63	53.10	58.31	51.92	30.27	42.99
200 °C	10	75.18	70.63	53.10	56.69	49.7	28.17	46.94
220 °C	0	75.18	70.63	53.10	75.18	70.63	53.10	0.00
220 °C	0.5	75.18	70.63	53.10	54.76	51.21	28.04	47.19
220 °C	1	75.18	70.63	53.10	51.85	52.22	27.08	49.01
220 °C	3	75.18	70.63	53.10	49.62	51.78	25.69	51.61
220 °C	5	75.18	70.63	53.10	50.5	48.27	24.38	54.09
220 °C	10	75.18	70.63	53.10	47.35	48.22	22.83	57.00
250 °C	0	75.18	70.63	53.10	75.18	70.63	53.10	0.00
250 °C	0.5	75.18	70.63	53.10	48.51	49.96	24.24	54.36
250 °C	1	75.18	70.63	53.10	46.58	48.24	22.47	57.68
250 °C	3	75.18	70.63	53.10	44.04	48.05	21.16	60.15
250 °C	5	75.18	70.63	53.10	42.81	47.71	20.42	61.54
250 °C	10	75.18	70.63	53.10	41.08	45.13	18.54	65.09

Calculation:

Concentration of VM = VM measured * Amount of sample

Volatile matter conversion (%) = $\frac{Initial\ concentration - Final\ concentration}{Initial\ concentration} * 100$

Example:

Initial feedstock weight = 70.63g, Initial feedstock VM measured (%) = 75.18%

Concentration of VM = 70.63 * 75.18/100 = 53.10g

Initial concentration = 53.10g, Hydrochar concentration = 18.54

Volatile matter conversion (%) = $\frac{53.10-18.54}{53.10} * 100$ = 65.09%

Liquid Characteristics (TOC)

รายงานผลการวิเคราะห์คุณภาพน้ำ

โครงการ : ตรวจวิเคราะห์คุณภาพน้ำ
ที่ตั้งโครงการ : -
ชื่อ/ที่อยู่ลูกค้า : สถาบันเทคโนโลยีแห่งเอเชีย
4 สถาบันเทคโนโลยีแห่งเอเชีย ตำบลคลองหนึ่ง
อำเภอคลองหลวง จังหวัดปทุมธานี 12120
วิธีเก็บตัวอย่าง : -
ผู้เก็บตัวอย่าง : สถาบันเทคโนโลยีแห่งเอเชีย

วันที่เก็บตัวอย่าง : -
วันที่รับตัวอย่าง : 26 กุมภาพันธ์ 2558
วันที่วิเคราะห์ : 26 กุมภาพันธ์-9 มีนาคม 2558
วันที่พิมพ์รายงาน : 9 มีนาคม 2558

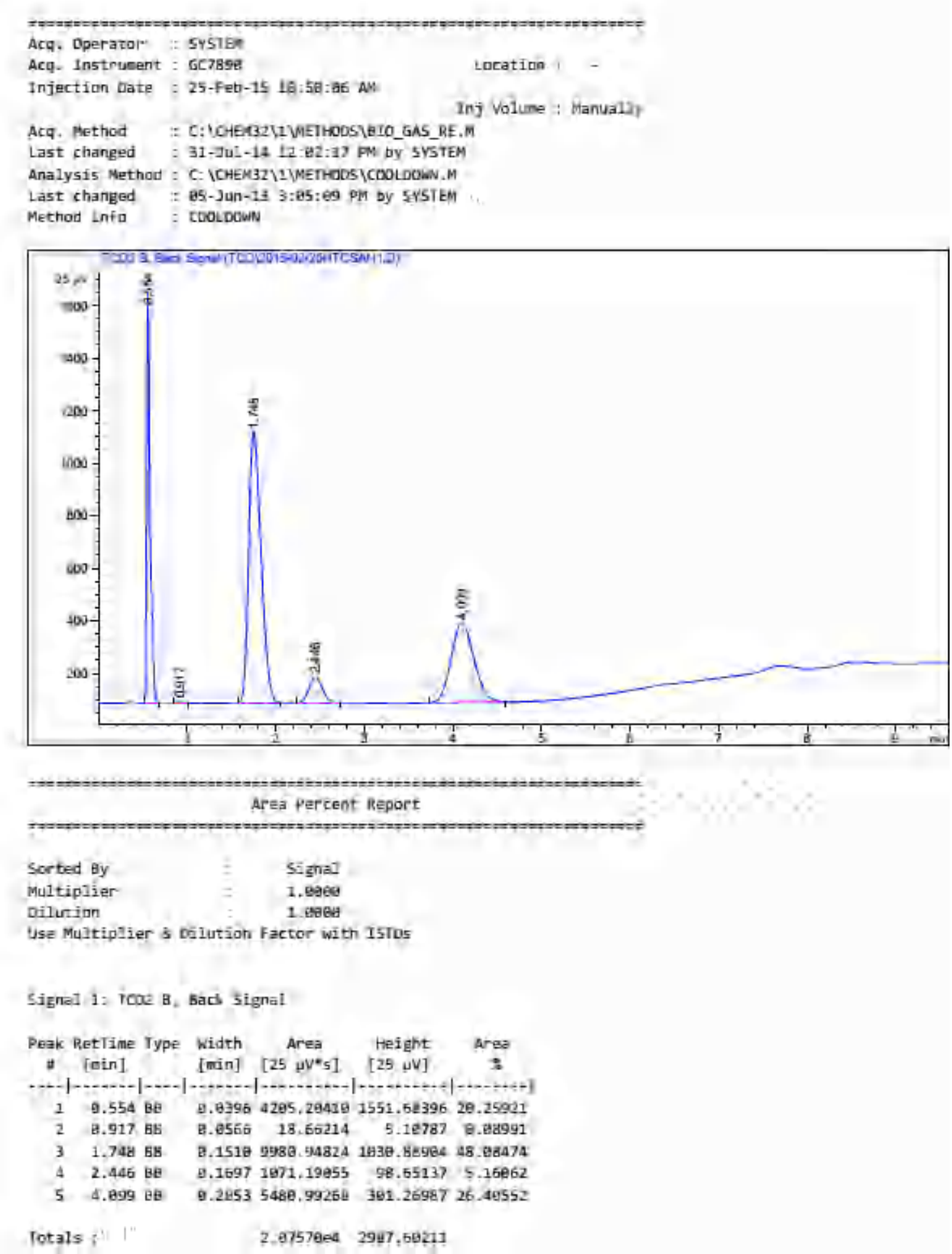
พารามิเตอร์	วิธีวิเคราะห์	สถานี	
		BARCH I	BARCH II
TOTAL ORGANIC CARBON (mg/L)	HIGH-TEMPERATURE COMBUSTION METHOD (5310-B)	17,020	19,035

หมายเหตุ
สภาพตัวอย่าง ;
1. BARCH I ; ขุ่นดำ ตะกอนมาก
2. BARCH II ; ขุ่นดำ ตะกอนมาก

ผลการวิเคราะห์นี้รับรองเฉพาะตัวอย่างที่ได้ทำการวิเคราะห์เท่านั้น
ห้ามคัดถ่ายรายงานผลการวิเคราะห์เพียงบางส่วนโดยไม่ได้รับอนุญาตจากห้องปฏิบัติการเป็นลายลักษณ์อักษร

Gas compositions (Gas chromatograph)

Sample 1



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Acq. Instrument : GC7890                          Location : -
Injection Date  : 25-Feb-15 10:50:06 AM
                                               Inj Volume : Manually

Acq. Method     : C:\CHEM32\1\METHODS\BIO_GAS_RE.M
Last changed    : 31-Jul-14 12:02:17 PM by SYSTEM
Analysis Method : C:\CHEM32\1\METHODS\COOLDOWN.M
Last changed    : 05-Jun-13 3:05:09 PM by SYSTEM
Method Info     : COOLDOWN
```

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: TCD2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [25 µV*s]   [25 µV]      %
----|-------|----|-------|----------|----------|--------|
   1   0.554 BB    0.0396 4205.20410 1551.68396 20.25921
   2   0.917 BB    0.0566   18.66214    5.10787  0.08991
   3   1.748 BB    0.1510 9980.94824 1030.88904 48.08474
   4   2.446 BB    0.1697 1071.19055   98.65137  5.16062
   5   4.099 BB    0.2053 5480.99260  301.26987 26.40552

Totals :                  2.07570e4  2987.60211
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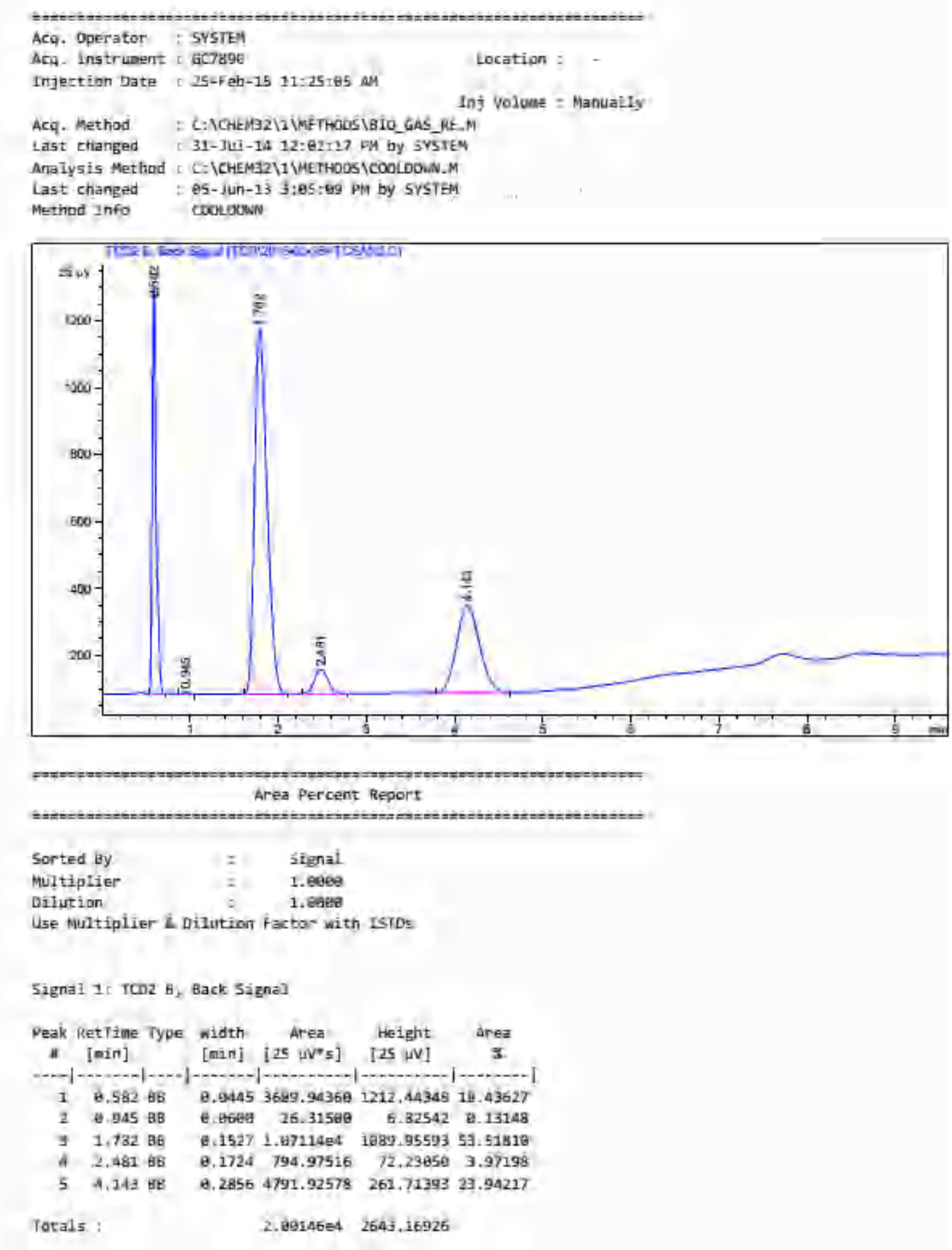
Sample 2



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=====================================================================
Acq. Operator   : SYSTEM
Acq. Instrument : GC7890                        Location :   -
Injection Date  : 25-Feb-15 11:25:05 AM
                                               Inj Volume : Manually
Acq. Method     : C:\CHEM32\1\METHODS\BIO_GAS_RE.M
Last changed    : 31-Jul-14 12:02:17 PM by SYSTEM
Analysis Method : C:\CHEM32\1\METHODS\COOLDOWN.M
Last changed    : 05-Jun-13 3:05:09 PM by SYSTEM
Method Info       COOLDOWN
```

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: TCD2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [25 µV*s]   [25 µV]      %
----|-------|----|-------|----------|----------|--------|
   1   0.582 BB    0.0445 3689.94360 1212.44348 18.43627
   2   0.945 BB    0.0600   26.31500    6.82542  0.13148
   3   1.782 BB    0.1527 1.07114e4  1089.95593 53.51810
   4   2.481 BB    0.1724  794.97516   72.23050  3.97198
   5   4.143 BB    0.2856 4791.92578  261.71393 23.94217

Totals :                  2.00146e4  2643.16926
```

Table B12. Parameters for Mass Balance

Before HTC				
Weight of feedstock	350	g	100.00	%
Dried input solids	70.63	g	20.18	%
Weight of dried feedstock	70.63	g		
Moisture content	279.37	g	79.82	%

After HTC		
Weight of coal-slurry product	342.26	g
Weight of filtrate	222.5	g
Liquid product	14.84	ml
Weight of hydrochar before drying	119.76	g
Weight of hydrochar after drying	48.05	g
Amount of water vaporized during drying	71.71	g
Amount of gas produced	7.74	g

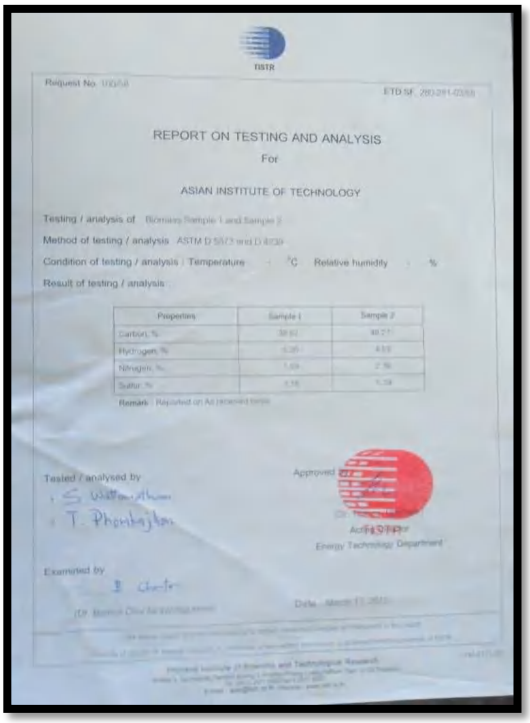
Input solids conversion = Hydrochar + Liquid products + Gas
= 48.05 + 14.84 +7.74
= 70.63g

Carbon Balance

Table B13. Parameters for Carbon Balance

Parameter	value	unit	value	unit
Input carbon	38.62	%C	27.2773	g
TOC	18.17	g/L	4.0428	g
Output carbon	48.27	%	23.19374	g
CO2	63.05	%	0.040746	g

Ultimate Analysis



TISTR

Request No. [illegible]

ETD SF. [illegible]

REPORT ON TESTING AND ANALYSIS
For
ASIAN INSTITUTE OF TECHNOLOGY

Testing / analysis of Biomass Sample 1 and Sample 2

Method of testing / analysis ASTM D 5373 and D 4239

Condition of testing / analysis : Temperature - °C Relative humidity - %

Result of testing / analysis :

Properties	Sample 1	Sample 2
Carbon, %	38.62	48.27
Hydrogen, %	[illegible]	[illegible]
Nitrogen, %	[illegible]	[illegible]
Sulfur, %	[illegible]	[illegible]

Remark : Reported on As received basis

Tested / analysed by

Approved by

Acting Director
Energy Technology Department

Examined by

Date [illegible]

Elemental compositions (C, H, N, S and O) (17.03.2015)

Table B14.Energy Balance

Time (min)	Temperature (°C)	Electricity power supplied (kWh)
0	15	0
1.5	15	0.06
3	18	0.09
5	19	0.16
7	26	0.22
9	68	0.28
10	93	0.32
12	130	0.34
14	140	0.40
16	155	0.47
18	169	0.52
20	180	0.58
22	192	0.65
24	203	0.72
26	214	0.78
27	220	0.82
30	230	0.91
32	240	0.97
34	250	1.10
94	256	1.60
154	250	2.25
180	254	3.00

*efficiency of the watt meter used ≈ 10% (Data recorded on (recorded on 12/02/2014))

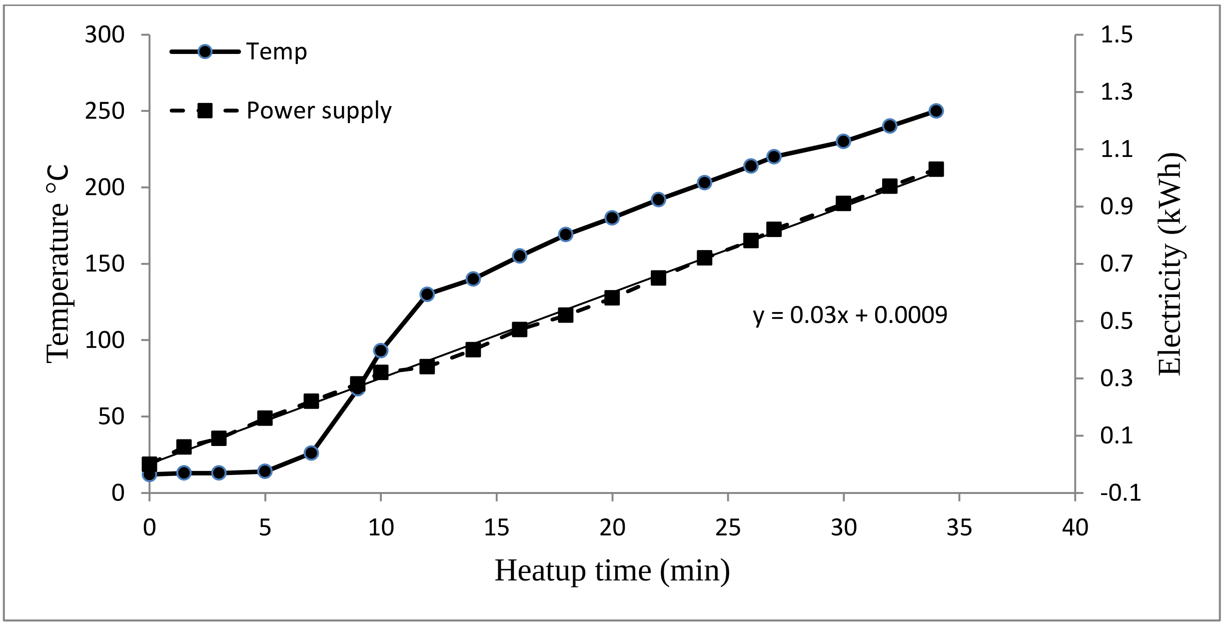


Figure B1. Heat up time of reactor vs temperature and electricity (recorded on 12/02/2014)

From graph,
Energy consumption rate to heat up the reactor (15 - 250°C) = 0.03 kWh/min

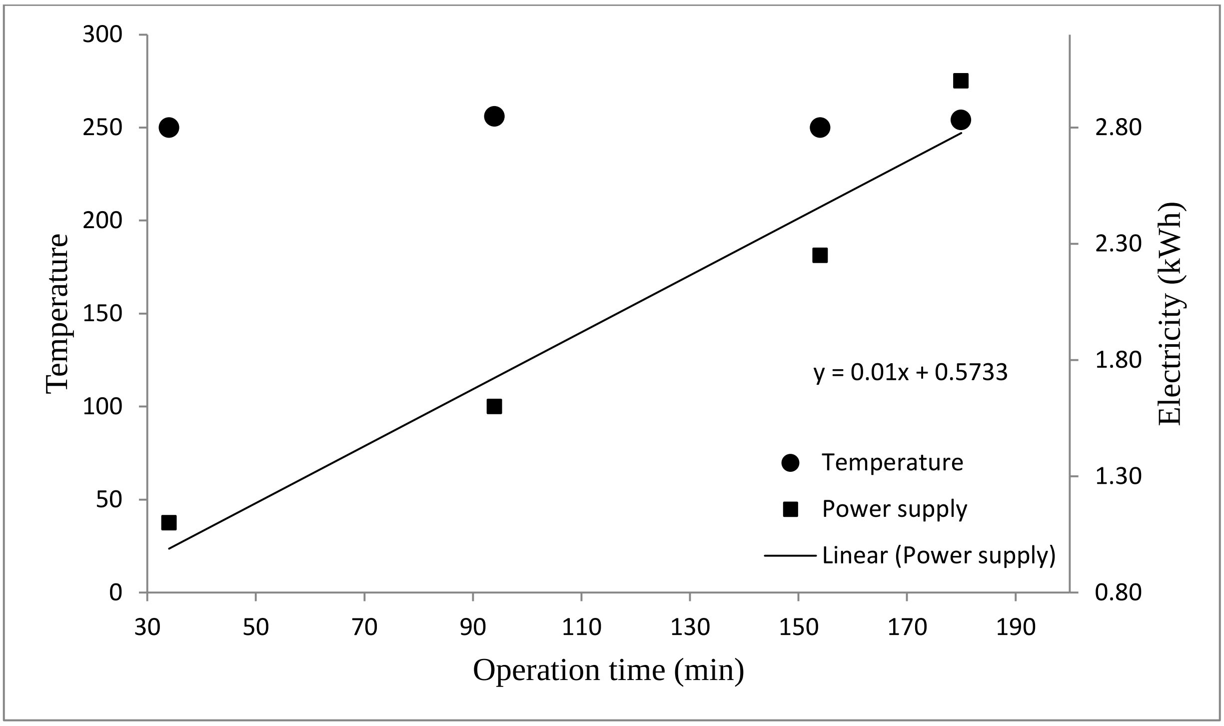


Figure B2. Operation time of reactor vs temperature and electricity (recorded on 12/02/2015)

From the graph,
Energy consumption rate to operate the reactor for 3 hours at 250 °C = 0.01kwh/min
= 34kJ/min

Table B15. Parameters for Energy Balance Calculation

Parameters	Value	Unit	Value	Unit
Initial temperature of feedstock	15	°C	288	K
Desired operation temperature	250	°C	523	K

Parameters	Value	Unit
Specific heat capacity of water (C_{pwater})	4.186	kJ/kg °C
Specific heat capacity of solids in sludge (C_{pFS})	1.95	kJ/kg °C
Latent heat of water (L)	2260	kJ/kg
Specific heat capacity of reactor (stainless steel) ($C_{Preactor}$)	0.5	kJ/kg °C

Theoretical calculation for energy requirement for 350ml feedstock

Moisture content = 79.82 %wt
Total solid content = 20.18%wt
Total feedstock volume = 350 mL (0.35 kg)
Operating temp of HTC = 250 °C
Initial temperature of feedstock = 15°C

Energy required for HTC
= $[m_{water} * C_{p\ water} * (T_p - T_i)] + [m_{FS} * C_{p\ FS} * (T_p - T_i)]$
= [(0.7982 x 0.35)*(4.186)*(250-15]+(0.2018 x 0.35)*(1.95)*(250-15)]
= 304.9817 kJ = 0.08 kWh

Actual supplied energy to heat up the reactor = 1.1 kWh

Therefore, efficiency of the reactor $= \frac{Actual\ energy\ required\ (theoretical)}{Actual\ energy\ supplied} * 100 = 7.7\% \approx$ 8%

Theoretical calculation for energy requirement for 1kg feedstock

Input feedstock	1000	g	1	kg
Moisture content	279.37	g	0.27937	kg
Total solids (dry basis)	70.63	g	0.07063	kg

Energy required for HTC to heat up (15 – 250 °C)

= [(0.7982 x1)*(4.186)*(250-15] + (0.2018 x 1)*(1.95)*(250-15)]

= 877.67 kJ

Energy required for HTC to operate the reactor at 250 °C for 3 hours (180min)

= [energy consumption rate * operation time)

= [34 kJ/min * 180 min)

=6480 kJ

If consider the efficiency of the watt meter used (10% = 0.10), the energy required for HTC becomes,

= 6480 * 0.1

=648kJ

Energy required for dewatering

energy of Vacuum pump (P) = 0.4 kWh (from the vacuum pump)

Operation time ($t_{dewater}$)= 5 min

= $P * t_{dewater}$

= 0.4 * 5/60

= 0.03kWh

=120 kJ

Energy required for drying into the oven from 25 - 105°C

= [$(m_{water})(C_{pwater})(T_{105°C} – T_{25°C})$+ $(m_{water})(L)$] + [$(m_{hydrochar})(C_{p,solid})(T_{105°C} – T_{25°C})$]

Wet hydrochar weight = 0.343 kg

Hydrochar weight (Dry basis) = 40%

Moisture evaporated = 60%

Hydrochar yield = 68%

= [0.60*0.343*4.186) (105 – 25) + (0.60*0.343*2260) + [0.40*0.343*1.95]

= 555.43 kJ

Energy recovery from produced hydrochar (measured on dry basis)

= 23.75 MJ/kg

Energy recovery based on wet feedstock
=energy recovered on dry basis * total solid content* hydrochar yield
= 23.75 * 0.2018* 0.68
=3.25907 MJ/kg of wet feedstock
=3259.07 kJ/kg of wet feedstock

Energy required for HTC operation from feeding feedstock towards hydrochar production
From the calculations,

Energy required to heat up the reactor = = 877.67 kJ
Energy required to operate the reactor = 648 kJ
Energy required for filtration = 120 kJ
Energy required for drying = 555.43 kJ
Sum of total energy = 2201.10 kJ

Energy efficiency = Energy recovered from hydrochar/ energy supplied to the reactor
= (3259.07 / 2201.10)*100 = 148.06 %

Heat loss

Table B16. Variables used for heat loss calculations

Variables	Formula	Units
Heat loss due to convection (Q)	$h_c * L_r * \beta * (T_p - T_a)$	J/S = W
heat transfer coefficient	h_c	$W/m^2.K$
Surface to transfer heat	S	m^2
Plate temperature	T_p	K
Air temperature	T_a	K
heat transfer coefficient due to convection (h_c)	(Nu*k)/L	$W/m^2.K$
Nusselt number (N_u)	$0.59 * Ra^{0.25}$	
Rayliegh number (R_a)	$Gr * P_r$	
Prandtl number (Pr)	$\mu * C_p / k$	
Air dynamic viscosity (μ)	$1.86 * 10^{-5}$	kg.m/s
Specific heat capacity of dryair (C_{pair})	1005	J/kg.K
Thermal conductiivity of air (k)	0.026	W/m*K
Grashof number (Gr)	$g * L^3 * \beta * (T_p - T_a) / \eta^2$	
Acceleration due to gravity (g)	9.81	m/s^2
Thermal expansion coefficient of air (gases) β	$1/T_a$	1/K
Kinematic viscosity of air (η) @30°C	$1.6 * 10^{-5}$	
Heat loss due to radiation (q)	$\sigma * \varepsilon * L_r * \beta * (T_p^4 - T_a^4)$	W=J/s
Stefan-Boltzmann constant (σ)	$5.67 * 10^{-8}$	$W/m^2.K^4$
Emissivity (ε) for ceramic	0.69	
Mass of the reactor	3.5	kg
Side length of the reactor (L_r)	0.12	m
Diameter of the reactor (bottom) (β)	0.06	m

No. of ceramic plates inside the heating jacket	4	
Plate temperature of the reactor (T_p)	722	°C (995 K)
Air temperature (T_a)	30	°C (303 K)

Prandtl number (Pr)
$= \mu *C_{pair} /k$
$=1.86*10^{-5}*1005*0.026$
$=0.71896$

Grashof number (Gr)
$= g*L_r^3*\beta*(T_p-T_a)/\eta^2$
$=9.81*0.12^3*0.06*(995 – 303)/ (1.6*10^{-5})^2$
$=151230469$

Rayliegh number (R_a)
$= Gr*P_r$
$= 151230469*0.71896$
$=108728658$

Nusselt number (N_u) (Selected for laminar flow)
$= 0.59*Ra^{0.25}$
$= 0.59*(108728658)^{0.25}$
$= 60.247$

Heat transfer coefficient due to convection (h_c)
$= (Nu*k)/L_r$
$= (60.247*0.026)/0.12$
= 13.053517 W/m^2.K.

Heat loss due to convection (Q)
$= h_c*L_r* \beta *(T_p -T_a)$
$=13.053517*0.12*0.06*(995 – 303)$
=65.037841 J/s
No. of ceramic plates presented inside the heat jacket = 4
Therefore,
Heat loss due to convection (Q) = 65.037841*4 = 260.15 J/s
But, actual operation time = 1.32 hrs = 1.32*3600 = 4752 s

Heat loss due to convection (Q)
= 260.15 * 4752 = 1236232 J
=1236.232 kJ

Heat loss due to radiation (q)
$= \sigma*\varepsilon* L_r* \beta *(T_p^4-T_a^4)$
$=5.67*10^{-8}*0.69*0.12*0.06*(995^4 – 303^4)$
=273.719 J/s

No. of ceramic plates presented inside the heat jacket = 4
Heat loss due to convection (Q) = 273.719 *4 = 1094.876 J/s
But, actual operation time = 1.32 hrs = 1.32*3600 = 4752 s

Heat loss due to radiation (q)
= 1094.876 * 4752 = 5202850.8 J
= 5202.850 kJ

Heat loss from the surface body of the reactor
$= (m_{reactor})(C_{p,\ reactor})(T_{250°C}-T_{15°C})$
= (3.5*0.5*(523-288))
= 411.25 kJ

Total heat loss (calculated) = 1236.232 kJ + 5202.850 kJ + 411.25 kJ = **6850.332 kJ**

Input total supplied energy = 3kWh = 10800 kJ

Energy required for HTC to heat up + Energy required for HTC to operate the reactor
= 877.67 +648 = 1525.6722 kJ

Other losses
= Total energy supplied – energy used for HTC operation – heat loss calculated
= 10800 – 1525.6722 - 6850.332
=2423.9958 kJ

% of heat losses = (heat loss calculated / total input supplied energy) * 100

Input supplied energy	100%
radiation	48%
convection	11%
Heat loss from the reactor body	4%
Heat required for HTC	14%
Other losses	22%

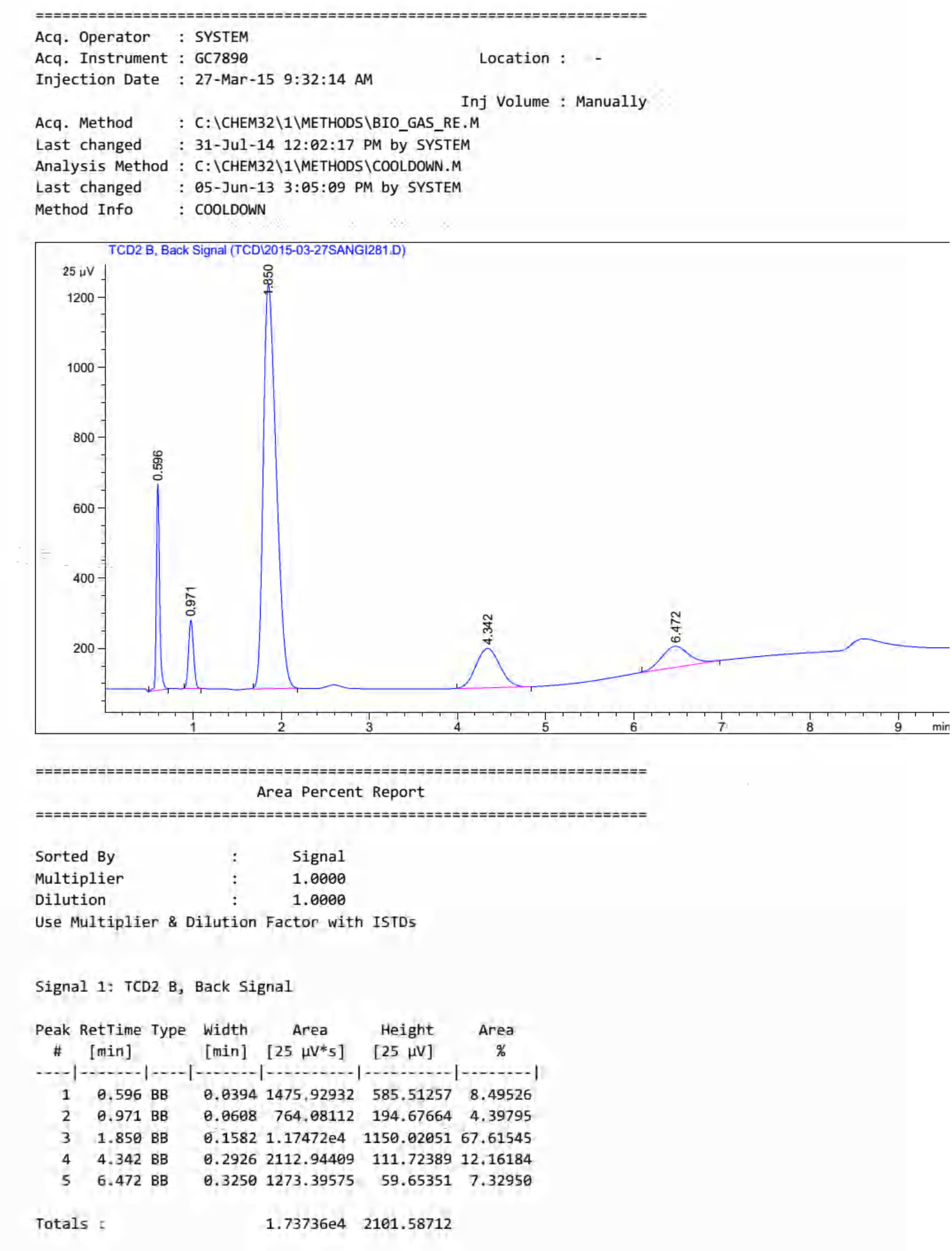
Phase III – Fermentation process

Table B17. Parameters Measured During Fermentation

SRT	pH	VFA (gCH3COOH/L)		CO_2	O_2	N_2	CH_4	CO
		Batch 1	Batch 2	(%)	**(%)**	**(%)**	**(%)**	**(%)**
0	5.62	11.70	11.24	0.00	0.00	0.00	0.00	-
7	4.55	21.90	22.74	36.55	6.297	40.865	16.288	-
14	4.39	21.76	21.36	46.44	4.78	21.821	26.959	-
21	4.27	21.71	19.62	56.33	3.72	2.31	37.63	-
28	4.43	23.92	21.94	75.22	4.89	4.71	15.28	-
35	4.41	11.70	11.24	58.17	1.52	25.81	7.31	7.19

Biogas Compositions

SRT – 28 days



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Acq. Instrument : GC7890                          Location :   -
Injection Date  : 27-Mar-15 9:32:14 AM
                                                Inj Volume : Manually
Acq. Method     : C:\CHEM32\1\METHODS\BIO_GAS_RE.M
Last changed    : 31-Jul-14 12:02:17 PM by SYSTEM
Analysis Method : C:\CHEM32\1\METHODS\COOLDOWN.M
Last changed    : 05-Jun-13 3:05:09 PM by SYSTEM
Method Info     : COOLDOWN
```

```
=====================================================================
                         Area Percent Report
=====================================================================

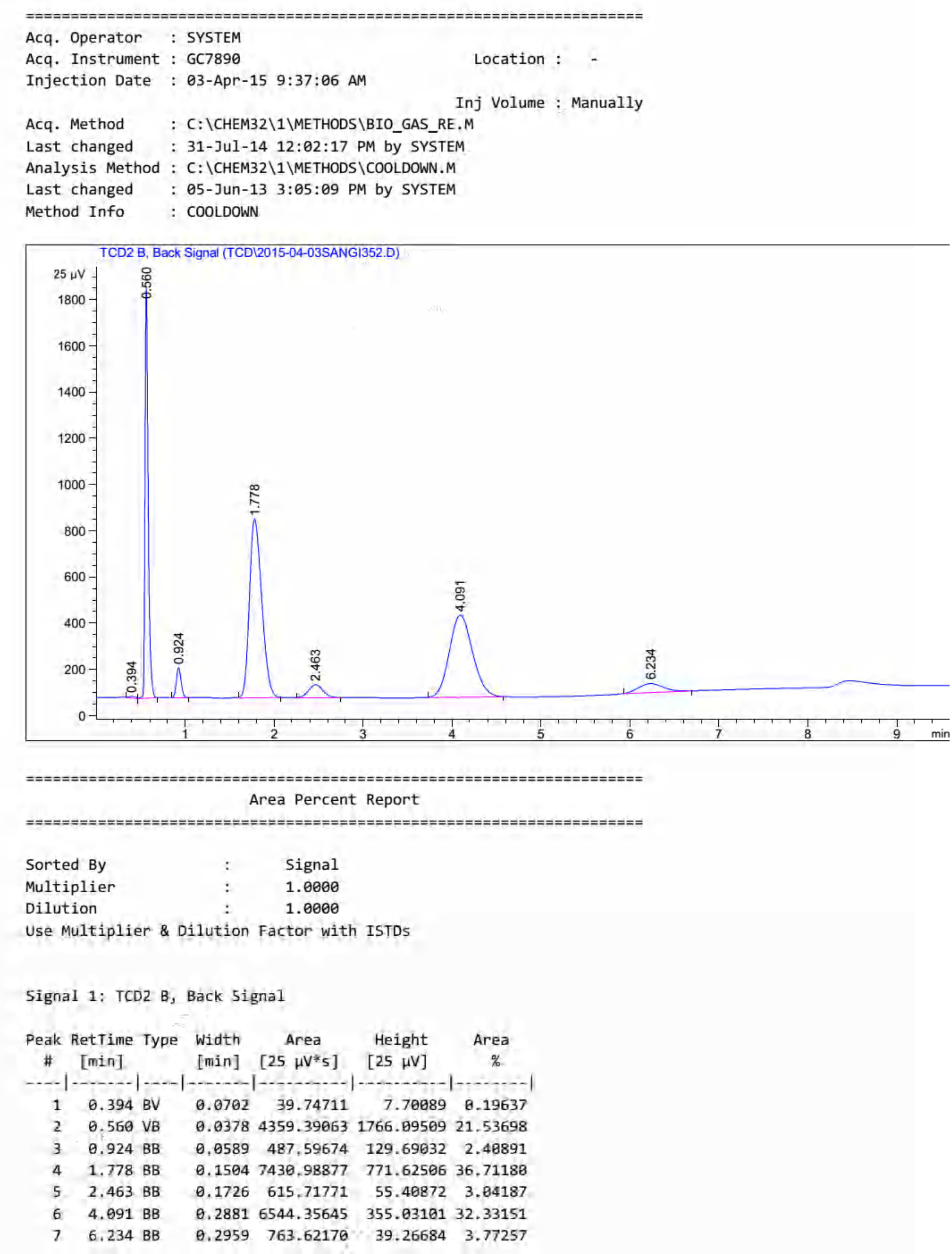
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: TCD2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [25 µV*s]   [25 µV]      %
----|-------|----|-------|----------|----------|--------|
   1   0.596 BB    0.0394 1475.92932  585.51257  8.49526
   2   0.971 BB    0.0608  764.08112  194.67664  4.39795
   3   1.850 BB    0.1582 1.17472e4  1150.02051 67.61545
   4   4.342 BB    0.2926 2112.94409  111.72389 12.16184
   5   6.472 BB    0.3250 1273.39575   59.65351  7.32950

Totals :                  1.73736e4  2101.58712
```

SRT – 35 days



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======================================================================
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Acq. Instrument : GC7890                          Location :   -
Injection Date  : 03-Apr-15 9:37:06 AM
                                                Inj Volume : Manually
Acq. Method     : C:\CHEM32\1\METHODS\BIO_GAS_RE.M
Last changed    : 31-Jul-14 12:02:17 PM by SYSTEM
Analysis Method : C:\CHEM32\1\METHODS\COOLDOWN.M
Last changed    : 05-Jun-13 3:05:09 PM by SYSTEM
Method Info     : COOLDOWN
```

```
======================================================================
                         Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: TCD2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #    [min]        [min]  [25 µV*s]   [25 µV]     %
----|-------|----|-------|----------|----------|--------|
   1   0.394 BV    0.0702   39.74711    7.70089  0.19637
   2   0.560 VB    0.0378 4359.39063 1766.09509 21.53698
   3   0.924 BB    0.0589  487.59674  129.69032  2.40891
   4   1.778 BB    0.1504 7430.98877  771.62506 36.71180
   5   2.463 BB    0.1726  615.71771   55.40872  3.04187
   6   4.091 BB    0.2881 6544.35645  355.03101 32.33151
   7   6.234 BB    0.2959  763.62170   39.26684  3.77257
```

Table B18. Parameters Measured During HTC

SRT	TS (%)	PH (Filtrate)	Calorific value (calorie/g)		Hydrochar weight (g)	
			Batch 1	Batch 2	Batch 1	Batch 2
0	15.4	4.67	5327.438	5366.1	34.33	36.55
7	14.79	4.6	4454.2	4316.1	29.81	31.21
14	13.83	4.24	4700.8	4545.1	29.72	28.92
21	13.54	4.27	4799.9	5018.5	28.4	26.94
28	13.73	4.19	4330.784	4390.535	26.85	28.12
35	12.79	4.3	4352.294	4211.281	27.47	25.12