# Evaluation of Hydrothermal Carbonization Reactions for Faecal Sludge Treatment and Hydrochar Production

by

Krailak Fakkaew

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| Examination Committee: | Dr. Thammarat Koottatep (Chairperson)<br>Prof. Chettiyappan Visvanathan<br>Prof. Rajendra Prasad Shrestha<br>Prof. Chongrak Polprasert (External Member) |
| External Examiner: | Prof. Tjandra Setiadi<br>Department of Chemical Engineering<br>Faculty of Industrial Technology<br>Institut Teknologi Bandung<br>Indonesia |
| Nationality: | Thai |
| Previous Degree: | Master of Engineering in Environmental Engineering<br>Chiang Mai University<br>Thailand |
| Scholarship Donor: | Bill & Melinda Gates Foundation<br>under the framework of the SaniUP Project |

Asian Institute of Technology
School of Environment, Resources and Development
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# Abstract

Faecal sludge management is a serious problem in developing countries which has caused environmental pollution and health risks. Hydrothermal carbonization (HTC) is a thermal conversion process which can be applied to treat faecal sludge (FS) and convert it into a valuable solid product called hydrochar. This research determined the applicability of conventional and two-stage HTC processes for FS treatment with respect to energy consumption and efficiency in hydrochar production. To investigate effects of process parameters, mass and energy balances, laboratory-scale HTC experiments were conducted with a 1-L high pressure reactor. Optimum conditions of HTC processes which could convert FS to hydrochar at the relatively high energy content and yield were determined and verified. HTC product characteristics were analyzed to identify their applications and post-treatment options.

Experimental results of the conventional HTC process indicated the significance of moisture content on energy content of the produced hydrochar. Likewise, increasing temperatures and reaction times resulted in increased energy contents of the produced hydrochar. Optimum conditions of the conventional HTC of FS to produce the highest normalized energy yield were moisture content of 80%, reaction time of 5 h and temperature of 250 °C. In these conditions, the energy content and hydrochar yield were 19-20 MJ/kg and 70-73%, respectively. In addition, a mathematical model which could estimate the energy content of the produced hydrochar using the relevant parameters such as moisture content of FS, temperature, reaction time and volatile solid concentration in FS was developed and validated satisfactorily with the literature data.

A low-energy HTC process named “Two-stage HTC” comprising of hydrolysis and carbonization stages using FS as feedstock was developed and optimized. The experimental results indicated the hydrolysis reaction time and carbonization temperature had significant effects on energy content of the produced hydrochar. Optimum conditions of the two-stage HTC of FS were hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C, and carbonization reaction time of 100 min. In these conditions, the energy content and hydrochar yield of 20-21 MJ/kg and 70-73%, respectively, could be achieved. The energy required for the two-stage HTC was about 25% lower than conventional HTC process. The energy efficiency of the two-stage HTC for treating faecal sludge was higher than that of conventional HTC and other thermal conversion processes such as pyrolysis and gasification. The two-stage HTC could be considered as a potential technology for treating FS and producing hydrochar.

Characteristics of HTC products including hydrochar, liquid and gas products were identified. The ranges of the energy content, H/C and O/C atomic ratios of the produced hydrochar were comparable to natural coals. Thus, it could be considered to apply as solid fuel in typical combustion processes. Other potential applications of the produced hydrochar based on its characteristics could be an anode in Li-ion battery, absorbent in water purification, and $CO_2$ sequestration. HTC liquid and gas by-products should be further managed to avoid environmental pollutions. As HTC is a relatively new technology shift from laboratory to pilot- or full-scale productions such as the FS treatment plant, opportunities and challenges related to HTC of FS still exist. Preliminary HTC plant design for FS treatment was proposed and discussed in this dissertation.

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## List of Abbreviations

| | |
|---|---|
| $A$ | Pre-exponential factor |
| AD | Anaerobic digestion |
| AIT | Asian Institute of Technology |
| ANOVA | Analysis of variance |
| BET | Brunauer-Emmett-Teller |
| BMP | Bio-methane potential |
| BOD | Biochemical oxygen demand |
| C | Carbon |
| C° | Celsius (unit) |
| CE | Carbon efficiency |
| CEC | Cation-exchange capacity |
| cfu | Colony-forming unit |
| $CH_4$ | Methane |
| $cm^3$ | Cubic centimeter (unit) |
| CO | Carbon monoxide |
| $CO_2$ | Carbon dioxide |
| COD | Chemical oxygen demand |
| $C_i$ | Mass of volatile matter in faecal sludge |
| $C_{p,M}$ | Heat capacity of input material |
| $C_{p,reactor}$ | Heat capacity of reactor body |
| $C_{p,W}$ | Heat capacity of water |
| $C_t$ | Mass of volatile matter in hydrochar |
| CSTR | Continuous stirred-tank reactor |
| Dist. | Distribution |
| $E_a$ | Activation energy |
| $E_{com}$ | Energy consumption rate |
| $E_{content}$ | Energy content of the input or product substrates |
| $E_{convection}$ | Energy loss to the environments by convection |
| $E_{dewater}$ | Energy used for vacuum filtration |
| $E_{dry}$ | Energy required for drying |
| $E_{feedstock}$ | Energy content of the dry initial feedstock |
| $E_{heat}$ | Heat of HTC reaction |
| $E_{hydrochar}$ | Energy content of the produced hydrochar |
| $E_{loss, reactor}$ | Energy loss for heating reactor body |
| $E_{radiation}$ | Energy loss to the environments by radiation |
| $E_{reaction}$ | Energy released from the HTC reaction |
| $E_{required, HTC}$ | Energy required for heating in HTC process |
| $E_{substrate}$ | Energy of the input or product substrates |
| $f$ | Correction factor |
| FC | Fixed carbon |
| FS | Faecal sludge |
| FSM | Faecal sludge management |
| FTIR | Fourier transform infrared spectroscopy |
| g | Gram (unit) |
| GHG | Greenhouse gas |
| h | Hour (unit) |
| $h$ | Convection coefficient |
| H | Hydrogen |

| | |
|---|---|
| $H_2S$ | Hydrogen sulfide |
| $H_2SO_4$ | Sulfuric acid |
| $H_3PO_4$ | Phosphoric acid |
| HCl | Hydrogen chloride |
| HMF | Hydroxymethylfurfural |
| $HNO_3$ | Nitric acid |
| HTC | Hydrothermal carbonization |
| HTG | Hydrothermal gasification |
| HTL | Hydrothermal liquefaction |
| J | Joule (unit) |
| $k$ | Reaction rate constant |
| K | Kelvin (unit) |
| $K_2O$ | Potassium oxide |
| L | Liter (unit) |
| LGC | Low gross calorific value |
| $M$ | Mass of input material |
| $m^2$ | Square meter (unit) |
| $m^3$ | Cubic meter (unit) |
| min | Minute (unit) |
| MNRE | Ministry of natural resources and environment |
| mol | Mole (unit) |
| $M_{substrate}$ | Mass of the input or product substrates |
| $M_{reactor}$ | Mass of HTC reactor body |
| $M_{vm}$ | Mass of volatile matter content in faecal sludge |
| MSW | Municipal solid waste |
| N | Nitrogen |
| $N_2O$ | Nitrous oxide |
| $NH_4$ | Ammonium |
| NiO | Nickel oxide |
| O | Oxygen |
| OSS | On-site sanitation |
| P | Phosphorous |
| $P$ | Power of vacuum pump |
| $P_2O_5$ | Phosphorous pentoxide |
| PCD | Pollution control department |
| ppm | Part per million (unit) |
| $r$ | Reaction rate |
| $R$ | Gas constant value |
| $R^2$ | Correlation coefficient |
| RSM | Response surface methodology |
| $s$ | Heater surface |
| S | Sulfur |
| SCWG | Supercritical water gasification |
| sec | Second (unit) |
| SEM | Scanning electron microscopy |
| Si | Silicon |
| $SnCl_4$ | Tin (IV) chloride |
| $SO_2$ | Sulfur dioxide |
| $t$ | Reaction time |
| $T$ | Temperature |

| | |
|---|---|
| $T_a$ | Air temperature |
| TN | Total nitrogen |
| TOC | Total organic carbon |
| TP | Total phosphorous |
| TS | Total solid |
| $T_s$ | Heater temperature |
| TVS | Total volatile solid |
| USD | United States dollar |
| VFA | Volatile fatty acids |
| VM | Volatile matter |
| VOC | Volatile organic carbon |
| VS | Volatile solid |
| $VS$ | Volatile solid concentration |
| $W$ | Moisture content in FS |
| WHC | Water-holding capacity |
| WHO | World health organization |
| wt | Weight |
| WWTP | Wastewater treatment plant |
| XPS | X-ray photoelectron spectroscopy |
| $\Delta H_{\mathrm{vap}}$ | Latent heat for vaporization of water |
| $\Delta T$ | Temperature difference |
| $\varepsilon$ | Emissivity of the surface |
| $\sigma$ | Stefan-Boltzman constant |

# Chapter 1

# Introduction

## 1.1 Background

Most developing countries do not provide sewer systems with centralized treatment for the majority of urban residents. Human excreta containing faeces and urine is commonly disposed into septic tanks, cesspools or pit latrines and the accumulated sludge from these systems, so called Faecal Sludge (FS), are periodically removed in urban areas for further treatment and disposal. Large amounts of FS in several developing countries such as Thailand, Vietnam and India are not properly treated and are being discharged into nearby canals, land and paddy fields (USAID, 2010). Because FS generally contains high concentrations of organic matter and pathogens, these untreated FS could cause serious environmental and health risk problems. Typical treatment technologies for treating FS and converting them into valuable products, such as drying bed, constructed wetland, composting, and digestion are well known. However, these technologies cannot be overcome the sanitation and environmental problems, and also selling the generated products is still not cover the collection and treatment costs.

Hydrothermal carbonization (HTC) is a thermal conversion process which is found to be effective in converting high moisture biomass into carbonaceous solids, commonly called "Hydrochar", within a short period of time (5-240 min) at a relatively low temperature range (180-250 °C) and corresponding pressures (20-60 bar) (Kambo and Dutta, 2015). According to previous reports (Falco et al., 2011; Funke and Ziegler, 2010; He et al., 2013; Sevilla and Fuertes, 2009), the hydrochar can be formed during HTC process via two major conversion pathways: (1) conversion of aqueous dispersion biomass materials which is dominated by reaction mechanisms including hydrolysis, dehydration, decarboxylation, fragmentation, polymerization and aromatization, and (2) direct solid–solid conversion of original biomass materials which undergoes devolatilization, intramolecular condensation, dehydration and decarboxylation.

HTC represents one possible means for treating FS. The main advantages of HTC over other thermal conversion processes (pyrolysis, gasification and incineration) are its ability to convert the wet biomass feedstock to become hydrochar at the relatively high yields without preliminary dewatering and drying (Libra et al., 2011; Lu et al., 2012) and, consequently, requiring less energy. The energy required for the HTC process is expected to be significantly lower than that required in the pyrolysis process of such wet feedstock (moisture content of 75-90%) (Libra et al., 2011). In addition, the chemical structure and energy content of hydrochar are similar to natural coal, which make it suitable for use as a solid fuel in conventional combustion processes. Moreover, hydrochar produced from HTC have already found in many applications such as, energy storage, soil amendment, absorbent in water purification, catalyst, and $CO_2$ sequestration (Titirici and Antonietti, 2010).

Some studies on HTC of human wastes (untreated faeces and FS) and sewage sludge have been previously reported. The experiments of Danso-Boateng et al. (2013) showed the decomposition kinetics of the organic matters in the HTC process be described by the first-order reaction, and energy contents of the produced hydrochar ranged from 21-23 MJ/kg. The HTC of sewage sludge to produce an alternative solid fuel was studied by He et al. (2013) who found fuel characteristics (e.g., energy content, H/C and O/C atomic ratios, and fuel ratio) of the produced hydrochar comparable with those of lignite. Probably due to the low organic matters and energy content of raw FS and its fluctuating characteristics as compared with other biomass materials, application of the HTC process for FS treatment has not been extensively studied and reported.

Although, the advantage of the HTC is a minimal requirement of FS drying, their challenges are the relatively high energy consumption and low energy content of the produced hydrochar. Therefore, to deal with these challenges, a low-energy HTC process named "Two-stage HTC" was explored in this research.

The concept of the two-stage HTC process is to separate reaction pathways into two stages, namely hydrolysis and carbonization stages which are different in the conversion reactions and operating temperatures. In the hydrolysis stage, biomass materials are broken down to become low-molecular weight compounds such as oligosaccharides, glucose (or fructose), and amino acids (Funke and Ziegler, 2010; He et al., 2013) which could be occurred in the temperature range of 100-175 °C (Abelleira et al., 2012). The carbonization stage consists of dehydration, polymerization, aromatization, and solid-solid conversion reactions which require relatively high temperatures in the range of 160-280 °C (Falco et al., 2011). In this stage, the hydrolyzed products (i.e. glucose or fructose) are dehydrated to 5-hydroxymethylfurfural (HMF) and subsequently polymerized and condensed to form the hydrochar (Sevilla and Fuertes, 2009). Simultaneously, the hydrochar is also formed via the solid–solid conversion of biomass materials (Falco et al., 2011). Based on this concept, the two-stage HTC should consume lower energy and result higher energy contents of the produced hydrochar than the conventional HTC.

## 1.2 Objectives

This research is to determine the applicability of two-stage HTC process for FS treatment with respect to energy consumption and efficiency in hydrochar production.

**Specific objectives:**

1. To investigate the hydrochar productions using the conventional and two-stage HTC of FS on the effects of process parameters, mass and energy balances
2. To optimize the conventional and two-stage HTC processes conditions taking into consideration of the energy content of the produced hydrochar and hydrochar yield
3. To evaluate characteristics of products and by-products from HTC of FS with emphasis on their applicability and treatment options to utilize their values and minimize the environmental impacts

## 1.3 Scope

This experimental study was conducted with the lab-scale 1 L high pressure reactor to operate the conventional and two-stage HTC. The experiments were carried out at Asian Institute of Technology (AIT), Thailand. FS samples were obtained from the sludge accumulated in septic tanks, collected by a municipal emptying truck, which serviced residential areas in a city located near Bangkok, Thailand. To investigate effects of process parameters, mass and energy balances, HTC experiments were performed with different process conditions: moisture content of 70-95%wt, temperature of 150-250 °C and reaction time of 0.5-10 h, and energy inputs during the HTC processes were measured using a watt-hour meter. The normalized energy yield was employed to determine optimum conditions of the conventional and two-stage HTC processes of FS which could produce the high energy content and hydrochar yield. The energy efficiencies of the conventional and two-stage HTC processes of FS were examined and compared to other thermal conversion processes (i.e., pyrolysis and gasification). The HTC products (hydrochar, liquid and gas products) were collected and analyzed their characteristics to identify their applications and treatment options.

# Chapter 2

# Literature Review

## 2.1 Faecal Sludge Management

### 2.1.1 Faecal sludge management practices and problems

Most developing countries, on-site sanitation (OSS) facilities such as septic tanks or latrines are provided in urban areas. These systems are typically emptied with vacuum trucks or manual labor. Collection, transportation, treatment and disposal of FS are the important steps in faecal sludge management (FSM). The disposal of FS is a serious situation. The FS is most commonly disposed of in a treatment plant, used in agriculture, and dumped directly into the environment (drainage ditches, lanes, inland waters, open urban spaces, estuaries and the sea). Using an average FS generation rate (1 liter FS per person per day), in a city of 1 million inhabitants, the FS of 1,000 $m^3$ should be collected and disposed. However, reported daily collections from Bangkok, Hanoi and Accra are rarely exceeded 300-500 $m^3$ (Koné and Strauss, 2004). This indicates that large quantities of collected FS are disposed of unrecorded within the urban settlement areas due to the improper of the FS collection, transport systems, and the lack of economic incentives for stakeholders throughout the FSM. To deal with these problems, the FS is not only treated to safe for the environment and human health, but also recovering and selling the generated products to cover the collection, transportation and treatment costs should be considered.

### 2.1.2 Faecal sludge treatment technology

Currently, technologies for FS treatment such as drying bed, constructed wetland, composting, and anaerobic digestion (AD) are well known. Overall advantages and disadvantages of these technologies are summarized in Table 2.1. The FS treatment options primarily depend on the FS characteristics, available technology and treatment objectives. The details of each technology are descripted in the following sections.

#### 2.1.2.1 Drying bed

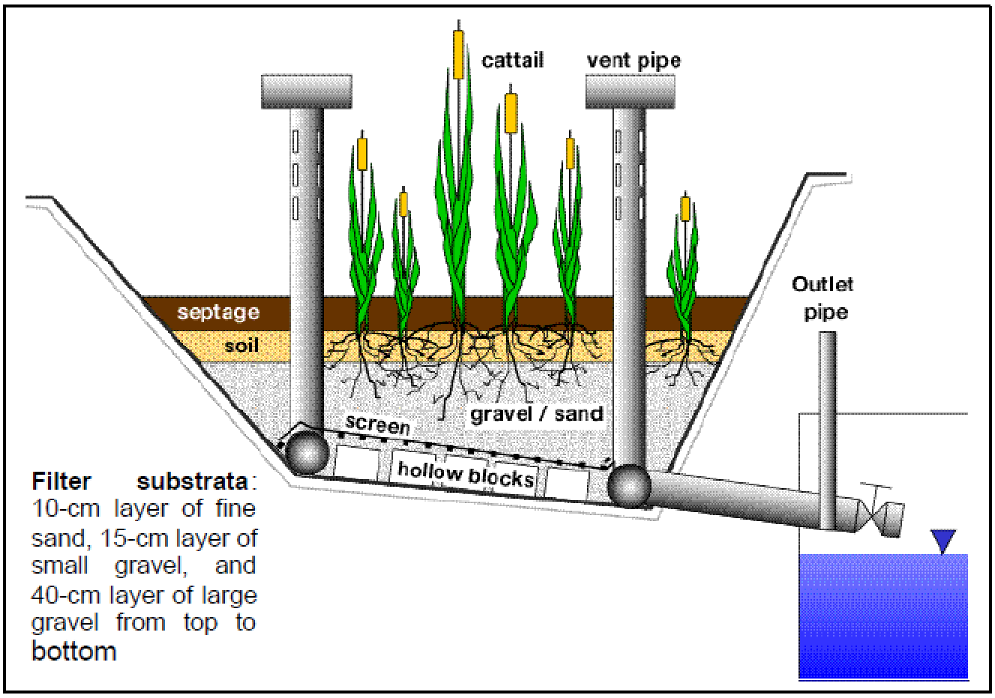
Drying beds or unplanted drying beds consist of a filter consisted of gravel and sand, equipped with a drainage system. Raw FS is loaded on the beds over a filter for dewatering and drying, which are responded by gravity percolation and evaporation. Performances of dewatering vary with the initial total solid (TS), total volatile solid (TVS) and the applied load (Pescod, 1971). 50-80% of the liquid in FS is removed as drained liquid (percolate) and 20-50% is evaporated from the filter bed (Heinss et al., 1998) while the solid is remained on the bed, allowed to dry and then scraped off. Levels of contaminants in the drying bed percolate are considerably lower compared to the settling tank supernatant. However, the drained liquid has to be further treated by suitable treatment such as facultative ponds. The solid, bio-solid, removed from the drying beds could be reused and requires further treatment for pathogen removal. The bio-solid product may be either directly used or co-composted as soil conditioner or fertilizer in agriculture (Cofie et al., 2006). Figure 2.1 shows an example of implementation of drying beds for treating FS at Niayes FS treatment plant in Dakar, Senegal.

**Figure 2.1 Drying beds at Niayes FS treatment plant (Strande et al, 2013)**

#### 2.1.2.2 Constructed wetland

Constructed wetland consists of a filter consisted of gravel, sand and soil, planted with emergent plants (i.e., bulrushes, reeds, and cattails). Raw FS is dewatered by the filter media and accumulated on the filter surface. The percolate (liquid fraction) is vertically drained through the filter media and collected at the bottom. Since early 1997, the constructed wetland system with cattail-planted was studied under different operating conditions at AIT (Figure 2.2). Process conditions of constructed wetland at maximum removal efficiency and minimum cattail wilting symptoms are: solids loading rate of 250 kg TS/m$^2$/year, percolate ponding of 6 days and sludge loading frequency of 1 time per week (Koottatep et al., 2001).

The advantages of constructed wetland over unplanted drying beds are that the roots and rhizome systems of the emergent plants generate a porous structure in the layers of accumulated solids, resulting in the dewatering capacity of the filter maintained for several years, lower removal frequency of accumulated solids, extended storage of the dewatered solids allows for biochemical stabilization, and operation costs considerably reduced. However, post-treatment of the percolate from constructed wetland will be required depending on local conditions and discharge regulations.



**Filter substrata**: 10-cm layer of fine sand, 15-cm layer of small gravel, and 40-cm layer of large gravel from top to bottom

**Figure 2.2 Pilot constructed wetland feed with FS at AIT (Koné and Peter, 2008)**

### 2.1.2.3 Composting

When FS and solid waste are available in sufficient quantity and quality for reusing as fertilizer in agriculture, composting becomes an interesting treatment option. Composting is the process that biodegradable wastes (organic materials) are biologically decomposed by microorganisms under controlled aerobic and thermophilic conditions. Temperatures in the piles can be reached to 55-60 °C which can kill all pathogens in FS and solid waste. The produced compost becomes a very good fertilizer and soil conditioner. In co-composting, two or more organic wastes are composted together. Organic wastes such as FS, animal manure, bark, food waste, municipal solid waste (MSW), sawdust, slaughterhouse waste, and wood chips can be used or subjected to co-composting (Strauss et al., 2003). Co-composting of the two materials such as FS and MSW is a most reasonable process due to they complement each other. FS has relatively high nitrogen and moisture contents, whereas MSW is relatively in high organic carbon contents with good bulking qualities (Strauss et al., 2003). FS can be co-composted with any organic wastes when composting process conditions such as mixing ratios, moisture content, thermophilic conditions, and frequency of turning are controlled.

### 2.1.2.4 Anaerobic Digestion

AD with biogas production has been widely applied for treating sludge and recovering energy. It may be suited for treating higher-strength FS which is emptied from unsewered public toilets with high frequencies and has not been degraded yet. Co-digestion of FS with MSW in landfill was studied by Valencia et al. (2009). The results indicate that the volatile solid (VS) removal efficiency of 60% and the increase of biogas production (0.60 $m^3$ biogas/kg $VS_{converted}$) are achieved. The advantages of co-digestion of FS with MSW in landfill are the safe and environmentally friendly disposals of FS and the overall performances of the landfill digester are improved due to increasing moisture retaining and providing a more acclimatized bacterial population. Although AD has been widely implemented, because of the relatively high investment cost and quite considerable of operating requirements, the number of the implementation of AD for FS treatment in developing countries is still relatively low.

**Table 2.1 Summary of Treatment Technologies**

| Technology | Valuable by-product | Advantage | Disadvantage |
|---|---|---|---|
| Drying bed | Bio-solid | 1. The bio-solid product that could be used as a soil conditioner in agriculture and co-composting with biodegradable solid waste<br>2. Moisture content of dried bio-solid is relatively low<br>3. Relatively good quality of percolate<br>4. Simple operation and maintenance, no skilled personnel required<br>5. Technology is reliable and well known | 1. Solids are not yet hygienically safe.<br>2. The percolate must be treated<br>3. Require larger area for the construction.<br>4. Manual labor is required to remove dried sludge or bio-solid from surface of beds<br>5. Applicable only during dry seasons and may needs a roof<br>6. Cause odor problems |
| Constructed wetland | Dewatered solid | 1. Dewatered solid can be used in agriculture without further treatment<br>2. Dewatering, stabilizing and hygiene are combined in a single treatment stage<br>3. Percolate quality compares favorably to other primary treatments | 1. Requires care for plant growth<br>2. Higher costs due to requires larger area |
| Composting | Compost or fertilizer | 1. Simple operation<br>2. Produce a good and pathogen free soil conditioner | 1. Proper aeration is required<br>2. Compost quality may be reduced by contaminants in FS or solid waste<br>3. Longer time is required to produce good quality compost product |
| Digestion | Biogas | 1. Production of combustible and generation of revenues<br>2. Safe and environmentally sound treatment of FS | 1. High initial investment cost<br>2. Operation requirements are quite considerable |

Source: HPCIDBC (2011)

## 2.2 Faecal Sludge Characteristics

FS is a sludge which comprises varying concentrations of settled faecal solids and other non-faecal matter accumulated in septic tanks, cesspools, pit latrines or other unsewer systems. Table 2.2 illustrates the characteristics of the different types of FS (public toilet and household sludge from septic tank and pit latrine) and sludge from wastewater treatment plant (WWTP). Concentrations of organic matters (as chemical oxygen demand (COD) and biochemical oxygen demand (BOD)), helminthes eggs, ammonium and TS measured in FS are normally greater values and higher variation than in wastewater and sludge produced in WWTP. Characteristics of FS vary greatly with the retention period, permeable of groundwater in septic tanks, temperature, septic tank type, performance of septic tanks, and degrees of biochemical stability through AD (Heinss et al., 1998; Ingallinella et al., 2002). FS in septic tanks is more stable bio-chemically and diluted form due to longer storage periods which result in variation of pollutant concentrations. FS characteristics also vary widely with the locality as shown in Table 2.3.

**Table 2.2 Characteristics of FS from OSS Systems and Sludge from WWTP**

| Parameters | Unit | Characteristics of FS and sludge (mean and range values) | | | |
|---|---|---|---|---|---|
| | | WWTP [a] | Public toilet [b, c] | Household (septic tank) [b, c] | Household (pit latrine) [d] |
| TS | mg/L | - | 30,000-52,500 | 12,000-35,000 | 19-71 [e] |
| TVS | % of TS | - | 65-68 | 45-73 | 6-62 |
| COD | mg/L | 50-2500 | 20,000-50,000 | 1,200-10,000 | 46-199 [f] |
| $BOD_5$ | mg/L | 20-229 | 7,600 | 840-2,600 | - |
| Total nitrogen (TN) | mg/L | 32-250 | - | 190-300 | - |
| $NH_4$-N | mg/L | 2-168 | 2,000-5,000 | 150-1,200 | - |
| Total phosphorus (TP) | mg P/L | 9-63 | 450 | 150 | - |
| Faecal coliforms | cfu/ 100 mL | $6.3 \times 10^4$ – $6.6 \times 10^5$ | $1 \times 10^5$ | $1 \times 10^5$ | - |
| Helminth eggs | | 300-2,000 | 20,000-60,000 | 4,000-5,700 | - |
| Moisture content | %wt | - | 95-97 | 96-98 | 29-81 |

[a] NWSC (2008)
[b] Koné and Strauss (2004)
[c] Heinss et al. (1998)
[d] Buckley et al. (2008)
[e] Unit: %wt of wet sample
[f] Unit: mg/g wet sample

**Table 2.3 Characteristics of FS in different locations**

| Locations | COD (g/L) | BOD/COD | TS (g/L) | TVS (% of TS) |
|---|---|---|---|---|
| Bangkok [a]<br>(256 samples) | 15.7 | 1:7 | 15.4 | 69 |
| Manila [b] | 37 | 1:10 | 72 | 76 |
| Accra/Ghana [c]<br>(68 samples) | 230 | - | 12 | 60 |
| Kathmandu [d] | - | - | 27 | 65 |

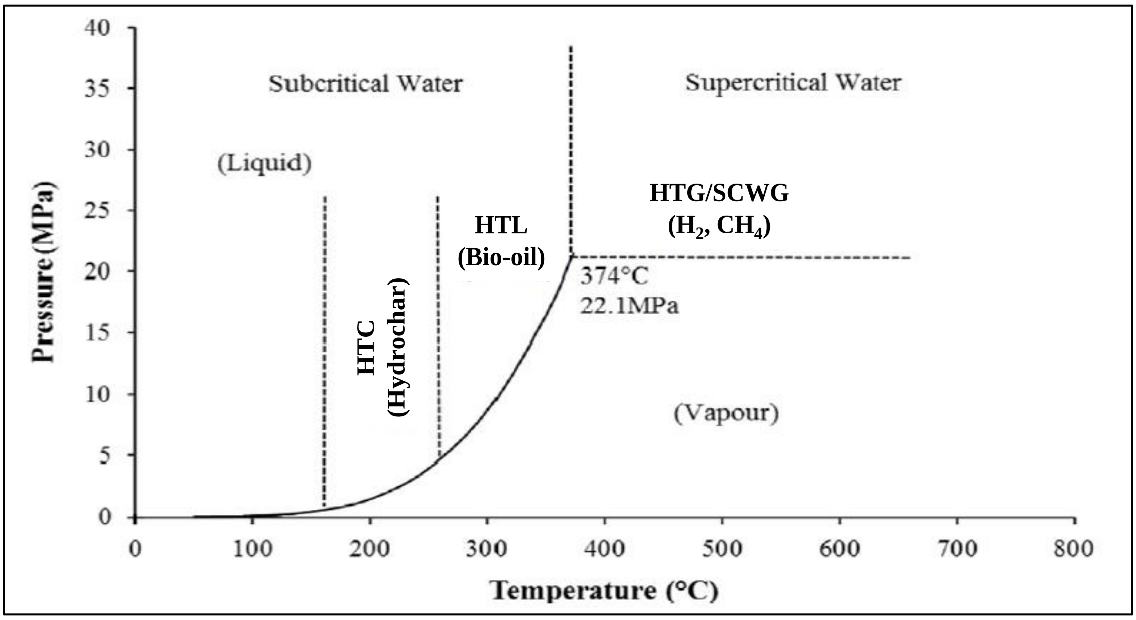
[a] Based on AIT (1997-2003)
[b] Based on University of Philippines (1997)
[c] Based on Achimota Faecal Sludge Treatment Plant, Accra, Ghana (1998)
[d] Based on analysis results of Kathmandu
Source: Sherpa (2005)

## 2.3 Hydrothermal Carbonization

HTC can be defined as a carbonization of biomass in water under temperature and pressure at the subcritical water (Figure 2.3), also called wet pyrolysis. In the HTC process, the solid material (biomass) is completely immersed in water during the operation in the closed systems with temperatures of 180-250 °C and corresponding pressures approximately 20-60 bar (2-6 Mpa) for reaction times of 5-240 min (Kambo and Dutta, 2015). At temperatures above 250 °C, the hydrothermal processes are further classified into hydrothermal liquefaction (HTL) and hydrothermal gasification or supercritical water gasification (HTG/SCWG). The HTC of biomass results in the 3 main products, including carbonaceous solids, commonly called “Hydrochar”, liquid (bio-oil) mixed with water, and small amount of gases (mainly $CO_2$) (Kambo and Dutta, 2015). The chemical structure and energy content of the hydrochar are similar to natural coal, which make it suitable for use as a solid fuel in conventional combustion processes. Moreover, hydrochar produced from HTC have already found in many applications such as, energy storage, soil amendment, absorbent in water purification, catalyst, and $CO_2$ sequestration (Titirici and Antonietti, 2010).

### 2.3.1 Feedstock

In theory, any kind of organic matter and biomass can be carbonized in the hydrothermal conditions. Feedstock such as cellulose, wood, microalgae, MSW, food waste, sewage sludge, and agriculture residues have been successfully treated by an HTC process (Berge et al., 2011; He et al., 2013; Heilmann et al., 2010; Li et al., 2013; Lu et al., 2012; Oliveira et al., 2013; Sevilla and Fuertes, 2009). Hydrochar production from different biomass feedstock and HTC process conditions showed in Table 2.4. Characteristics of biomass feedstock such as chemical composition, moisture content, volatile matter (VM), fixed carbon (FC), noncombustible matter (ash) and energy content significantly affect products (hydrochar, liquid and gas phases) distribution, product characteristics, conversion efficiencies and process energetics.



Note; HTC: Hydrothermal carbonization
HTL: Hydrothermal liquefaction
HTG/SCWG: Hydrothermal gasification or supercritical water gasification

**Figure 2.3 Pressure-temperature phase charge diagram of water and classification of hydrothermal process of biomass (Kambo and Dutta, 2015)**

The influence of different feedstock on the particle morphology, chemical composition and structural of hydrochar is reported by Titirici et al. (2008). They compared the characteristics of hydrochar produced from HTC of diverse biomass (xylose, glucose, sucrose, maltose, amylopectin and starch) and biomass derivatives (furfural and HMF), as shown in Figure 2.4. Their results showed that significant structural and morphological difference in the produced hydrochar from pentoses and hexoses can be observed, but all produced hydrochar from sugar in hexose form showed astonishing similarities, suggesting that the difference of sugar structures is not effect to carbonization mechanisms.

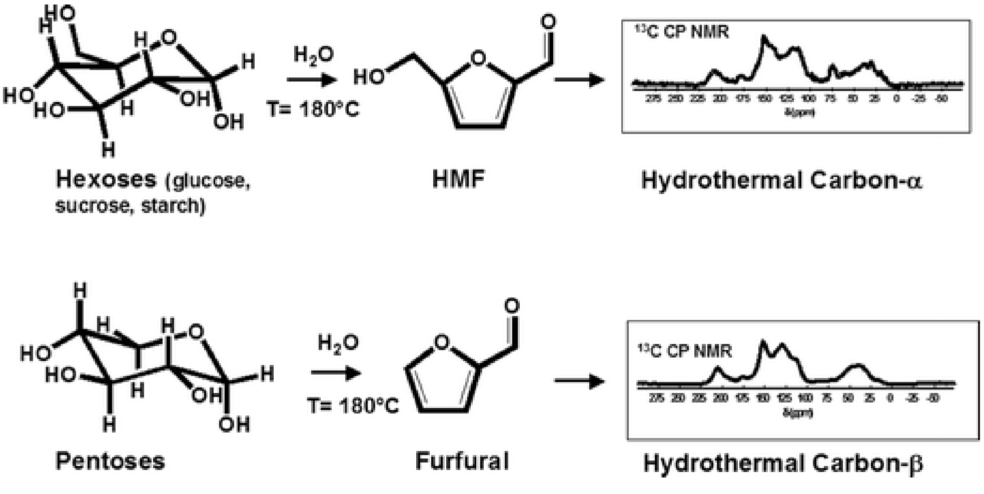


**Figure 2.4 HTC of sugar in hexoses and pentoses forms (Titirici et al., 2008)**

**Table 2.4 Hydrochar Production from Different Feedstock and HTC Process Conditions**

| Feedstock information | | | | | | | | HTC process condition | | | Hydrochar | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type | Ultimate analysis (% wt) | | | Proximate analysis (% wt) | | | Energy content (MJ/kg) | Moisture content (% wt) | Temperature (°C) | Reaction time (h) | Yield (%) | Energy content (MJ/kg) | |
| | C | H | O | VM | FC | Ash | | | | | | | |
| Sewage sludge | 36.7 | 6.4 | 35.9 | 70.0 | 1.4 | 28.6 | 14.7 | 85 | 200 | 4-12 | 60 | 14.4-15.0 | He et al. (2013) |
| Water Hyacinth | 29.8 | 5.4 | 24.7 | 49.9 | 6.3 | 38.1 | 13.8 | 94 | 240 | 0.5 – 24 | - | 16.8-20.6 | Gao et al. (2013) |
| Sewage Sludge | 46.9 | 5.8 | 50.9 | 70.3 | 5.3 | 16.0 | 18.0 | 96 | 140 – 200 | 4 | 60 – 74 | 21.4-23.1 | Danso-Boateng et al. (2013) |
| Palm empty fruit bunches | 55.4 | 6.7 | 43.7 | 82.2 | 10.4 | 3.0 | 19.5 | 90 | 150 – 350 | 0.3 | 49 – 76 | 20.0-27.2 | Parshetti et al. (2013) |
| Corn silage | 46.9 | 6.2 | 41.9 | 96.2 | - | - | 19.6 | 85 | 220 | 4 | 53 | 26.6 | Oliveira et al. (2013) |
| Poultry manure | 46.8 | 6.3 | 30.1 | 84.4 | - | - | 18.8 | 85 | 220 | 4 | 53 | 24.3 | Oliveira et al. (2013) |
| Bedding material | 40.7 | 5.1 | 30.5 | 78.2 | - | - | 16.9 | 85 | 220 | 4 | 31 | 20.9 | Oliveira et al. (2013) |
| Separated digestate | 45.1 | 5.5 | 36.7 | 88.7 | - | - | 18.4 | 85 | 220 | 4 | 59 | 23.5 | Oliveira et al. (2013) |
| Dry straw | 46.8 | 6.0 | 42.0 | 95.3 | - | - | 18.7 | 85 | 220 | 4 | 50 | 26.3 | Oliveira et al. (2013) |
| Cabbage residues | 45.8 | 5.4 | 35.2 | 90.0 | - | - | 18.0 | 85 | 220 | 4 | 34 | 25.3 | Oliveira et al. (2013) |
| Dough residues | 44.1 | 6.5 | 44.4 | 97.1 | - | - | 17.8 | 85 | 220 | 4 | 44 | 28.3 | Oliveira et al. (2013) |

**Table 2.4 Hydrochar Production from Different Feedstock and HTC Process Conditions (cont.)**

| Feedstock information | | | | | | | | HTC process condition | | | Hydrochar | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type | Ultimate analysis (% wt) | | | Proximate analysis (% wt) | | | Energy content (MJ/kg) | Moisture content (% wt) | Temperature (ºC) | Reaction time (h) | Yield (%) | Energy content (MJ/kg) | |
| | C | H | O | VM | FC | Ash | | | | | | | |
| Forest wood chips | 46.2 | 0.6 | 37.6 | 90.1 | - | - | 18.4 | 85 | 220 | 4 | 61 | 21.5 | Oliveira et al. (2013) |
| Landscape wood chips | 49.6 | 5.8 | 39.4 | 95.2 | - | - | 19.4 | 85 | 220 | 4 | 46 | 24.3 | Oliveira et al. (2013) |
| Paper | 36.0 | 5.0 | 48.1 | 79.6 | 9.6 | 10.9 | 14.0 | 80 | 250 | 20 | 29 | 23.9 | Berge et al. (2011) |
| Food | 42.5 | 5.8 | 40.8 | 77.6 | 14.8 | 7.5 | 18.1 | 80 | 250 | 20 | 44 | 29.1 | Berge et al. (2011) |
| Mixed MSW | 28.5 | 3.8 | 38.7 | 62.0 | 9.6 | 28.4 | 16.5 | 80 | 250 | 20 | 63 | 20.0 | Berge et al. (2011) |
| AD waste | 32.6 | 4.8 | 20.3 | 55.9 | 8.2 | 35.9 | 15.5 | 80 | 250 | 20 | 47 | 13.7 | Berge et al. (2011) |
| Corn stalk | 46.8 | 6.3 | 40.7 | - | - | - | 17.5 | 90 | 250 | 4 | 35 | 29.2 | Xiao et al. (2012) |
| Forest waste | 48.0 | 6.6 | 43.4 | - | - | - | 17.9 | 90 | 250 | 4 | 38 | 28.4 | Xiao et al. (2012) |
| Coconut fiber | 47.8 | 5.6 | 45.5 | 80.9 | 11.0 | 8.1 | 18.4 | 90 | 220-375 | 0.5 | 56-77 | 24.7-30.6 | Liu et al. (2013b) |
| Eucalyptus leaves | 47.0 | 5.2 | 44.8 | 79.2 | 10.3 | 10.5 | 18.9 | 90 | 220-375 | 0.5 | 43-87 | 25.0-29.0 | Liu et al. (2013b) |
| Walnut shell | - | - | - | 71.8 | 15.9 | 1.3 | 19.6 | 95 | 230 | 20 | 36 | 27.1 | Roman et al. (2012) |
| Sunflower stem | - | - | - | 82.3 | 3.6 | 1.5 | 16.4 | 95 | 230 | 20 | 29 | 28.5 | Roman et al. (2012) |

### 2.3.2 Mechanisms of HTC

According to previous reports (Falco et al., 2011; Funke and Ziegler, 2010; He et al., 2013; Sevilla and Fuertes, 2009), the hydrochar can be formed via two major conversion pathways:

1. Conversion of aqueous dispersion biomass materials which is dominated by reaction mechanisms, including hydrolysis, dehydration, fragmentation, decarboxylation, polymerization, and aromatization.
2. Solid–solid conversion of the original biomass materials which is dominated by reaction mechanisms, including dehydration, devolatilization, intramolecular condensation and decarboxylation.

Based on the abovementioned pathways, hydrochar formation during HTC of cellulose (represent of organic materials) is proposed in Figure 2.5.

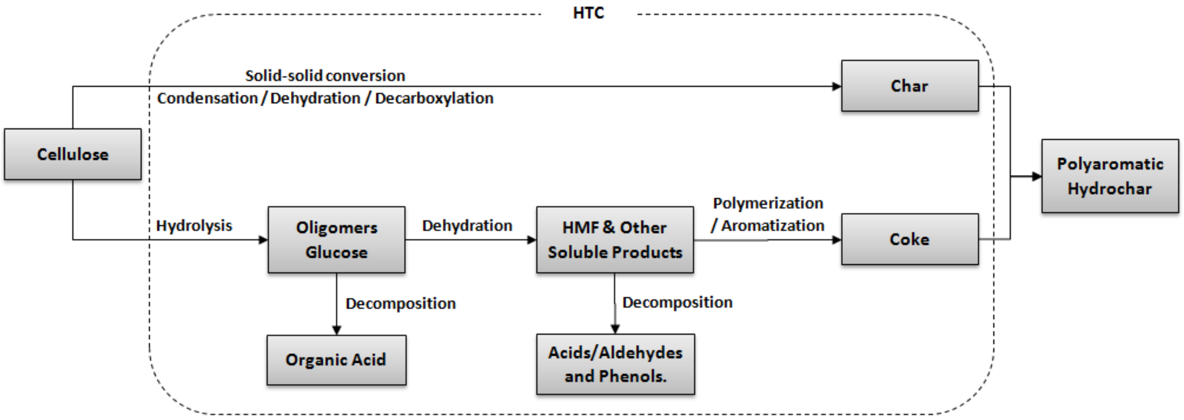


Figure 2.5 Schematic hydrochar formation pathways during HTC of cellulose

According to Sevilla and Fuertes (2009), the hydrochar can be formed by the following steps:

***Hydrolysis***: When cellulose is heated up in water, the initial reaction taking place. The cellulose chains hydrolyze giving different oligomers (i.e. oligosaccharides) and glucose or fructose. The decomposition of the glucose or fructose produces organic acids such as acetic, lactic, propenoic, levulinic and formic acids, as shown in Figure 2.6.

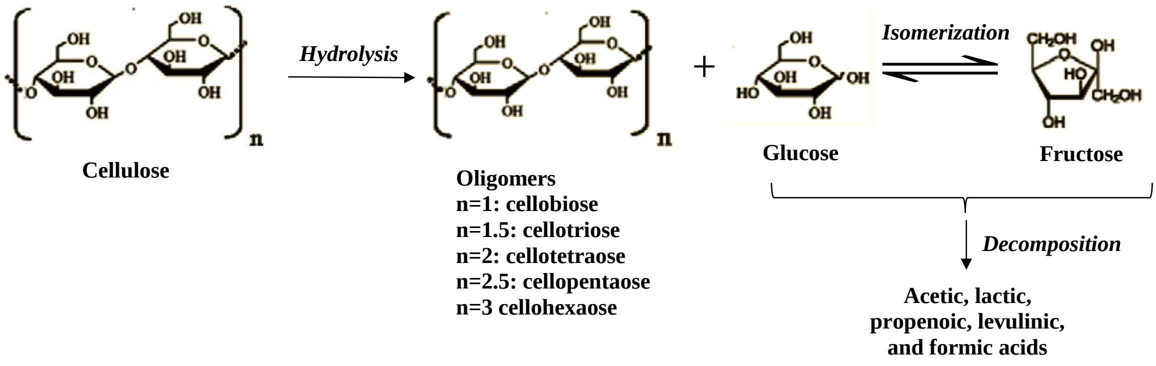


Figure 2.6 Hydrolysis of cellulose in HTC (Sevilla and Fuertes, 2009)

***Dehydration and fragmentation**:* The oligomers further hydrolyze into their monomers (i.e. glucose or fructose). Dehydration and fragmentation (C-C bond breaking and ring opening) of these monomers generate the various soluble products such as furfural-like compounds (HMF, 5-methylfurfural, furfural), 1,6-anhydroglucose, erythrose, 1,2,4-benzenetriol and aldehydes, as shown in Figure 2.7. The decomposition of these soluble products also produces organic acids, aldehyde and phenol.

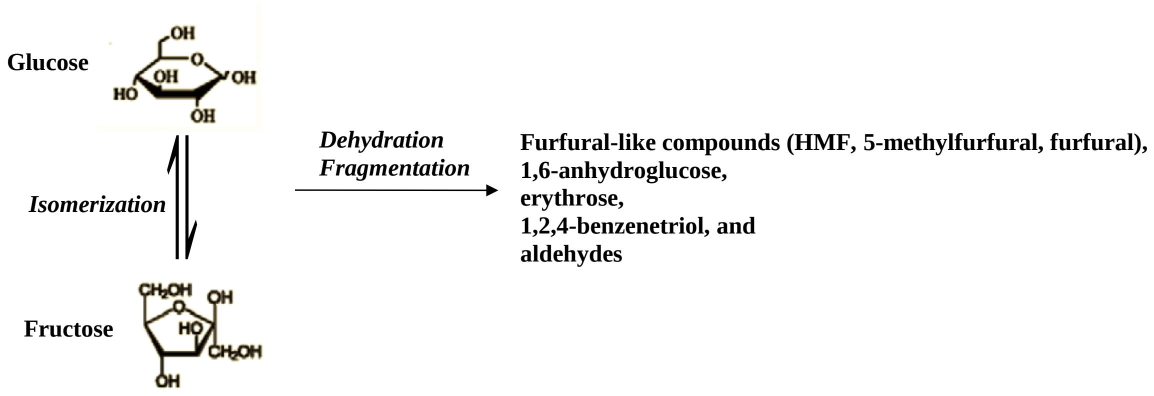


**Figure 2.7 Dehydration and fragmentation of glucose or fructose in HTC (Sevilla and Fuertes, 2009)**

***Polymerization and aromatization**:* As shown in Figure 2.8, the subsequent polymerization reaction leads to the generation of soluble polymers. This reaction is induced by intermolecular dehydration or aldol condensation. Simultaneous, aromatization of the soluble polymers takes place. The dehydration and decomposition of the oligosaccharides or monosaccharide generated in the hydrolysis of cellulose may produce the aromatized molecules which could be condensed to be aromatic clusters.

***Particle growth:*** When the aromatic clusters concentration reaches the critical limiting supersaturation, a burst nucleation and diffusional growth take place. The produced nuclei grow outwards by diffusion of the chemical species present in the solution.

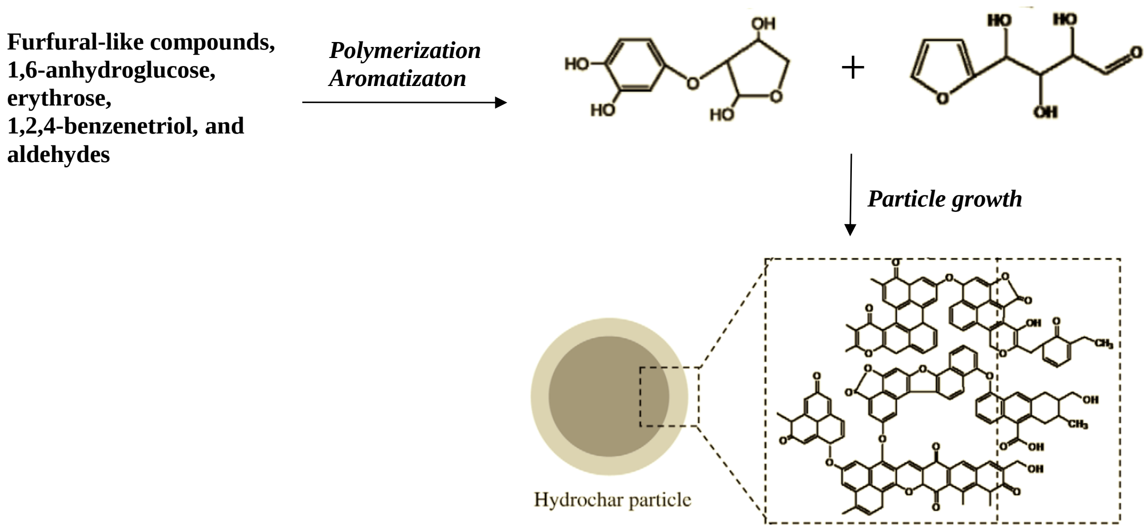


**Figure 2.8 Polymerization, aromatization, and particle growth in HTC (Sevilla and Fuertes, 2009)**

### 2.3.3 Influence of process parameters

As above mentioned in the feedstock of HTC, characteristics of feedstock determine the hydrochar properties. In addition, hydrochar production also depends on the HTC process parameters such as moisture content of feedstock, operating temperature, reaction time, pressure, solid load, and pH value.

#### 2.3.3.1 Moisture content

It has been reported in previous experiments that carbonization of biomass is accelerated by water, biomass above the surface of water does not carbonize, and biomass is possible carbonized in oil as well as in water (Funke and Ziegler, 2010). The presence of sufficient water is an important part associated with the HTC process (Lu et al., 2012). The roles of water in the HTC process are:

1. Temperature peaks during HTC process which may result from exothermal reactions can be avoided because water is a good heat transfer and storage medium (Siskin and Katritzky, 2001).
2. Distribution of substance and transportation of fragments out of the matrix of the feedstock are impacted by the amount of water (as a solvent), which may become a rate-determining step (Behar et al., 2003).
3. At high temperatures, solvent properties of water are significantly enhanced. The solubility of dissolved organic and inorganic components is increased.
4. The heated water has been shown to have an autocatalytic effect on carbonization, hydrolysis reaction, ionic condensation, and bond cleavage (Funke and Ziegler, 2010; Siskin and Katritzky, 2001).

#### 2.3.3.2 Temperature

Temperature has a decisive effect on the hydrolysis of biomass, for examples, hemicellulose is almost completely hydrolyzed at the temperature of 180-200 °C, lignin 180-220 °C, and cellulose approximately greater than 220 °C (Bobleter, 1994). As above mentioned reactions in the HTC process, the temperatures required for activating the reactions are different. The hydrolysis can be occurred in the temperature range of 100-175 °C (Abelleira et al., 2012), dehydration and polymerization require temperatures greater than 160 °C, and solid-solid conversion requires relatively high temperatures in the range of 200-280 °C (Falco et al., 2011). Additionally, the temperature also indirectly affects HTC by changing water properties as already described. The viscosity of water is changed which results in an easier penetration of porous media of biomass and, consequently, enhances the decomposition of biomass (Funke and Ziegler, 2010).

Effects of temperature on energy content, hydrochar yield and carbon distribution are reported in the literatures. The increasing temperature results in increased energy content of the produced hydrochar and correlated well with the carbon content in the produced hydrochar (Danso-Boateng et al., 2013). Fraction of carbon transferred to the hydrochar and liquid products decreases with increasing temperature, thus higher hydrochar production yields at lower operating temperatures (Lu et al., 2013). Effect of temperature on the hydrochar yield is shown in Figure 2.9. From the HTC processes of coconut fiber and eucalyptus leaves at various temperatures, the similar trends of hydrochar yield are observed. The hydrochar yield decreased rapidly (90 to 45%) with increasing temperatures (150 to 300

°C), followed by a further gradual decrease to about 30% at a temperature of 350 °C (Liu et al., 2013b).

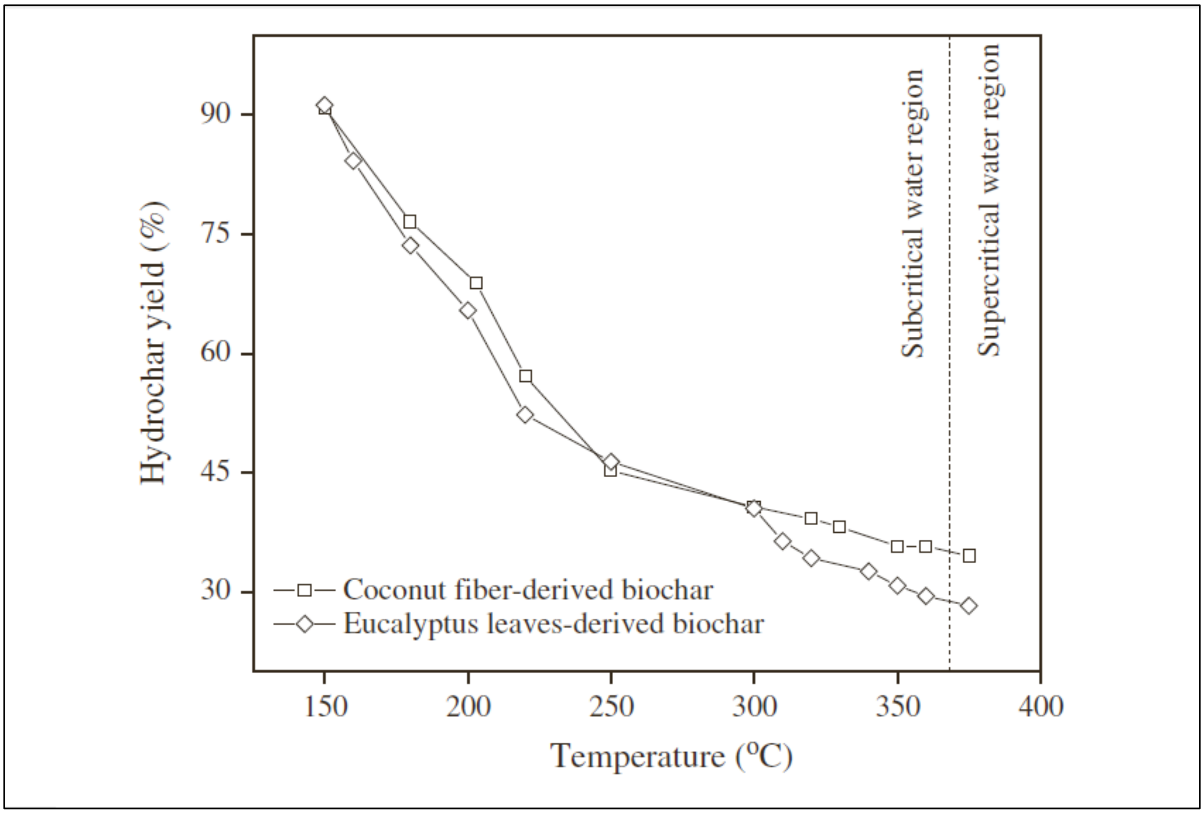


**Figure 2.9 Hydrochar yields of HTC of coconut fiber and eucalyptus leaves at various temperatures (Liu et al., 2013b)**

### 2.3.3.3 Reaction time

Reaction time of HTC process can be range from some minutes up to several hours. The effects of reaction time on carbon distribution, energy content, hydrochar formation, and chemical and structural properties of the hydrochar are previously reported in the literatures. The carbon distribution changes with reaction time following two apparent periods (at temperatures of 225, 250, and 275 °C). The first period (0 to 8 h) is characterized by significant changes of carbon content in the HTC products. During this period, a rapid decrease of carbon content in solid-phase (hydrochar) is observed. The second period (exceeding 8 h) is characterized by slower and less significant changes of carbon content in the HTC products (Lu et al., 2013). With an increase in reaction time, energy content of the produced hydrochar was increased. In addition, longer reaction time increases the hydrochar formation where lignocellulosic biomass is hydrolyzed and underwent dehydration and polymerization processes, resulting in rich carbon microspheres (Gao et al., 2013).

#### 2.3.3.4 Solid content

The initial solid content of feedstock is also considered to be a significant factor for the HTC of biomass. The effects of solid content on carbon distribution, energy content and hydrochar yield are previously investigated. Results indicate that, during HTC operation, the mass of carbon in the biomass transfer to the liquid phase, particularly at low solid content. At the solid content of 5 %wt, the carbon content in liquid phase is significantly different from that obtained from the experiments conducted at the solid content of 20 and 32 %wt at all reaction times (Li et al., 2013). HTC using feedstock with high solid contents (25 %wt) produces the hydrochar yield greater than using feedstock with low solid contents (5% wt). In addition, energy content of the produced hydrochar could be increased by increasing solid content (Danso-Boateng et al., 2013).

#### 2.3.3.5 pH value

During the HTC operation, decreasing of pH is observed, which is the result from an organic acids such as acetic, formic, lactic and levulinic acids are formed (Sevilla and Fuertes, 2009). Applications of acids and bases additions to adjust pH in the HTC process have been studied and the significant effects on the product characteristics and reaction rate have been observed. Liang et al. (2011) investigated the effect of pH, at a different starting pH value of feedstock, on hydrochar yield in the HTC of starch. The results indicate that, at pH of 1, the strong acid accelerates the hydrolysis reaction in the early stage of HTC. The polysaccharide (e.g., starch and cellulose) is hydrolyzed to low molecule monomers and hastily formed microsphere. On the other side, the strong acid inhibits the polymerization and carbonization of the produced monomers, and also the produced HMF is more decomposed into levulinic and formic acid (Jeong et at., 2012). The hydrochar yields of about 25 % reach maximum very quickly and keep constant. At pH of 3, 5 and 7, the hydrochar yields increased with reaction time and, after 3 h, reached their maximum yields which are very similar (43.57%, 44.6%, and 43.69% for pH of 3, 5, and 7, respectively). Therefore, it can conclude that the suitable pH value of feedstock for the HTC process ranges from 3 to 7.

### 2.3.4 HTC compared to other thermal conversion processes

Thermal conversion process is the typical process for producing chars (biochar and charcoal). The various thermal conversion processes differ in type of feedstock, heating rate, operating temperature, reaction time, and the product distribution (solid, liquid and gas phases). According to the operating conditions and the product yields, the thermal conversion process can be classified and compared in Table 2.5 and discussed in the following section.

#### 2.3.4.1 Pyrolysis

Pyrolysis is a thermochemical conversion of biomass at elevated temperature (400-500 °C) in the absence of oxygen. It is the main process for char production (charcoal and tar-like substances) with significant yields, which has been used by mankind for millennia. Besides char, it can be produced the other products such as bio-oil and gas (CO, $CO_2$, $CH_4$ and $H_2$) (Kambo and Dutta, 2015). For slow and intermediate pyrolysis processes, the moderate heating rates and long reaction times are employed to produce gases (30-35 %wt), liquids (30-50 %wt) and char (20-35 %wt) (Antal and Grønli, 2003).

Fast pyrolysis involves fast heating of the feedstock and rapid cooling of the generated vapour. In the fast pyrolysis process, a liquid is the desired product which can be used as a primer for fuels. The liquid products yield is about 75 %, which is higher than other products (char and gas product yields are 12 and 13 %, respectively) (Bridgwater and Peacocke, 2000). In addition, the fast pyrolysis process is required special reactors for operating at high heating rates and good mixing conditions.

#### 2.3.4.2 Gasification

Gasification is the partial combustion process where feedstock is oxidized in the atmosphere using the addition of oxygen, air, steam or carbon dioxide or a mixture thereof at a high temperature (500-800 °C) for short reaction time (10-20 sec) (Higman and Burgt, 2003; Libra et al., 2011). The gas products of gasification process are mainly $H_2$, CO, $CO_2$ and $CH_4$. The mixture of these gases can be used directly as a fuel gas in the catalytic conversion processes to produce syngas, methanol, and many more products. Generally, gasification produces maximum gas with yields of approximately 85% in a continuous mode; only a small amount of char (10%) and liquid product (5%) are produced. Although large amounts of input biomass could produce char at the lower yield, the produced char could be recovered at acceptable costs (Libra et al., 2011).

#### 2.3.4.3 Thermal conversion process comparison

Table 2.5 compared the data of operation, feedstock and product distribution associated with HTC process and other thermal conversion processes such as pyrolysis and gasification. The differences of HTC from pyrolysis and gasification processes are that the HTC process occurs at comparative lower temperatures and relative longer reaction times, and requires a wet feedstock (or addition of water). During the HTC process, the feedstock is converted into the products by conversion reactions similar to those in pyrolysis. However, the biomass is initially degraded in the hydrothermal condition by a hydrolysis reaction which is a low activation energy reaction compared to the other pyrolytic decomposition reactions (Libra et al., 2011). The advantages of HTC over pyrolysis and gasification processes are that wet biomass feedstock can be processed without dewatering and drying. While pyrolysis and gasification processes require the dried feedstock. Therefore, the energy required for drying wet feedstock can be significant, depending on moisture content of the biomass feedstock. In addition, HTC produces higher hydrochar yields (50-80%) and more soluble organic compounds presented in liquid products. Hydrochar characteristics (e.g., energy content, elemental composition, structure, and functionality) can be varied by changing the HTC process conditions (e.g., temperature and reaction time), feedstock type, and moisture content, as well as by using additives (Lu et al., 2012). Gas products from HTC process, particularly carbon dioxide, are small in comparison to other thermal conversion processes.

**Table 2.5 Comparison of Operating Conditions and Product Distribution for Thermal Conversion Processes**

| Process | Operation | | Feed stock | Product distribution | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Char | | Liquid | | Gas | |
| | Temp (°C) | Time | | Dist. (%wt.) | Energy (MJ/kg) | Dist. (%wt.) | Energy (MJ/kg) | Dist. (%wt.) | Energy (MJ/m$^3$) |
| Pyrolysis: slow | 400 | h – week | Dry | 35 | 11 -35 | 30 | 10 -35 | 35 | 5 -30 |
| Pyrolysis: intermediate | 500 | 10-20 sec | Dry | 20 | 11 -35 | 50 | 10 -35 | 30 | 5 -30 |
| Pyrolysis: fast | 500 | 1 sec | Dry | 12 | 11 -35 | 75 | 10 -35 | 13 | 5 -30 |
| Gasification | 500-800 | 10 -20 sec | Dry | 10 | Not available | 5 | Not available | 85 | 2 -20 |
| HTC | 180 -250 | 1 -12 h | Wet | 50 -80 | 18 -36 | 5 -20 | Not available | 2 -5 | Not available |

Source: Libra et al. (2011) and Lu et al. (2012)

#### 2.3.4.4 Energetic comparison

Energetic considerations, as some guidance, can be used to provide information in the technology selection among HTC, pyrolysis, and gasification for processing biomass. From a thermodynamic point of view, moisture content in the biomass feedstock makes the uneconomical uses of pyrolysis and gasification. Pyrolysis process could be operated economically to convert the biomass feedstock with moisture content below approximately 50–70%. By contrast, HTC typically operates with the feedstock at the moisture content of 75–90% or even higher. The energy required for the HTC process is substantially lower than for the pyrolysis process of such feedstock. HTC of dry biomass with moisture content less than 40%, is unlikely to have any energetic advantages over pyrolysis (Libra et al., 2011). In the HTC case, energy consumptions related to the transport of wet biomass feedstock and post-processing of the produced hydrochar such as filtration and drying process have to be considered. An energetic advantage of the HTC process can be expected either when the produced hydrochar can be used without pre-drying or when its dewatering property is improved compared to the initial feedstock.

## 2.4 HTC Products

There are various products involved in the HTC reaction pathways. The product distribution, as illustrated in Figure 2.10, mainly depends on process conditions and feedstock types. By HTC process, initial biomass can be converted into 3 phases of products including solid, liquid, and gas phases. The HTC product characteristics are explained in the following sections.

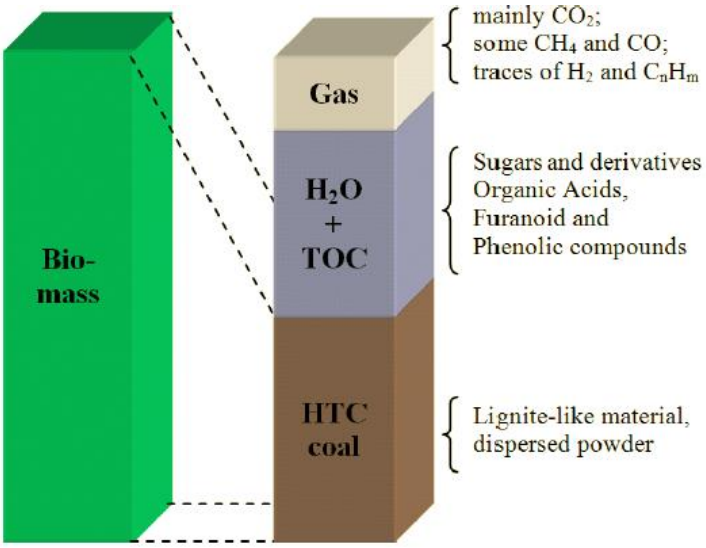


**Figure 2.10 Product distribution of HTC (Funke and Ziegler, 2010)**

### 2.4.1 Hydrochar

#### 2.4.1.1 Characteristics of hydrochar

Energy content, elemental composition and surface morphology of the produced hydrochar have been intensively characterized. Several analysis techniques (e.g. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), elemental analyzer, and calorimeter) and theoretical model have been used to accomplish such characteristics.

***Energy content***

Figure 2.11 shows the low gross calorific values (LGC) or energy contents for hydrochar and some natural fuels. Hachured bars present the hydrochar samples produced from the HTC of cellulose and pine sawdust (Guiotoku et al., 2009). It can be seen that energy contents of the produced hydrochar are comparable to ethanol, coal (fossil fuel), and charcoal. Moreover, similar results of the energy contents of the hydrochar produced from other feedstocks (in the range 20-30 MJ/kg) are shown in Table 2.4. However, energy contents of the gasoline and diesel oil (petroleum-based fuels) are still higher than the hydrochar.

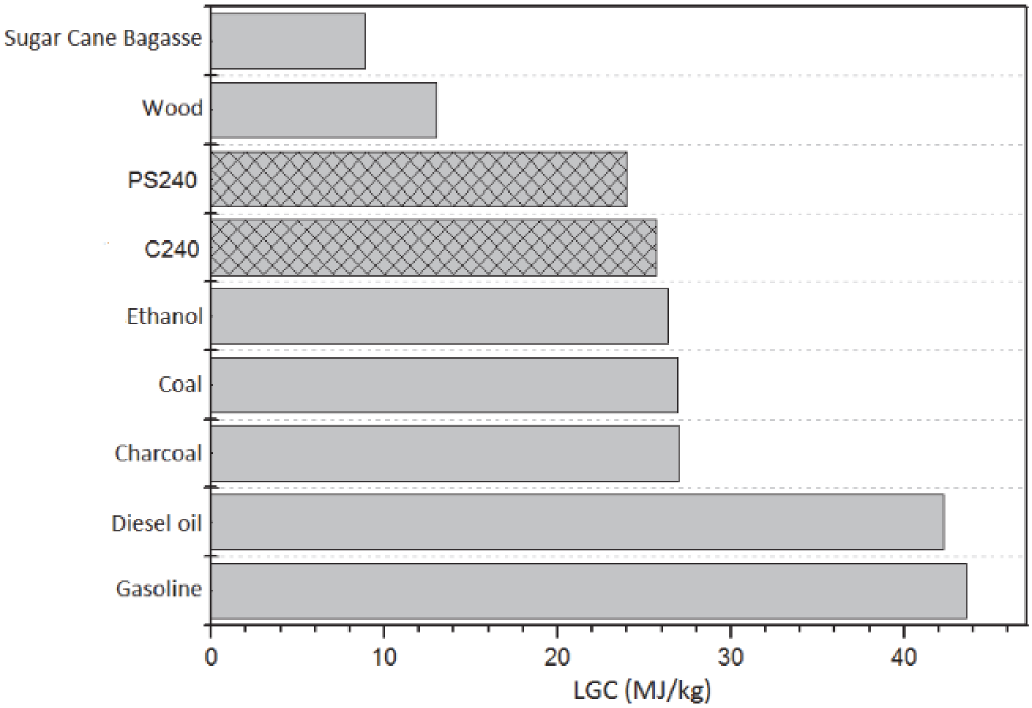


**Figure 2.11 Energy contents of solid and liquid fuels and hydrochars (PS240: pine sawdust and C240: cellulose) (Guiotoku et al., 2011)**

Feedstock such as cellulose, wood, microalgae, MSW, food waste, sewage sludge, and agriculture residues have been successfully treated by HTC process (Berge et al., 2011; He et al., 2013; Heilmann et al., 2010; Li et al., 2013; Lu et al., 2012; Oliveira et al., 2013; Sevilla and Fuertes, 2009), most of which could obtain the relatively low energy content of the produced hydrochar. Few of researchers studied on the improvement of energy content of the hydrochar. Lynam et al. (2011 and 2012) reported about 30% increase in energy contents of the produced hydrochar from HTC of lignocellulosic biomass with the additions of acetic acid and salt catalysts (i.e., calcium lactate, calcium chloride and lithium chloride). On the other hand, using zeolites (Jadhav et al., 2012; Moreau et al., 1996; Ordomsky et al., 2012; Shimizu et al., 2009) and borax (Titirici, 2013) as a catalyst in dehydration reaction of glucose or fructose could produce HMF, an intermediate product, at the yield greater than 70%. In addition, the study of Oliveira et al. (2013) found that adding easily-hydrolyzed carbohydrate biomass such as dough residues and corn silage into feedstock of the HTC process resulted in about 15% increase in energy content of the produced hydrochar.

### *Elemental composition*

The main factors influencing the produced hydrochar composition include the operating temperature, reaction time are nature of the feedstock. Elemental composition of the hydrochar produced from different process conditions and biomass feedstock is compared in Table 2.6. It can be implied that the carbon content increased from 44.44% in the cellulose feedstock to 71.66% in the produced hydrochar (Sevilla and Fuertes, 2009). The similar results are also obtained from other feedstocks.

**Table 2.6 Elemental Composition of Produced Hydrochar from Different Biomass Feedstock and HTC Process Conditions**

| Feedstock | Process conditions | | Elemental composition | | | | O/C (atomic) | H/C (atomic) |
|---|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (h) | C (wt%) | H (wt%) | O (wt%) | N (wt%) | | |
| Cellulose[*,a] | - | - | 44.44 | 6.17 | 49.38 | - | 0.833 | 1.666 |
| Cellulose [a] | 250 | 4 | 71.66 | 4.55 | 23.79 | - | 0.249 | 0.762 |
| Corn stalk [b] | 250 | 4 | 71.36 | 5.60 | 16.27 | 2.00 | 0.171 | 0.935 |
| Sewage sludge [c] | 200 | 4 | 46.17 | 5.81 | 49.39 | 1.88 | 0.80 | 1.51 |
| MSW [d] | 250 | 20 | 33.50 | 2.70 | 14.20 | 0.63 | 0.32 | 0.97 |
| Coconut fiber [e] | 220 | 0.5 | 62.47 | 5.28 | 31.09 | 0.90 | 0.37 | 1.01 |
| Micro algae [f] | 203 | 2 | 72.7 | 9.7 | - | 7.3 | - | 1.60 |

*Initial cellulose feedstock prior to HTC

[a] Sevilla and Fuertes (2009)

[b] Xiao et al. (2012)

[c] Danso-Boateng et al. (2013)

[d] Berge et al. (2011)

[e] Liu et al. (2013b)

[f] Heilmann et al. (2010)

During the HTC process, the dehydration and decarboxylation reactions cause a decrease in the H/C and O/C atomic ratios (Funke and Ziegler, 2010). For comparison, H/C and O/C atomic ratios of four natural coals (i.e., lignite, sub-bituminous, bituminous and anthracite) can be illustrated by the Van Krevelen diagram as in Figure 2.12. The H/C and O/C atomic ratios of the produced hydrochars are approached to the area of lignite, which are generally 0.8-1.3 and 0.2-0.38, respectively (Park and Jang, 2011). In this regard, the coal characteristics of the produced hydrochar are comparable to lignite. Thus, the hydrochar could be used as a solid fuel in the typical combustion process.

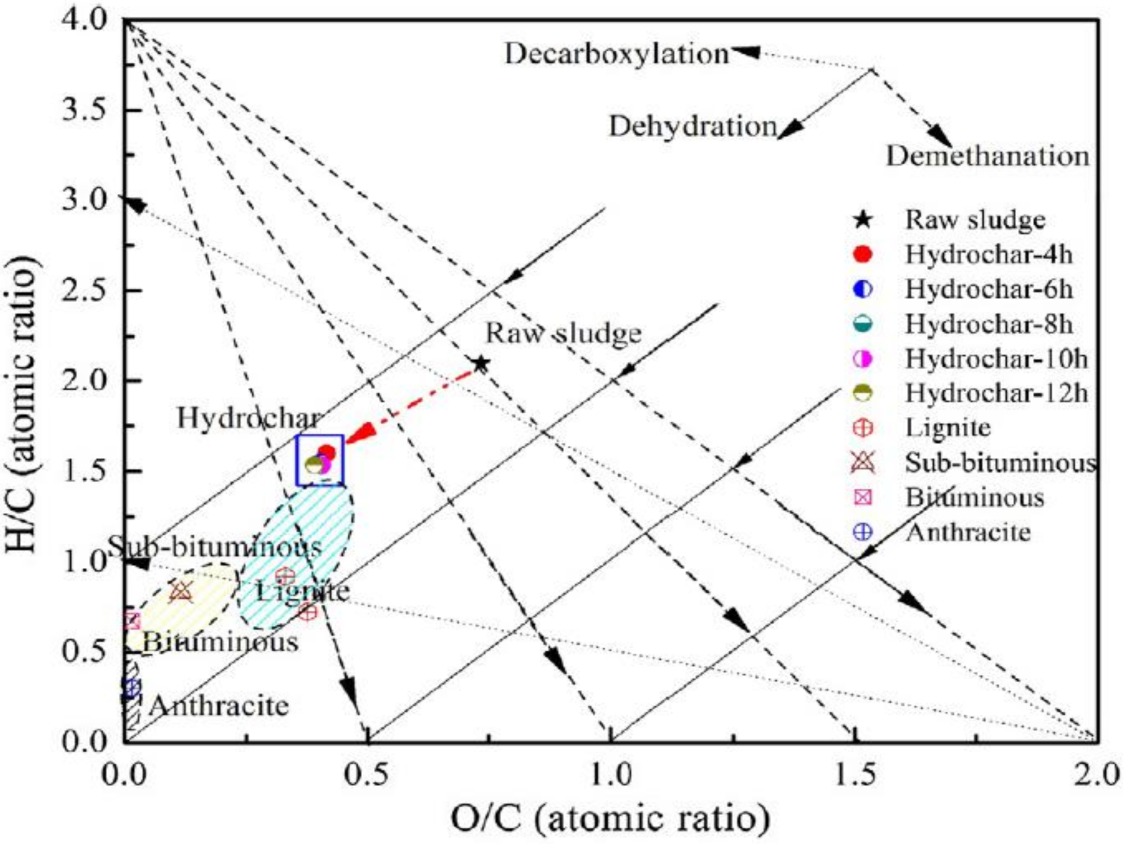


**Figure 2.12 Van Krevelen diagram of raw sludge, produced hydrochars at various times and four natural coals, i.e., lignite, sub-bituminous, bituminous, and anthracite (He et al., 2013)**

### *Surface morphology*

Surface morphology of the produced hydrochar from HTC of glucose and cellulose at different operating temperature are shown in Figures 2.13 and 2.14, respectively. At low HTC operating temperature (i.e., 160 °C), cellulose is resistant to hydrothermal treatment. The fibrous structure of cellulose is still intact (Figure 2.14 a and b). On the other hand, with increasing the operating temperature (i.e., 220 °C), spherical particles in the produced hydrochar start forming (Figure 2.14 c and d), which is similar to the hydrochar obtained from glucose (Figure 2.13). In addition, the surface morphology of the hydrochar produced from HTC using rye straw as a feedstock at different operating temperature is shown in Figure 2.15. The morphological transformation of rye straw with the HTC process is similar to that observed for cellulose. Structural disruption of the lignocellulosic biomass (i.e., rye straw) does not occur at low temperature (i.e., 160 °C), and the fibrous structure of rye straw is maintained (Figure 2.15 a and b). At a higher operating temperature (i.e., 240 °C), the fiber network in rye straw is disrupted and spherical particles in the produced hydrochar start forming similar to cellulose (Falco et al., 2011).

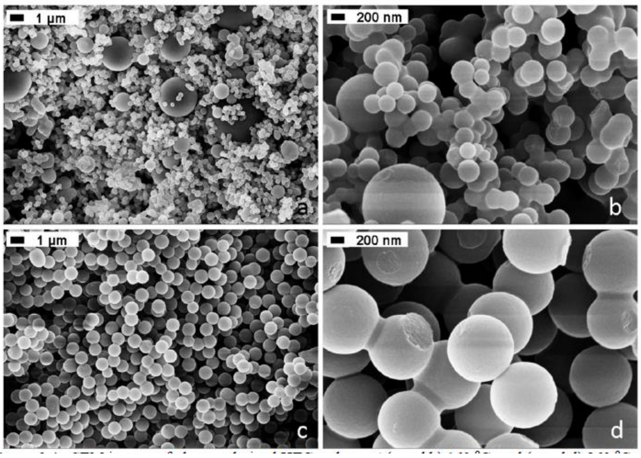


**Figure 2.13 SEM images of glucose-derived hydrochar at (a and b) 160 °C, and (c and d) 260 °C (Falco et al., 2011)**

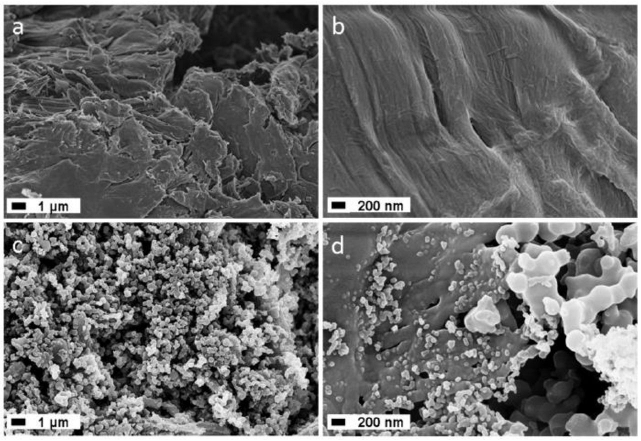


**Figure 2.14 SEM images of cellulose-derived hydrochar at (a and b) 160 °C, and (c and d) 220 °C (Falco et al., 2011)**

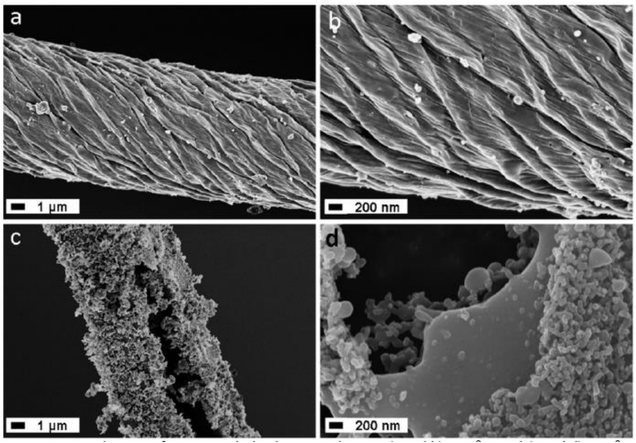


**Figure 2.15 SEM images of rye straw derived hydrochar at (a and b) 160 °C, and (c and d) 240 °C (Falco et al., 2011)**

#### 2.4.1.2 Applications of hydrochar

HTC process is an environmental friendly, easy and scalable process which produces the various carbon materials as the hydrochar with various practical applications. Currently, applications of the hydrochar have already been found in many fields such as solid fuel, energy storage, soil amendment, absorbent in water purification, catalyst, and $CO_2$ sequestration.

***Solid fuel***

As abovementioned, the energy content of hydrochar and elemental composition (H/C and O/C atomic ratios) are similar to natural coals. Thus, the hydrochar can be considered to apply as solid fuel. The investigations of the hydrochar application as a substitute for natural coals (fossil fuels) in the typical combustion process have been reported. The combustion of hydrochar produces a more stable flame due to low VM content (He et al., 2013). In addition, the co-combustion of hydrochar with coals can improve the combustion performance of low rank coal, by reducing ignition temperatures and increasing burnout temperatures (Parshetti et al., 2013).

***Energy storage***

One of the most promising applications of hydrochar is in the field of energy storage. Hydrochar can be processed further to make it suitable for use as electrodes in Li-ion batteries. The application of hydrochar as an anode in Li-ion batteries was reported in some literatures. There are 2 main techniques to produce this specific hydrochar: (1) Carbonization of the produced hydrochar under argon at 1000 °C for 5 h or, (2) the specific anode materials (such as Si nanoparticles, NiO, and $SnCl_4$) are dispersed into the feedstock and subsequently treated by HTC to produce hydrochar nanocomposites (Titirici and Antonietti, 2010). Moreover, using carbon colloids prepared by the HTC process for increasing the efficiency of the indirect carbon fuel cell has also been reported (Paraknowitsch et al., 2009).

***Soil amendment***

Application of hydrochar in the soil will affect to the soil properties such as reducing the tensile strength of hard-setting soils, enhancing the water-holding capacity and increasing the hydraulic conductivity of soils (Libra et al., 2011). There has been a lot of research regarding the application of biochar produced from pyrolysis to increase soil fertility. However, very little application of the hydrochar for soil amendment has been reported. The comparison of hydrochar and biochar in term of their application in soil amendment is explained in section 2.4.1.3.

***Absorbent in water purification***

One of the most important applications of hydrochar is adsorption purposes, especially for water purification. In order to increase the sorption capacity, using acrylic acid in the hydrochar production results in a high amount of carboxylic groups on the hydrochar surface which produces the materials with high functional surface area. This produced hydrochar, as an adsorbent, was successfully tested for lead and cadmium adsorptions. Sorption capacities of the hydrochar are higher than standard synthetic ion exchange resins and other types of sorption materials (Demir-Cakan et al., 2009).

### *Catalyst*

To produce the functional catalyst hydrochar from the HTC of biomass, it obviously should be hybridized with functional inorganic materials. The HTC operation with added noble metal salts results in the hydrochar loaded with the metallic nanoparticles which would be especially located in the hydrophobic core of the hydrochar (Titirici and Antonietti, 2010). For example, $Pd^0$ nanoparticles are prepared inside the carbon matrix of hydrochar. This functional catalyst hydrochar can be used successfully as a catalyst for the selective hydrogenation of phenol to cyclohexanone (Makowski et al., 2008).

### *$CO_2$ sequestration*

Biomass can be the carbon converter with the high efficiency of binding $CO_2$ out of the atmosphere, and using HTC process can transfer biomass into hydrochar could represent a most efficient process for $CO_2$ sequestration (Titirici et al., 2007). Figure 2.16 is an example to compare carbon transfer diagram of carbohydrates, including carbon efficiency (CE) and combustion energy from different renewable energy pathways. It showed the HTC process is the most efficient means for carbon fixation, with CE close to 1.

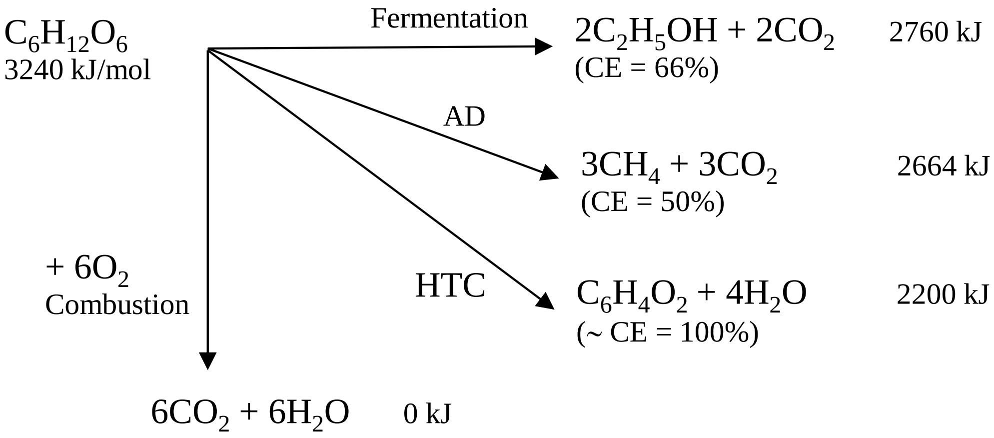


**Figure 2.16 Comparison of carbon transfer diagram of carbohydrates from different renewable energy pathways (Titirici and Antonietti, 2010)**

### 2.4.1.3 Comparison of hydrochar and biochar

There is a variety of terms to describe the chars produced from pyrolysis and HTC.

| | |
|---|---|
| Char | *"a solid decomposition product of a natural or synthetic organic material"* (IUPAC, 1997) |
| Charcoal | *"char obtained from pyrolysis of wood, peat or some to mean charred organic matter"* (Libra et al., 2011) |
| Biochar | *"a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment"* (IBI, 2013) and |

| | |
|---|---|
| | *"biochar distinguished from charcoal and similar materials by the fact that biochar is produced with the intent to be applied to soil as a means to improve soil health, to filter and retain nutrients from percolating soil water, and to provide carbon storage"* (Lehmann and Joseph, 2009) |
| Hydrochar | *"char produced from HTC process"* (Libra et al., 2011) |

Physical and chemical characteristics of biochar compared to hydrochar produced from the same feedstock (i.e., corn silage) are differed, as results in Table 2.7. However, both types of char have higher carbon and nitrogen contents and lower hydrogen and oxygen contents than the feedstock. Other properties of biochar and hydrochar are compared and explained in the following section.

**Table 2.7 Characteristics of Biochar, Hydrochar and Corn Silage (Feedstock)**

| Samples | Chemical composition (%wt) | | | | |
|---|---|---|---|---|---|
| | C | H | O | N | Ash |
| Biochar | 77.9 | 2.3 | 6.4 | 2.0 | 11.4 |
| Hydrochar | 51.6 | 5.7 | 19.6 | 1.9 | 21.3 |
| Corn silage | 54.1 | 6.8 | 43.9 | 1.1 | 3.1 |

Source: Malghani et al. (2013)

### *Biochar production and characteristics*

Biochar is produced by pyrolysis of organic material or biomass such as wood, leaves or manure in a closed system at relatively low temperatures (<700 °C) under limited supply of air or oxygen (Lehmann and Joseph, 2009). Biochar production is one of the most primitive industrial technologies developed by mankind. As defined above, the difference of biochar from other chars and similar materials is that it is produced with the purpose to be used for soil amendment. The characteristics of biochar are very varied, consisting of carbon, hydrogen, oxygen, nitrogen, sulfur and ash (Duku et al., 2011), depending on pyrolysis conditions and raw material. Feedstock type and operating temperature are the two main process factors which effect on the properties of biochar. Chun et al. (2004) produced biochar from the pyrolysis of wheat residue and found that increasing pyrolysis temperatures result in the increase of surface area of the produced biochar. At temperatures of 500−700 °C, biomass is carbonized, resulting a relatively high surface area (more than 300 $m^2/g$), low organic matter (less than 3%), and low oxygen content (less than 10%). Whereas, at low temperatures of 300−400 °C, the produced biochar is only partially carbonized, resulting significantly different characteristics such as organic carbon of 40−50%, oxygen content of >20% and surface area of <200 $m^2/g$.

### *Comparison of hydrochar and biochar in term of their application as soil amendment*

1. Stability of biochar and hydrochar in soil

The stability of biochar presented in Terra preta soil has been found to be 500-2000 years old (Glaser et al., 2002). Hydrochar probably decompose faster than biochar but slower than uncarbonized materials. The biochar and hydrochar are the longest organic carbon contain in soils. However, they cannot be considered inert because of the decomposition and mineralization of biochar and hydrochar over sufficiently long time periods. The exposed surfaces and the increase of total surface area caused from physical forces (swelling–shrinking and freeze–thaw of clay minerals) and biological forces (fungal hyphae and in-growth of plant roots), can be resulted in further oxidation and degradation of the biochar and hydrochar. Another cause of biochar and hydrochar loss from soils is the surface erosion, which occurs from either the transport of small size particles or dissolution of dissolved organic carbon in the water (Libra et al., 2011).

2. Change of soil characteristics

Application of biochar in soils has showed many beneficial effects in improving soil properties, such as (Libra et al., 2011):

- enhancing aeration
- increasing water-holding capacity (WHC)
- enhancing hydraulic conductivity of soils
- increasing cation-exchange capacity (CEC) of soils
- reducing tensile strength of hard-setting soils
- stimulating growth, activity and the metabolic efficiency of the microbial biomass
- improving nutrient retention and efficiency of nutrient use
- attracting earthworm activity

With application of hydrochar, it will affect soil properties, such as enhancing soil WHC, increasing hydraulic conductivity and reducing tensile strength. Due to the lower operating temperature of the HTC process, the hydrochar will have less internal surfaces than biochar. In addition, hydrochar is more acidic than biochar; hence, in acidic soils, the Al toxicity may not be reduced by using acidic hydrochar in such soils. Thus, the effect of the biochar and hydrochar on soil biology may be very different.

3. Soil fertility and crop yield

For biochar application in soil, it can enhance crop yields with combination with N, P, and K fertilizers, especially in tropical soils (Libra et al., 2011). Some of the nutrients in biochar has been found to lose during the pyrolysis process (e.g., via volatilization) and the nutrients included in aromatic stable structures may become unavailable for plants. While hydrochar, operating at lower temperatures, may retain more available nutrients either in the hydrochar or in the liquid products. Hydrochar contains higher fractions of labile carbon (i.e., carboxylates and carbohydrates) than biochar which may lead microbial growth and promote nutrient cycling in soil after a lag phase.

4. Carbon sequestration potential and greenhouse gas (GHG) emissions

Hydrochar decomposition in soils is rapid (50% in 100 days) and stimulates substantially higher GHG emissions like $CH_4$ and $CO_2$ than biochar application in soil, but it can reduce $N_2O$ fluxes in the spruce forest and agricultural soils. In contrast, biochar application in soil results in the decrease $CO_2$ emission from soil with no significant effect on $CH_4$ emission, and produces moderate levels of $N_2O$ emission (compare hydrochar application in soil) (Kammann et at, 2012). Although biochar and hydrochar are produced from the same biomass feedstock, biochar has a significantly higher carbon sequestration potential than hydrochar (Malghani et al., 2013).

### 2.4.2 Liquid products

Liquid products (some called “process water”) have a high concentration of organic and inorganic materials. From the conversion of feedstock in the HTC process, the produced soluble organic matters fraction is contained in the liquid phase. About 15% of carbon in the initial biomass feedstock are solubilized (Stemann et al., 2013). The total organic carbon (TOC) and COD of liquid products resulting from the HTC have been investigated for the various feedstocks (Berge et al., 2011; Danso-Boateng et al., 2013; Stemann et al., 2013). For example, the TOC and COD concentrations of the liquid products produced from HTC of wood chips are about 17 g/L and 50 g/L, respectively (Stemann et al., 2013). Concentrations of these parameters are equal to those commonly found in landfill leachate (Berge et al., 2011). Moreover, about 30-50% of the TOC come from the produced organic acids during the HTC process, such as acetic acid, glycolic acid, levulinic acid and formic acid, resulting the low pH of liquid products (less than 5) (Lu et al., 2012; Stemann et al., 2013). The other components in the liquid products formed during the HTC process are the various monomers and organic acids, as shown in Table 2.8. It is apparent that these liquid products need to be further treated such as by AD (Oliveira et al., 2013; Poerschmann et al., 2014) to minimize environmental pollution and producing useful biogas.

**Table 2.8 Analysis of Components in HTC Liquid Products**

| Components | Concentration (mg/L) | |
|---|---|---|
| | HTC of maize silage [a] | HTC of wood chips [b] |
| Glucose | 0-152 | 140-220 |
| Xylose | 0-80 | Not analyzed |
| Sucrose | 416-458 | Not analyzed |
| Lactic acid | 4296-6116 | Not analyzed |
| Formic acid | 2611-5062 | 1380-2080 |
| Acetic acid | 300-1923 | 7300-9700 |
| HMF | 0-2120 | 1080-1380 |
| Furfural | 8-646 | 150-170 |
| Phenol | 48-109 | 530-610 |

[a] HTC conditions: temperature of 200-250 °C and reaction times of 3-5 h (Reza et al., 2014)

[b] HTC conditions: temperature of 220 °C and reaction times of 4 h (Stemann et al., 2013)

### 2.4.3 Gas products

A carbon fraction is also shifted to gas phase. The gas formed during the HTC process is small and mainly consists of $CO_2$ as a result of decarboxylation reaction. Minor fractions of $CH_4$, CO, and $H_2$ as well as traces of hydrocarbon gases such as butane, propene, and ethane and have also been reported widely (Berge et al., 2011; Funke and Ziegler, 2010; Lu et al., 2012). To achieve a high energy content of the produced hydrochar, the removals of hydrogen and oxygen from the biomass by dehydration and decarboxylation reactions, reducing H/C and O/C atomic ratios, are favorable (Peterson et al., 2008). However, to allow for the $CO_2$ sequestration potential and to keep a high carbon content in the produced hydrochar, it might be considered to maintain the decarboxylation reaction as low as possible (Titirici et al., 2007).

## 2.5 Introduction of Two-Stage Hydrothermal Carbonization

Concept of the two-stage HTC process is to separate reaction pathways into two stages, namely hydrolysis and carbonization stages which are different in the conversion reactions and operating temperatures (Figure 2.17). In the hydrolysis stage, biomass materials are broken down to become low-molecular weight compounds such as oligosaccharides, glucose (or fructose), and amino acids (Funke and Ziegler, 2010; He et al., 2013) which can be occurred at temperature in the range of 100-175 °C (Abelleira et al., 2012). The carbonization stage consists of the dehydration, polymerization, aromatization and solid-solid conversion reactions, which require relatively high temperatures in the range of 160-280 °C (Falco et al., 2011). In this stage, the hydrolyzed products (i.e. glucose or fructose) are dehydrated to HMF and subsequently polymerized and condensed to form the hydrochar (Sevilla and Fuertes, 2009). Simultaneously, the hydrochar is also formed via the solid–solid conversion of biomass materials (Falco et al., 2011). More details of each stage are explained in the following sections.

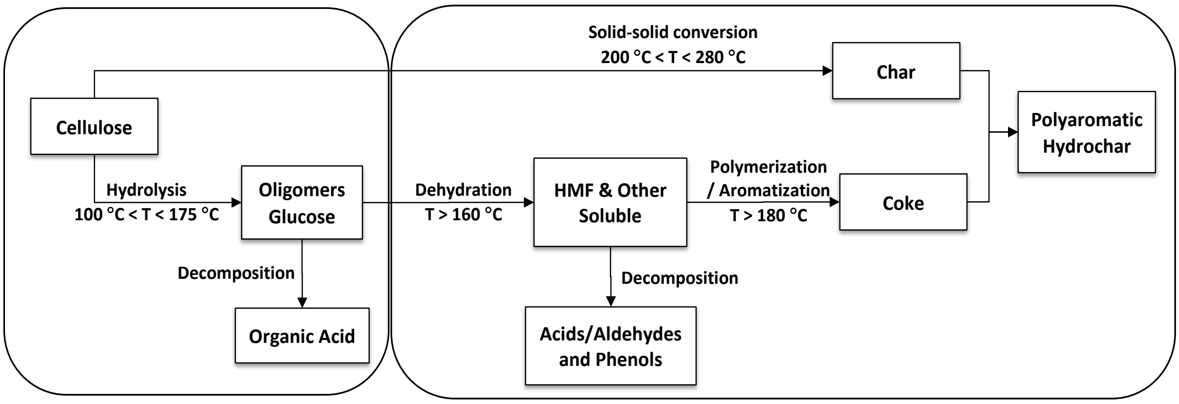


**Figure 2.17 Conceptual design of two-stage HTC**

### 2.5.1 Hydrolysis stage

Hydrolysis of the bio-macromolecules such as cellulose, hemicellulose and lignin, adding 1 mole of water, results in the cleavage of mainly ester and ether bonds, producing a wide range of products such as (oligo-) saccharides, glucose monomers, and amino acids (Funke and Ziegler, 2010; He et al., 2013). Cellulose from different biomass types and sources has different characteristics, depending on its physical and chemical structures (Peterson et al., 2008). In the thermal hydrolysis process, operating temperatures are in the range of 100–175 °C at low corresponding pressure (max 13 bar). Optimum conditions are the operating temperature and times of about 170 °C and 30–60 min, respectively (Abelleira et al., 2012). To enhance the hydrolysis reaction rate of the biomasses at elevated temperatures and pressures, the acid catalysts such as $H_2SO_4$, HCl, $H_3PO_4$, and $HNO_3$ have been investigated. From the results of Jeong et al. (2012), $H_2SO_4$ is the most suitable catalyst for hydrolysis of cellulose, producing maximized glucose at 160.7 °C, 2.0% (w/v) $H_2SO_4$, and 40 min.

### 2.5.2 Carbonization stage

Carbonization generally is the reactions involved in the fuel productions from biomass. The overall objective of the carbonization of biomass is to remove its oxygen content which often contains 40-60 %wt oxygen while the typical fuels and oil normally have oxygen contents less than 1 %wt (Peterson et al., 2008). Oxygen removal can occur through decarboxylation and dehydration reactions which remove oxygen in the forms of $CO_2$ and $H_2O$, respectively. Although an amount of water is present in HTC process, dehydration reactions can occur in aqueous media under high temperatures and pressures. The carbonization in the HTC process is the complex reactions, including dehydration, decarboxylation, polymerization and aromatization.

#### *Dehydration*

Dehydration in the HTC process includes both physical process (dewatering) and chemical reaction. Considering chemical dehydration, it is generally described by elimination of hydroxyl groups in biomass, resulting in reducing H/C and O/C atomic ratios (Funke and Ziegler, 2010). More details of dehydration reaction can be explained using the hydrothermal degradation of glucose to HMF as an example. Qi and Xiuyang (2008) investigated the dehydration of glucose solution at temperatures of 180-220 °C under pressure of 10 Mpa. The dehydration reaction pathway from glucose to HMF (main product), levulinic and formic acids (by-products) is illustrated in Figure 2.18. Glucose is completely decomposed at temperature of 220°C for 90 min without adding catalysts. The kinetic model of the dehydration rate of glucose to HMF is found to follow the first order reaction, having the reaction rate constants of 0.012, 0.018, and 0.036 $min^{-1}$ at 200, 210, and 220°C, respectively. The kinetic analysis indicated higher yield of HMF significantly depending on higher temperature and shorter reaction time. Further, the Arrhenius equations for dehydration of glucose are determined. The activation energies for dehydration of glucose to HMF and decomposition of HMF to by-products are found to be 108 and 136 kJ/mol, respectively, indicating that high temperature leads the formation of by-products.

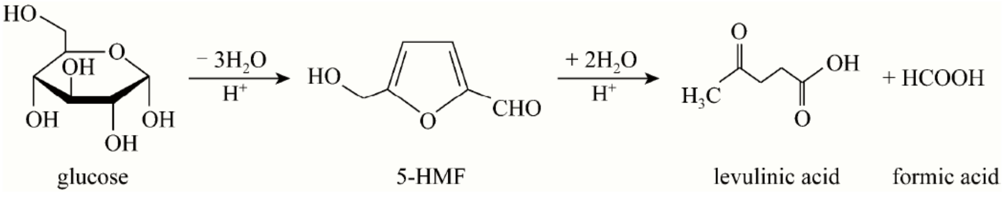


**Figure 2.18 Dehydration of glucose to HMF and by-product (Qi and Xiuyang, 2008)**

### *Decarboxylation*

Decarboxylation reaction is a second method for removing oxygen from biomass feedstock during the HTC process, generating $CO_2$ gas. It results in increased the H/C atomic ratio and decreasing the O/C atomic ratio, which typically lead to more attractive fuels. Unfortunately, fewer studies on decarboxylation reaction have been initiated, compared to dehydration reaction.

### *Polymerization*

Dehydration and decarboxylation of hydrolyzed substrates (glucose or fructose) generate the unsaturated compounds (HMF and furfural) which can be polymerized easily. During HTC, the formation of hydrochar is mostly explained by condensation polymerization, specifically aldol condensation (Sevilla and Fuertes, 2009; Kabyemela et al., 1999). At subcritical conditions of water in the HTC process, the low rate of polymerization reaction was found which indicates that the condensation polymerization reaction is likely controlled by step-growth polymerization (Kuster, 1990).

### *Aromatization*

Dehydration of the monosaccharide such as glucose produces the aromatized molecules which present a high stability under subcritical conditions of water or hydrothermal conditions. These molecules could be condensed to be aromatic clusters and may be considered as a basic structure of the producing hydrochar (Sevilla and Fuertes, 2009). Cross-linking condensation of these aromatic structures is also found in the main configurations of natural coal, which may explain the good agreement between HTC process and natural coalification. Similar chemical characteristics of hydrochar and natural coal have been reported in several publications (Funke and Ziegler, 2010).

### *HTC of glucose*

Glucose is used as a precursor in the HTC, which can be represented the carbonization stage of the two-stage HTC. From the experimental results of Falco et al. (2011), as show in Figure 2.19, the recovery yield from the HTC of glucose is not significant at lower temperatures (150-160 °C) for reaction time of 24 h, resulting in less amount of solid (hydrochar) is formed. From the yield analysis of the produced hydrochar, it indicates that the operating conditions of the HTC of glucose can be varied to optimize the HTC recovery yield. At the temperature of 200 °C, the highest hydrochar yield can be achieved. At the temperatures of 200-250 °C, the HTC recovery yield decreases due to oxygen losses by decarboxylation and dehydration reactions. On the other hand, the carbon content in the produced hydrochar decreases and subsequently remains relatively constant. At the temperatures of 250-280 °C, the decrease of carbon content in the produced hydrochar is observed, presumably due to the loss of unstable VM by gasification processes.

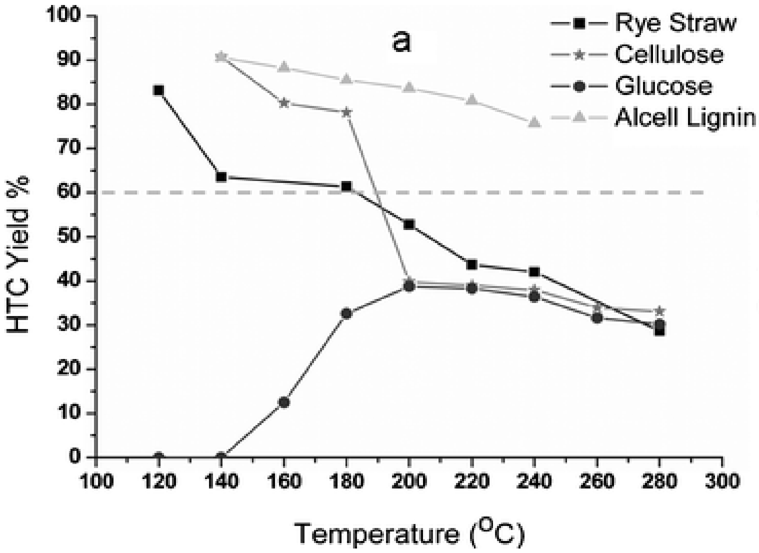


**Figure 2.19 HTC yields obtained from glucose, cellulose, rye straw, and alcell lignin at different operating temperatures (Falco et al., 2011)**

## 2.6 Summary and Research Gaps

FSM is a serious problem in most developing countries which has caused water and soil pollutions and health risks. Typical treatment technologies such as drying bed, constructed wetland, composting, and digestion cannot be overcome the sanitation and environmental problems. HTC is an alternative technology that can be used to treat FS and convert it into hydrochar. The advantage of the HTC process for treating FS over other thermal conversion processes such as pyrolysis and gasification is that it requires minimal FS drying. Moreover, hydrochar produced from HTC have already found in many applications such as solid fuel in combustion process, energy storages, soil amendment, absorbent in wastewater treatment, catalyst, and $CO_2$ sequestration.

Although several authors have reported using HTC of many kinds of organic feedstock for hydrochar production, application of HTC process on FS has not been extensively studied and reported. The HTC of raw FS which was the accumulated sludge emptied from septic tanks was studied and reported in this dissertation. Research study for HTC is still lacking of design criteria and operation condition and need to be developed. Therefore, in addition to this research area, A linear regression model was developed which could estimate energy content of the produced hydrochar at various operating conditions.

The challenges of HTC process are the high energy consumption and relatively low energy content of the produced hydrochar. Therefore, a low-energy HTC process named “Two-stage HTC” for FS treatment was explored in this research. The concept of the two-stage HTC process is to separate reaction pathways into two stages, namely hydrolysis and carbonization stages which are different in the conversion reactions and operating temperatures. Based on this concept, the two-stage HTC consumes lower energy and results higher energy content of the produced hydrochar than the conventional HTC. In addition, hydrochar formation mechanisms in the hydrolysis and carbonization stages of two-stage HTC were studied and proposed in this dissertation.

# Chapter 3

# Methodology

The study of HTC of FS has been conducting at AIT, Thailand. The experiments were set up in lab-scale to study hydrochar production by conventional and two-stage HTC of FS. The influences of moisture content, temperature and reaction time on energy content of the produced hydrochar and hydrochar yield were investigated and optimized. The HTC product characteristics were analyzed to identify their applications and treatment options. Research outline is summarized in Table 3.1 and explained in the following sections.

## 3.1 Materials and Apparatus

### *Faecal sludge*

FS which is the accumulated sludge in septic tanks, cesspools or pit latrine was collected from a municipal emptying truck, which serviced residential areas in a city located near Bangkok, Thailand. Moisture contents of the collected FS samples, which were originally about 95%wt with the VS concentration of about 40 g/L, were adjusted to be 90, 80 and 70%wt using a water bath before feeding to the HTC reactor, while VS concentrations of these samples were about 70, 150, and 340 g/L, respectively.

### *Acetic acid and Cassava pulp*

Acetic acid (RCI labscan, 99.7% min) and cassava pulp were selected to mix with FS in order to increase energy content of the produced hydrochar (Tajai, 2015; Pradeep, 2015). The FS samples were mixed with acetic and cassava pulp at the mixing ratio of 1:0.4:1 by weight prior feed into HTC reactor.

### *HTC reactor*

Experiments were conducted with a 1-L high pressure reactor made of stainless steel and equipped with pressure gauge, thermocouple and gas collecting ports, as illustrated and described in Figure 3.1 and Table 3.2. An electrical heater equipped with a control panel (Figure 3.1a) was used to adjust the temperature and reaction time of the reactor. For the cooling system, a cooling jacket (Figure 3.1b) was used to cool down the reactor after finish each HTC experiment.

**Table 3.1 Research Outline**

| | | |
|---|---|---|
| **Experiment of conventional HTC** | **Purposes**<br>1. To investigate the hydrochar production using conventional HTC with relevant process parameters such as moisture content (70-95 %wt), temperature (180-250 °C), and reaction time (0.5-10 h)<br>2. To optimize the conventional HTC process conditions taking into consideration of energy content of the produced hydrochar and hydrochar yield | **Expected outcomes**<br>1. Effects of moisture content, temperature and reaction time on energy content of the produced hydrochar and hydrochar yield<br>2. Optimum conditions of HTC for FS treatment would result in maximum energy content and hydrochar yield<br>3. Characteristics of the HTC products<br>4. A mathematical model for estimate energy content of the produced hydrochar at various operating conditions |
| **Experiment of two-stage HTC** | **Purposes**<br>1. To investigate the hydrochar production using two-stage HTC with relevant process parameters such as hydrolysis temperature (150-180 °C), hydrolysis reaction time (20-200 min), carbonization temperature (200-250 °C), and carbonization reaction time (30-300 min)<br>2. To optimize the two-stage HTC process conditions taking into consideration of energy content of the produced hydrochar and hydrochar yield | **Expected outcomes**<br>1. Effects of temperatures and reaction times in the hydrolysis and carbonization stages on energy content of the produced hydrochar and hydrochar yield<br>2. Optimum conditions of two-stage HTC for FS treatment would result in maximum energy content and hydrochar yield, while minimizing energy input<br>3. Characteristics of the HTC products<br>4. Reaction pathways of the two-stage HTC (hydrolysis and carbonization)<br>5. Reaction kinetics of FS degradation<br>6. Comparison results of the two-stage HTC with the conventional HTC and literatures |
| **Application of HTC for FS treatment and its products** | **Purposes**<br>1. To study the technical feasibility of HTC for FS treatment<br>2. To identify the applications and treatment options of the HTC products | **Expected outcomes**<br>1. Concept of HTC application for FS treatment<br>2. Applications and treatment options of HTC products to utilize their value and minimize the environmental impacts |

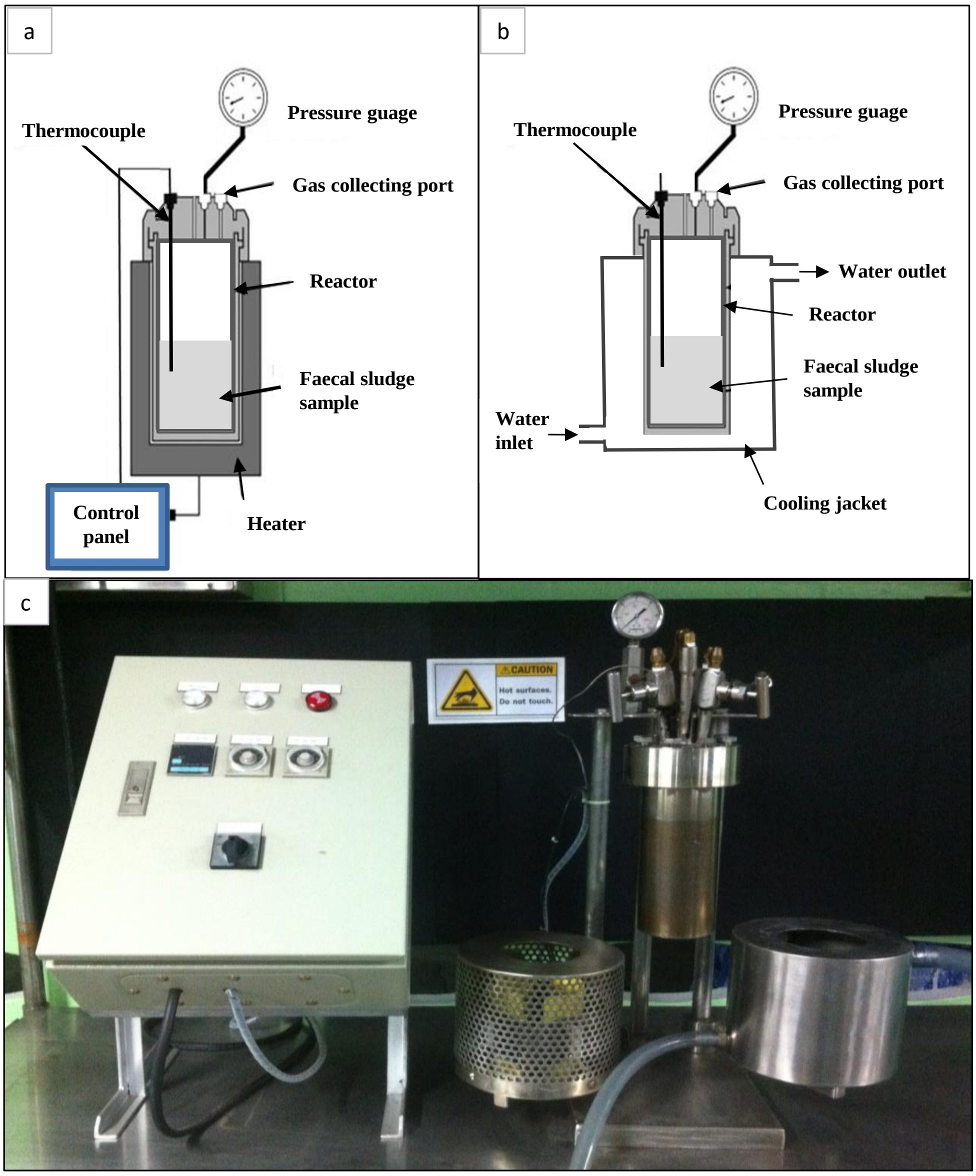


**Figure 3.1 Schematic of HTC reactor: (a) heating system; (b) cooling jacket; (c) photograph of HTC reactor**

**Table 3.2 Specifications of Main Parts of HTC Reactor**

| Parts | Specifications |
|---|---|
| Reactor tube | Material : stainless steel<br>Total volume : 1 L<br>Inside depth : 5.4 inches, inside diameter : 4 inches |
| Tube head | Material : stainless steel<br>Consist of : gas collection port, thermocouple and pressure gauge |
| Heater | Ceramic heater bar<br>Electrical heater, 2000W |
| Cooling bucket | Water cooling |
| Control panel | Control systems for operating temperature and time |

## 3.2 Experiments of Conventional HTC

Preliminary experiments were conducted to study the conventional HTC for FS treatment and the effect of process parameters on energy content of the produced hydrochar and hydrochar yield. The design of experiments was listed in Table 3.3. Each HTC experiment was performed in the triplicate with 350 mL of FS sample, and the operating conditions were controlled at temperatures of 180, 220, and 250 °C and reaction times of 0.5, 1, 5, and 10 h. The generated pressure was monitored and recorded during HTC operation. After desired temperature and reaction time of each experiment were reached, the HTC reactor was fast cooled down with water in a cooling bucket at the cooling rate of about 45 °C/minute to stop the reactions. The gas sample was collected after the HTC reactor was cooled to the ambient temperature. The carbonized FS remaining in the HTC reactor was separated for solid (hydrochar) and liquid products using vacuum filtration (Whatman filter paper, 1.2 µm). The liquid sample was collected in the containers. The produced hydrochar was subsequently dried in an oven at 105 °C for at least 12 h to remove the remaining moisture. The hydrochar, liquid and gas samples were analyzed for their physical and chemical characteristics as listed in the section 3.7.1.

**Table 3.3 Design of Experiments for Conventional HTC of FS**

| Experiment no. | Process parameters | | |
|---|---|---|---|
| | Moisture content (%wt) | Temperature (°C) | Reaction time (h) |
| 1 | 70 | 220 | 5 |
| 2 | 80 | 220 | 5 |
| 3 | 90 | 220 | 5 |
| 4 | 95 | 220 | 5 |
| 5 | 80 | 180 | 0.5 |
| 6 | 80 | 180 | 1 |
| 7 | 80 | 180 | 5 |
| 8 | 80 | 180 | 10 |
| 9 | 80 | 220 | 0.5 |
| 10 | 80 | 220 | 1 |
| 11 | 80 | 220 | 5 |
| 12 | 80 | 220 | 10 |
| 13 | 80 | 250 | 0.5 |
| 14 | 80 | 250 | 1 |
| 15 | 80 | 250 | 5 |
| 16 | 80 | 250 | 10 |

## 3.3 Experiments of Two-Stage HTC

The two-stage HTC experiments were conducted by varying the hydrolysis temperature, hydrolysis reaction time, carbonization temperature, and carbonization reaction time, while energy content of the produced hydrochar and hydrochar yield were the responsive values. The design of the two-stage HTC experiments showed in Table 3.4 was according to the response surface methodology (RSM) with central composite design (Montgomery, 2005) which is used to examine the relationship between the responsive values and process parameters, and to optimize the two-stage HTC process conditions. The Minitab-17 software was employed for designing experiments and analyzing experimental data.

For each of the two-stage HTC experiment, 350 mL of the FS sample was fed to the HTC reactor, which was operated at the designed temperature and reaction time of the hydrolysis stage, and subsequently at the designed temperature and reaction time of the carbonization stage (Table 3.4). At the end of each experiment, the cooling method, filtration and hydrochar drying were performed following procedures of the conventional HTC experiments (explained in section 3.2). The hydrochar, liquid and gas samples were collected and analyzed for their physical and chemical characteristics as listed in the section 3.7.1.

**Table 3.4 Design of Experiments for Two-Stage HTC of FS**

| Experiment no. | Hydrolysis stage | | Carbonization stage | |
|---|---|---|---|---|
| | Temperature (°C) | Reaction time (min) | Temperature (°C) | Reaction time (min) |
| 1 | 150 | 110 | 225 | 165 |
| 2 | 158 | 65 | 213 | 98 |
| 3 | 158 | 65 | 213 | 233 |
| 4 | 158 | 65 | 238 | 98 |
| 5 | 158 | 65 | 238 | 233 |
| 6 | 158 | 155 | 213 | 98 |
| 7 | 158 | 155 | 213 | 233 |
| 8 | 158 | 155 | 238 | 98 |
| 9 | 158 | 155 | 238 | 233 |
| 10 | 165 | 20 | 225 | 165 |
| 11 | 165 | 110 | 200 | 165 |
| 12 | 165 | 110 | 225 | 30 |
| 13 | 165 | 110 | 225 | 165 |
| 14 | 165 | 110 | 225 | 165 |
| 15 | 165 | 110 | 225 | 165 |
| 16 | 165 | 110 | 225 | 165 |
| 17 | 165 | 110 | 225 | 165 |
| 18 | 165 | 110 | 225 | 165 |
| 19 | 165 | 110 | 225 | 300 |
| 20 | 165 | 110 | 250 | 165 |
| 21 | 165 | 200 | 225 | 165 |
| 22 | 173 | 65 | 213 | 98 |
| 23 | 173 | 65 | 213 | 233 |
| 24 | 173 | 65 | 238 | 98 |
| 25 | 173 | 65 | 238 | 233 |
| 26 | 173 | 155 | 213 | 98 |
| 27 | 173 | 155 | 213 | 233 |
| 28 | 173 | 155 | 238 | 98 |
| 29 | 173 | 155 | 238 | 233 |
| 30 | 180 | 110 | 225 | 165 |

## 3.4 Experiments of Reaction Kinetics Determination

Experiments for determining the reaction kinetics of the FS degradation in the HTC process were designed and listed in Table 3.5. Each HTC experiment was performed in the triplicate with 350 mL of FS sample and the operating conditions were controlled at temperatures of 140, 160, 180, 200 °C and reaction times of 0.5, 1, 3, 5, and 10 h. At the end of each experiment, the cooling method, filtration and hydrochar drying were performed following procedures of the conventional HTC experiments (explained in section 3.2). FS samples and the produced hydrochars were analyzed for the VM content by proximate analysis. The $1^{st}$-order reaction model and Arrhenius equation were determined following explanation in the section 3.7.4.

**Table 3.5 Design of Experiments for Determining Reaction Kinetics of FS Degradation**

| Experiment no. | Process parameters | | |
|---|---|---|---|
| | Moisture content (%wt) | Temperature (°C) | Reaction time (h) |
| 1 | 80 | 140 | 0.5 |
| 2 | 80 | 140 | 1 |
| 3 | 80 | 140 | 3 |
| 4 | 80 | 140 | 5 |
| 5 | 80 | 140 | 10 |
| 6 | 80 | 160 | 0.5 |
| 7 | 80 | 160 | 1 |
| 8 | 80 | 160 | 3 |
| 9 | 80 | 160 | 5 |
| 10 | 80 | 160 | 10 |
| 11 | 80 | 180 | 0.5 |
| 12 | 80 | 180 | 1 |
| 13 | 80 | 180 | 3 |
| 14 | 80 | 180 | 5 |
| 15 | 80 | 180 | 10 |
| 16 | 80 | 200 | 0.5 |
| 17 | 80 | 200 | 1 |
| 18 | 80 | 200 | 3 |
| 19 | 80 | 200 | 5 |
| 20 | 80 | 200 | 10 |
| 21 | 80 | 220 | 0.5 |
| 22 | 80 | 220 | 1 |
| 23 | 80 | 220 | 3 |
| 24 | 80 | 220 | 5 |
| 25 | 80 | 220 | 10 |
| 26 | 80 | 250 | 0.5 |
| 27 | 80 | 250 | 1 |
| 28 | 80 | 250 | 3 |
| 29 | 80 | 250 | 5 |
| 30 | 80 | 250 | 10 |

## 3.5 Experiments of Energy Content Improvement

The mixtures of FS, acetic acid and cassava pulp were selected as an example to determine energy contents of the produced hydrochar from conventional and two-stage HTC processes. Each conventional HTC experiment was performed in the triplicate with 350 mL of the mixture of FS, acetic acid and cassava pulp and the operating conditions were controlled at temperatures of 200, 220, and 250 °C and reaction times of 0.5, 1, 3, 5, and 10 h, following experiments designed in Table 3.6. At the end of each experiment, the cooling method, filtration and hydrochar drying were performed following procedures of the conventional HTC experiments (explained in section 3.2). For two-stage HTC, each experiment was performed in the triplicate with 350 mL of the mixtures of FS, acetic acid and cassava pulp and operated under optimum of the two-stage HTC conditions. The produced hydrochars from conventional and two-stage HTC experiments were collected and analyzed for the energy content as listed in the section 3.7.1.

**Table 3.6 Design of Experiments of Energy Content Improvement**

| Experiment no. | Process parameters | | |
|---|---|---|---|
| | Mixing ratio of FS: acetic acid : cassava pulp (by weight) | Temperature (°C) | Reaction time (h) |
| 1 | 1:0.4:1 | 200 | 0.5 |
| 2 | 1:0.4:1 | 200 | 1 |
| 3 | 1:0.4:1 | 200 | 3 |
| 4 | 1:0.4:1 | 200 | 5 |
| 5 | 1:0.4:1 | 200 | 10 |
| 6 | 1:0.4:1 | 220 | 0.5 |
| 7 | 1:0.4:1 | 220 | 1 |
| 8 | 1:0.4:1 | 220 | 3 |
| 9 | 1:0.4:1 | 220 | 5 |
| 10 | 1:0.4:1 | 220 | 10 |
| 11 | 1:0.4:1 | 250 | 0.5 |
| 12 | 1:0.4:1 | 250 | 1 |
| 13 | 1:0.4:1 | 250 | 3 |
| 14 | 1:0.4:1 | 250 | 5 |
| 15 | 1:0.4:1 | 250 | 10 |

## 3.6 Bio-Methane Potential Test

To determine biogas production from AD of the HTC liquid by-product, the bio-methane potential (BMP) tests were conducted. The HTC liquid by-products collected from the filtration process of the HTC of FS operating at temperature of 250 °C and reaction time of 5 h were used as a substrate. An anaerobic inoculum was obtained from an anaerobic co-digestion of cassava pulp and pig manure in the continuous stirred-tank reactor (CSTR) at mesophilic condition.

The BMP tests, as shown in Table 3.7, were performed in triplicate using 1000 mL glass bottles (Figure 3.2). Each glass bottle of test I was filled with the mixture of HTC liquid by-product and inoculum at the substrate/inoculum ratio of 0.5 gVS/gVS (Esposito et al., 2012) and each glass bottle of test II was filled with inoculum alone, to estimate the biogas resulting from digestion of organic substrates contained in the inoculum. Water was filled up to 500 mL total volume in each glass bottle. To prevent pH drop, $Na_2CO_3$ powder of 0.10 g was added. Nitrogen gas was filled into each glass bottle to purge the excessive oxygen gas inside the bottle and maintaining the anaerobic condition. All glass bottles were shaken for 30 min and kept inside an incubator (INE800, Memmert, Japan) maintaining at a constant temperature of 37 ± 1 °C. Amount of biogas was measured daily and methane production was measured every 7 days using gas chromatograph instrument (GC 7890A, Agilent, USA).

**Table 3.7 BMP Test Design**

| BMP test | HTC liquid by-product [a] (g) | Inoculum [b] (g) | Total volume (adjusted with water) (mL) |
|---|---|---|---|
| I | 150 | 273 | 500 |
| II | - | 273 | 500 |

[a] TVS = 2.67 gVS/100 g

[b] TVS = 2.93 gVS/100 g

**Figure 3.2 Photograph of BMP test reactors**

## 3.7 Analytical Methods

### 3.7.1 Product characteristics

FS, hydrochar, liquid and gas samples collected from the experiments were analyzed following the parameters and method/equipment listed in Table 3.8.

**Table 3.8 List of Analysis Parameters and Methods/Equipment**

| Samples | Parameters | Methods/Equipment |
|---|---|---|
| FS sample (dried FS) | Dry weight | Oven (105 °C at least 12 h) |
| | Proximate analysis | Thermogravimetric analyzer<br>(TGA701, Leco, USA) |
| | Ultimate analysis | CHNS analyzer<br>(Truspec, Leco, USA) |
| | Energy content | Bomb calorimeter<br>(AC500, Leco, USA) |
| | Surface morphology | Scanning electron microscopy<br>(S-3400N, Hitachi, Japan) |
| | Bulk density | Gravimetric and weight method |
| | Surface area | Brunauer-Emmett-Teller (BET) analysis with adsorption isotherm (Lohwacharin et al., 2010) |
| | Porosity characteristics (total pore volume and pore diameter) | Nitrogen adsorption analysis at 77 K in a BELSORP-mini II volumetric adsorption analyzer (BEL Japan Inc., Japan) |
| FS sample | TOC | High temperature combustion method<br>(TOC-V CPH, Shimadzu, Japan) |
| | COD | Closed dichromate reflux method<br>(APHA/AWWA/WEF, 2005) |
| | BOD | 5 days BOD test (5210-B)<br>(APHA/AWWA/WEF, 2005) |
| | TN | Persulfate method<br>(APHA/AWWA/WEF, 2005) |
| | TP | Colorimetric method<br>(APHA/AWWA/WEF, 2005) |
| | Volatile fatty acids (VFA) | Distillation method<br>(APHA/AWWA/WEF, 2005) |
| | pH | pH meter<br>(Sevengo, Metter Toledo, USA) |
| Hydrochar | Dry weight | Oven (105 °C at least 12 h) |
| | Proximate analysis | Thermogravimetric analyzer<br>(TGA701, Leco, USA) |
| | Ultimate analysis | CHNS analyzer<br>(Truspec, Leco, USA) |
| | Energy content | Bomb calorimeter<br>(AC500, Leco, USA) |
| | Surface morphology | Scanning electron microscopy<br>(S-3400N, Hitachi, Japan) |

**Table 3.8 List of Analysis Parameters and Methods/Equipment (cont.)**

| Samples | Parameters | Methods/Equipment |
|---|---|---|
| Hydrochar | Bulk density | Gravimetric and weight method |
| | Surface area | BET analysis with adsorption isotherm (Lohwacharin et al., 2010) |
| | Porosity characteristics (total pore volume and pore diameter) | Nitrogen adsorption analysis at 77 K in a BELSORP-mini II volumetric adsorption analyzer (BEL Japan Inc., Japan) |
| Liquid product | TOC | High temperature combustion method (TOC-V CPH, Shimadzu, Japan) |
| | COD | Closed dichromate reflux method (APHA/AWWA/WEF, 2005) |
| | BOD | 5 days BOD test (5210-B) (APHA/AWWA/WEF, 2005) |
| | TN | Persulfate method (APHA/AWWA/WEF, 2005) |
| | TP | Colorimetric method (APHA/AWWA/WEF, 2005) |
| | $NH_4$-N | Titrimetric method (APHA/AWWA/WEF, 2005) |
| | Available phosphorous ($P_2O_5$) | AOAC (2012) |
| | Available potassium ($K_2O$) | AOAC (2012) |
| | VFA | Distillation method (APHA/AWWA/WEF, 2005) |
| | pH | pH meter<br>(Sevengo, Metter Toledo, USA) |
| | Phenol | Direct photometric method (5530-D) (APHA/AWWA/WEF, 2005) |
| Gas product | $CO_2$, $CH_4$, $O_2$, and $N_2$ | Gas chromatograph instrument<br>(GC 7890A, Agilent, USA) equipped with FID detector |
| | $H_2S$ and CO | Multiple gas measuring device with infrared sensors<br>(Multitec 540, Sewerin) |
| | Total volatile organic carbon (VOC) | VOC analyzer<br>(MiniRAE 2000, RAE systems, USA) |
| | VOCs composition | Gas chromatography-mass spectrometry (GC-MS 5975C, Agilent, USA) |

### 3.7.2 Normalized energy yield

In order to determine the optimum conditions, it is useful to compare energy content of the produced hydrochar and hydrochar yield as the normalized energy yield. Hydrochar yield (%) is the percentage of dry weight produced hydrochar per dry initial feedstock (He et al., 2013), as shown in Equation (3.1). The normalized energy yield (MJ/kg-FS) is defined as "the energy of the produced hydrochar per mass of dry initial feedstock" (Li et al. 2013), as shown in Equation (3.2).

$$Hydrochar\ yield = \frac{mass\ of\ hydrochar\ x\ 100}{mass\ of\ dry\ initial\ feedstock} \tag{3.1}$$

$$Normalized\ energy\ yield = \frac{energy\ content\ of\ hydrochar\ x\ \ mass\ of\ hydrochar}{mass\ of\ dry\ initial\ feedstock} \tag{3.2}$$

### 3.7.3 Energy balance

With respect to energy balance, the thermodynamic boundaries were considered into the HTC reactor (Figure 3.3) and the HTC process (Figure 3.4), the energy balances could be determined by:

HTC reactor

*Energy input from electricity heating* = *Energy required for HTC operation* + *Energy losses* (3.3)

HTC process

*Energy required for HTC operation* (Eq. 3.3) + *Energy required for dewatering* + *Energy required for drying* + *Energy of FS*
= *Energy of products* + *Heat of reaction* + *Energy losses* (3.4)

Actual energy input from the electricity heating during the HTC operation of these experiments was measured by a watt-hour meter (Mitsubishi, Thailand). The energy required for the HTC operation was determined by Equation (3.5). Energy losses can be occurred mainly due to heat transferring to environments and heating HTC reactor body. The energy loss between the surface of the heater and environments is appeared due to convection and radiation, which was calculated using Equation (3.10) and (3.11), respectively (ASHRAE, 1989). Equation (3.12) was used for calculating energy loss due to heating reactor body.

Figure 3.4 showed a flow diagram of energy balance of the HTC process. Energy inputs to the HTC process, including energy required for the HTC operation, dewatering by vacuum filtration, drying hydrochar and energy of FS, were determined using Equations (3.5), (3.6), (3.7) and (3.8), respectively. Energy outputs included the energies of the products (hydrochar, filtrate and gas) and heat of HTC reaction can be calculated using Equation (3.8) and (3.9), respectively, while energy losses occurred during the cooling and drying processes were determined using Equation (3.5) and (3.7), respectively.

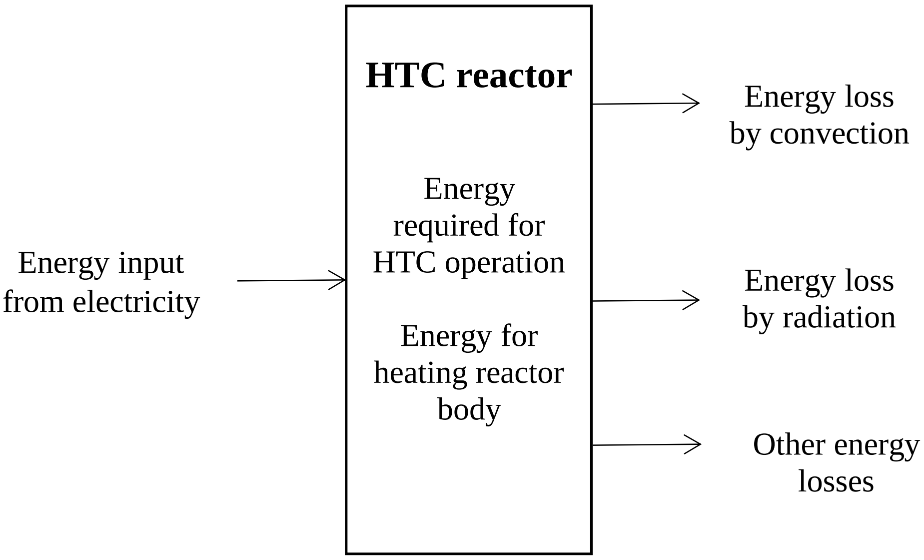


Figure 3.3 Energy balance for HTC reactor

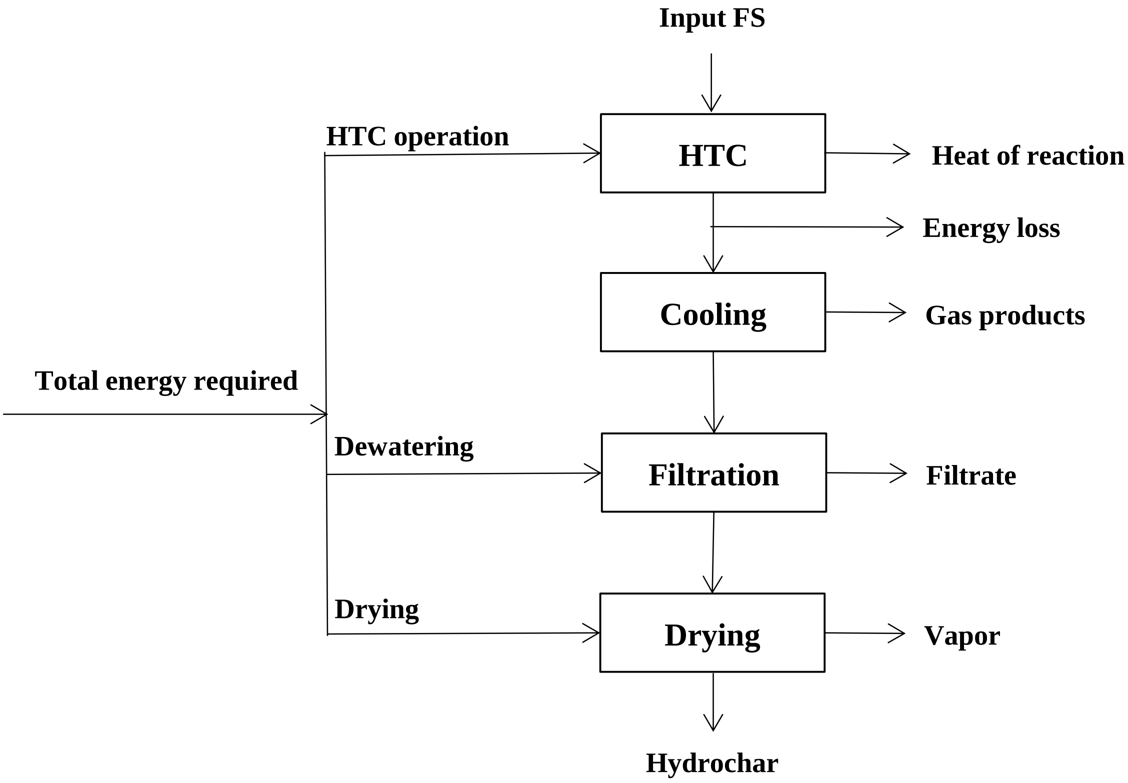


Figure 3.4 Energy balance for HTC process

Equations:

$$E_{required,\ HTC} = M \text{ x } W \text{ x } (C_{p,W} \text{ x } \Delta T) + [M \text{ x } (1\text{-}W)] \text{ x } C_{p,M} \text{ x } \Delta T + [E_{com} \text{ x } t] \tag{3.5}$$

$$E_{dewater} = P \text{ x } t \tag{3.6}$$

$$E_{dry} = M \text{ x } W \text{ x } [(C_{p,W} \text{ x } \Delta T) + \Delta H_{vap}] + [M \text{ x } (1\text{-}W)] \text{ x } C_{p,M} \text{ x } \Delta T \tag{3.7}$$

$$E_{substrate} = E_{content} \text{ x } M_{substrate} \tag{3.8}$$

$$E_{reaction} = E_{heat} \text{ x } M_{VM} \tag{3.9}$$

$$E_{convection} = h \text{ x } s \text{ x } (T_s - T_a) \tag{3.10}$$

$$E_{radiation} = \sigma \text{ x } s \text{ x } \varepsilon \cdot (T_s^{\ 4} - T_a^{\ 4}) \tag{3.11}$$

$$E_{loss,\ reactor} = M_{reactor} \text{ x } C_{p,reactor} \text{ x } \Delta T \tag{3.12}$$

Notations:

| | |
|---|---|
| $C_{p,M}$ | is the heat capacity of input material (kJ/kg/°C) |
| $C_{p,W}$ | is the heat capacity of water (4.186 kJ/kg/°C) |
| $C_{p,reactor}$ | is the heat capacity of reactor body (kJ/kg°C) |
| $E_{com}$ | is the energy consumption rate (kJ/min) |
| $E_{content}$ | is the energy content of the input or product substrates (MJ/kg) |
| $E_{convection}$ | is the energy loss to the environments by convection (W) |
| $E_{dewater}$ | is the energy required for vacuum filtration of slurry from HTC process (kJ) |
| $E_{dry}$ | is the energy required for drying the wet FS from initial temperature to 105 °C (kJ) |
| $E_{heat}$ | is the heat of HTC reaction (MJ/kg) |
| $E_{loss,\ reactor}$ | is the energy loss for heating reactor body (kJ) |
| $E_{reaction}$ | is the energy released from HTC reaction (kJ) |
| $E_{radiation}$ | is the energy loss to the environments by radiation (W) |
| $E_{required,\ HTC}$ | is the energy required for HTC process to heat FS from the initial temperature to the operating temperature (kJ) |
| $E_{substrate}$ | is the energy of the input or product substrates (kJ) |
| $h$ | is the convection coefficient (W/m$^2$K) |
| $M$ | is the mass of input material (kg) |
| $M_{reactor}$ | is the mass of HTC reactor body (kg) |
| $M_{substrate}$ | is the mass of the input or product substrates (kg) |
| $M_{VM}$ | is the mass of volatile matter content in FS (kg) |
| $P$ | is the power of vacuum pump (W) |
| $s$ | is heater surface (m$^2$) |
| $T_a$ | is the air temperature (K) |
| $T_s$ | is the heater temperature (K) |
| $t$ | is reaction time (h) |
| $W$ | is the moisture content in FS (%wt) |
| $\Delta H_{\text{vap}}$ | is the latent heat for vaporization of water (2,260 kJ/kg) |
| $\Delta T$ | is temperature difference (°C) |
| $\varepsilon$ | is the emissivity of the surface |
| $\sigma$ | is the Stefan-Boltzman constant (5.67 ×10$^{-8}$ W/m$^2$ K$^4$) |

### 3.7.4 Energy efficiency

Regarding to Xu and Lancaster (2008), the net energy efficiency or “energy output/input ratio” is defined as “the ratio of energy of the objective product to the energy input to produce it”, as shown in the Equation (3.13). For simplification of the energy efficiency calculation, the following assumptions are made: (1) the feedstock used is law FS of zero energy value, (2) the heat loss of the reactor was negligibly small, and (3) the energy consumption by the experimental operations (e.g., electricity supply to control panel, etc.) were negligible.

$$Energy\ efficiency = \frac{energy\ content\ of\ product \times mass\ ofproduct}{energy\ input} \qquad (3.13)$$

### 3.7.5 Reaction kinetics

A typical HTC reaction is as follow:

$$\text{FS} \xrightarrow{\text{HTC}} \text{Hydrochar + By-product (liquid and gas)} \qquad (3.14)$$

To understand the reaction kinetics of FS degradation in the HTC process, the first-order reaction and Arrhenius equation were determined considering VM in the FS as a substrate. The reaction rate of FS degradation depends on the conversion of substrate (VM in the FS) and reaction time which can be expressed as the first-order differential rate equations (Equation (3.14) and (3.15)). The reaction rate constants, depending on the temperatures, can be expressed as the Arrhenius equation (Equation (3.16)).

Equations:

$$r = -\frac{dC_t}{dt} = kC_t \qquad (3.15)$$

$$ln\frac{C_i}{C_t} = kt \qquad (3.16)$$

$$k = Ae^{-\frac{E_a}{RT}} \qquad (3.17)$$

Notations:

| | |
|---|---|
| $A$ | is the pre-exponential factor |
| $C_i$ | is the mass of VM in the initial FS (dry weight) |
| $C_t$ | is the mass of VM in the produced hydrochar at reaction time ($t$) |
| $E_a$ | is the activation energy |
| $k$ | is the reaction rate constant |
| $r$ | is the reaction rate |
| $R$ | is the gas constant (8.314 J/mol.K) |
| $t$ | is the reaction time |
| $T$ | is the temperature (K) |

# Chapter 4

# Results and Discussion

## 4.1 Conventional HTC

In the preliminary experiments, effects of process parameters such as moisture content of FS, temperature and reaction time on energy content of the produced hydrochar and hydrochar yield were investigated. Results of these experiments were also used to optimize the conventional HTC process conditions, to provide mass and energy balances and to develop a mathematical model which could estimate energy content of the produced hydrochar.

### 4.1.1 Effects of process parameters

#### 4.1.1.1 Effects of moisture content

Effects of moisture content on energy content of the produced hydrochar were firstly investigated by conducting HTC of the FS samples at the moisture contents of 70, 80, 90, and 95%, while the temperature and reaction time were maintained at 220 °C and 5 h, respectively. Under these operating conditions, the pressure inside the HTC reactor was measured to be about 30 bar. The results from three replicates of batch experiments shown in Figure 4.1 (Appendix B-1) indicated the significance of moisture content on energy content of the produced hydrochar ($p \leq 0.05$). The relatively high energy contents of about 19.5 and 19.0 MJ/kg could be obtained, when the moisture contents were varied at 80 and 90%, respectively.

According to Funke and Ziegler (2010), the moisture content in FS acts not only as a solvent, but also serves as a catalyst for carbonization, facilitating hydrolysis, ionic condensation, and bond cleavage at elevated temperatures. However, the energy content of the produced hydrochar was decreased to about 17.6 MJ/kg when the moisture content was reduced to 70%, probably because of insufficient water as a catalyst for various reactions in the HTC process. Because water acts predominantly as a solvent, giving a low concentration of the hydrolyzed products which generally results in a decreased reaction rate, at the 95% moisture content, the energy content of the produced hydrochar was also decreased to about 18.0 MJ/kg.

With respect to hydrochar yield, Figure 4.1 shows that HTC fed with higher moisture contents of FS could generate lower hydrochar yields because the high amount of water (acting as a solvent) increased solubility of the FS, hydrolyzed product (glucose or fructose) and intermediate products (HMF and furfural-like compounds), resulting in less hydrochar formation. However, the hydrochar yields of 65-80% were found comparable with those of the other studies (Mumme et al., 2011; Li et al., 2013), the remaining portions were in mostly liquid by-products and trace amount of gases.

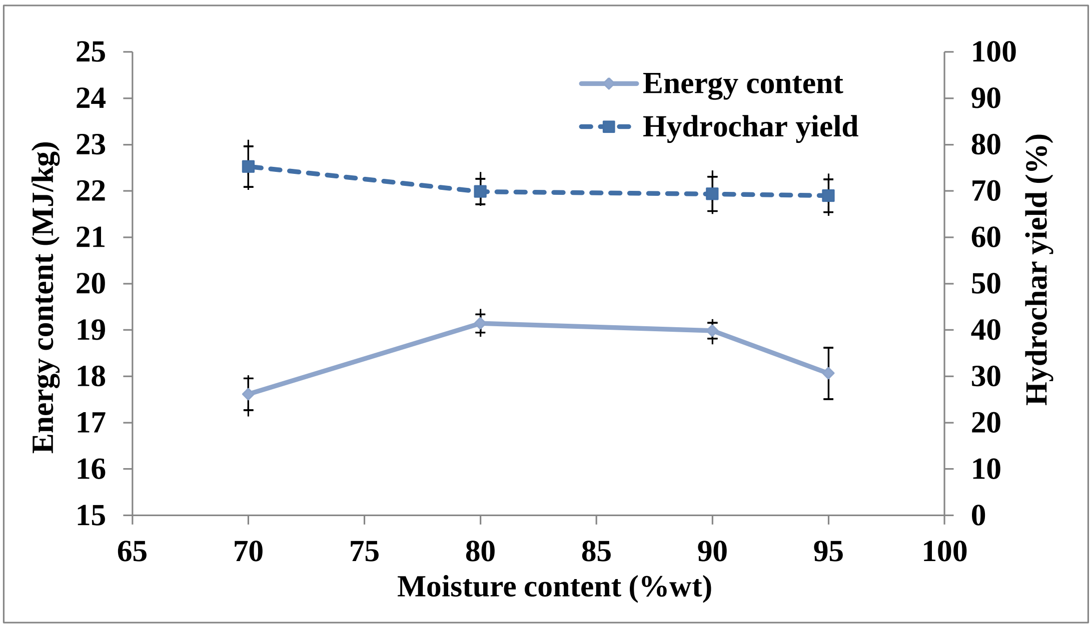


**Figure 4.1 Energy contents and hydrochar yields at various moisture contents, operating at temperature of 220 °C and reaction time of 5 h**

### 4.1.1.2 Effects of temperature and reaction time

The effects of temperature and reaction time on energy content of the produced hydrochar are shown in Figure 4.2 (Appendix B-1). The highest energy content of 20.3 MJ/kg could be achieved at the temperature of 250 °C and reaction time of 10 h, while the lowest energy content of hydrochar was found at the temperature and reaction time of 180 °C and 0.5 h, respectively. These energy contents were comparable with the results of Escala et al. (2013) who found hydrochar produced from sewage sludge with energy contents of 18.2-19.1 MJ/kg.

In general, increasing the temperature in the HTC reactor would result in more dehydration of the hydrolyzed products which could produce HMF. The higher energy content of HMF (22.1 MJ/kg) compared to FS (13.5-14.1 MJ/kg) and hydrolyzed product (glucose is 15.6 MJ/kg) may increase the overall energy content of the produced hydrochar (Kambo and Dutta, 2015). From these experimental results, increasing temperatures from 180 to 220 °C and from 220 to 250 °C resulted in about 10% and 4% increases in the energy contents of the produced hydrochar, respectively. The effects of temperature on the energy content of the produced hydrochar were previously reported in the literatures for the other substrates such as sewage sludge, coconut fibre, eucalyptus leaves, cellulose, and empty fruit bunches (Danso-Boateng et al., 2013; Liu et al., 2013b; Lu et al., 2013; Parshetti et al., 2013).

According to Titirici (2013), the typical operating temperatures of HTC are in the range 130-250 °C. At higher temperatures up to 350 °C, hydrothermal liquefaction could take place (Kruse et al., 2013) resulting in generation of more liquid and gas by-products and consequently, less hydrochar yield (<45%) (Liu et al., 2013b). Therefore, the HTC process should not be operated at temperatures more than 250 °C because it would result in less hydrochar yields and high operation costs.

With respect to reaction time, it can be seen from Figure 4.2 that increasing reaction times led to increased energy contents, especially when operating the HTC at 250 °C, which had the statistically significant *p* value $\leq 0.05$. At a temperature of 250 °C, energy contents of the initial dried FS were increased to 18.2, 18.8, 19.7, and 20.3 MJ/kg in the hydrochar at HTC reaction times of 0.5, 1.0, 5.0, and 10.0 h, respectively (Figure 4.2).

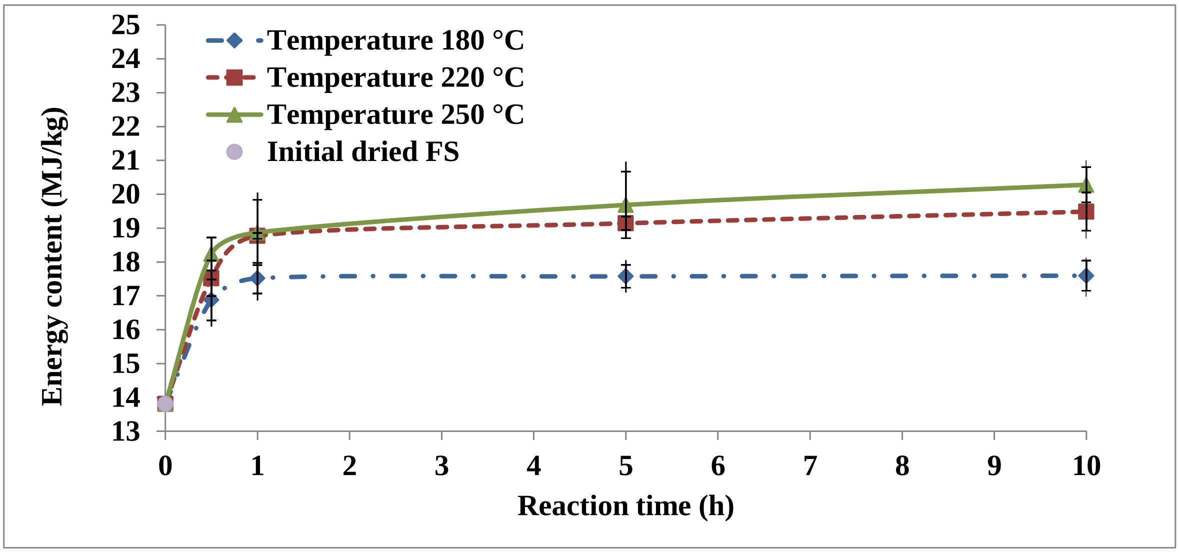


**Figure 4.2 Energy contents at various temperatures and reaction times, operating at moisture content of 80%**

### 4.1.2 Optimum conditions

In order to determine the optimum conditions, the normalized energy yields (defined in section 3.7.2) at various moisture contents were analyzed and showed the results in Figure 4.3. It indicated that moisture content of 80% was found to be optimum in producing the highest normalized energy yield of 13.4 MJ/kg-FS. The normalized energy yields of the produced hydrochar at various temperatures and reaction times, shown in Figure 4.4, were found to decrease with increasing reaction time, but the temperature of 250 °C still produced a higher normalized energy yield than those at 220 °C and 180 °C. It can be deduced from the results of Figure 4.4 that the reaction time of 5 h was optimum in producing the highest normalized energy yield of 13.8 MJ/kg-FS. As reported earlier that operating the HTC temperatures more than 250 °C could result in less hydrochar yields and more energy consumptions, it can be assumed that the temperature of 250 °C was optimum for the HTC in producing the highest normalized energy yield.

Based on analysis results of the normalized energy yields, it can be concluded that the optimum conditions for the conventional HTC of FS were: moisture content of 80%, temperature of 250 °C, and reaction time of 5 h. To verify these optimum conditions, 3 replicates of the conventional HTC experiments using different FS samples were conducted. These experimental results showed energy contents of the produced hydrochar and hydrochar yield to be 19.4, 19.9 and 19.3 MJ/kg and 72.5, 72.1 and 70.2%, respectively, while the normalized energy yields of about 14.0 MJ/kg-FS were achieved.

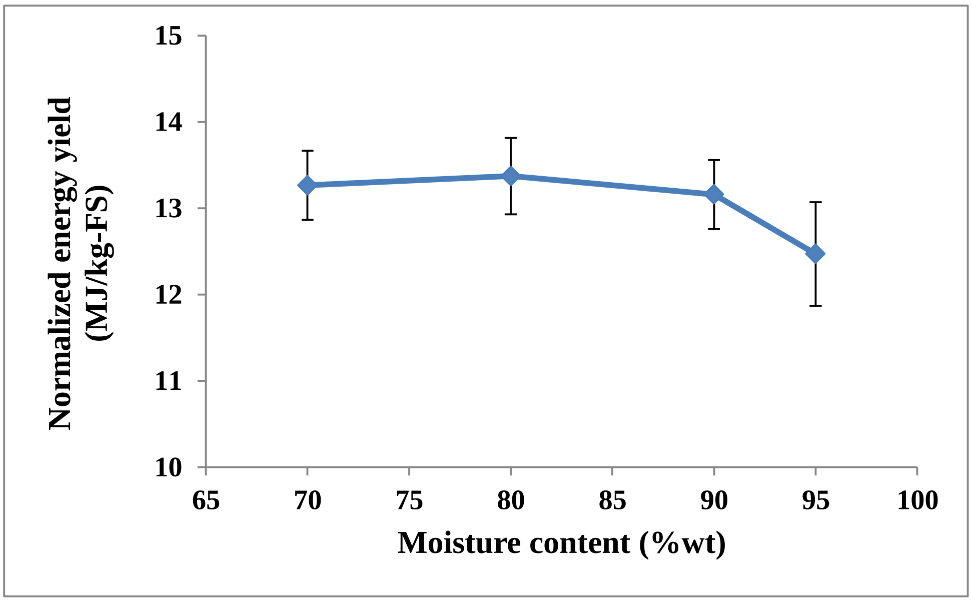


Figure 4.3 Normalized energy yields at various moisture contents, operating at temperature of 220 °C and reaction time of 5 h

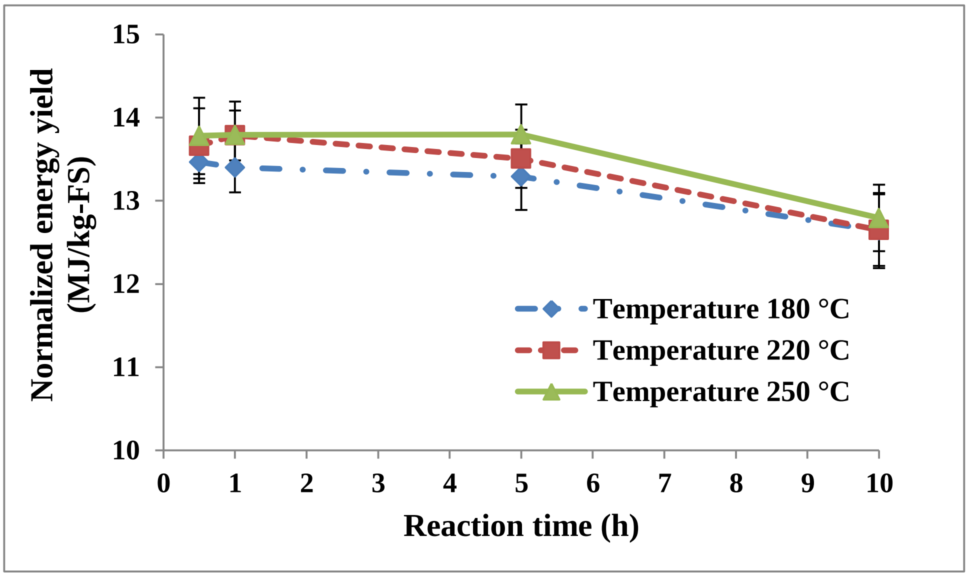


Figure 4.4 Normalized energy yields at various temperatures and reaction times, operating at moisture content of 80%

### 4.1.3 Mass balance and carbon distribution

Mass balance and carbon distribution of the FS were carried out at the optimum HTC conditions, as illustrated in Figure 4.5. The initial dried FS consisting of carbon of 38.4%wt and the other elements (e.g. hydrogen, nitrogen, oxygen, and sulfur) of 61.6%wt was hydrothermally carbonized into the hydrochar, liquid and gas by-products of 69.9%wt, 20.7%wt and 9.4%wt, respectively. The carbon distribution indicated a significant proportion of carbon in the initial dried FS retained within the hydrochar of 28.7%wt. The rest of the carbon was shifted into either the liquid or gas by-products. TOC concentration of the liquid samples was used to calculate the carbon content in the liquid by-product which was 6.9%wt. From the mass balance analysis, a small fraction of carbon in the initial dried

FS was transferred into gas by-products of 2.8%wt, which was predominantly $CO_2$. High carbon efficiency of the HTC process was obtained and discussed further in section 4.4.1.5.

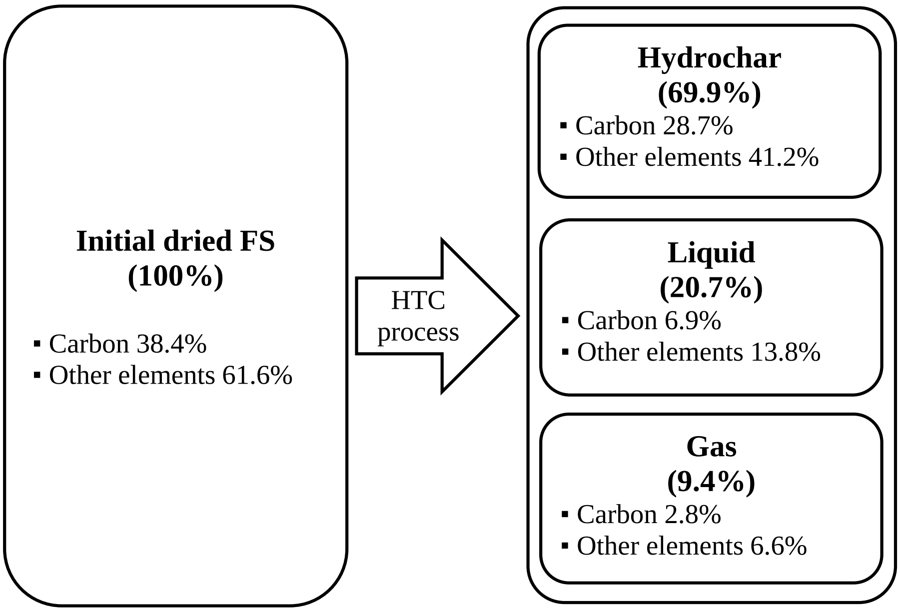


**Figure 4.5 Mass balance and carbon distribution for conventional HTC of FS**

### 4.1.4 Energy balance

Energy balance of the conventional HTC reactor showed in Figure 4.6. It can be seen that only about 14% of energy input was used for the HTC operation while energy losses due to heat transferring to the environments and heating reactor body were about 78% and 3% of energy input, respectively. To minimize these energy losses, insulation should be well installed and heating and cooling processes should be separated to reduce the quantity of heat that will be absorbed by the reactor body. The energy balance of the conventional HTC process was further discussed compare to the two-stage HTC process in the section 4.2.6.

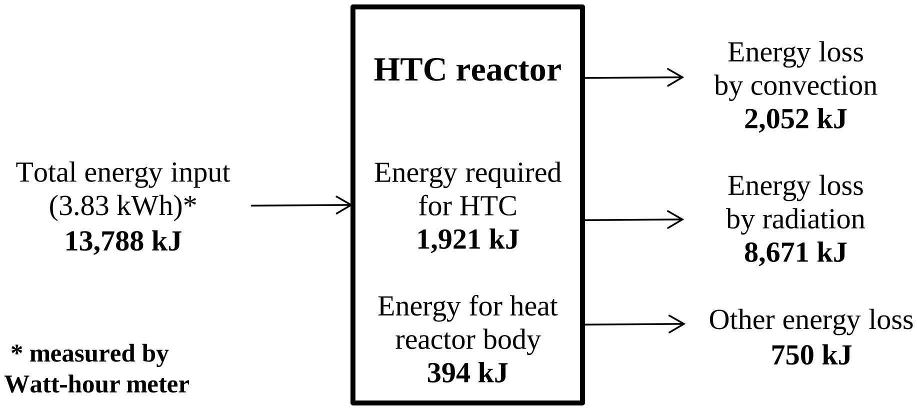


**Figure 4.6 Energy balance for conventional HTC reactor**

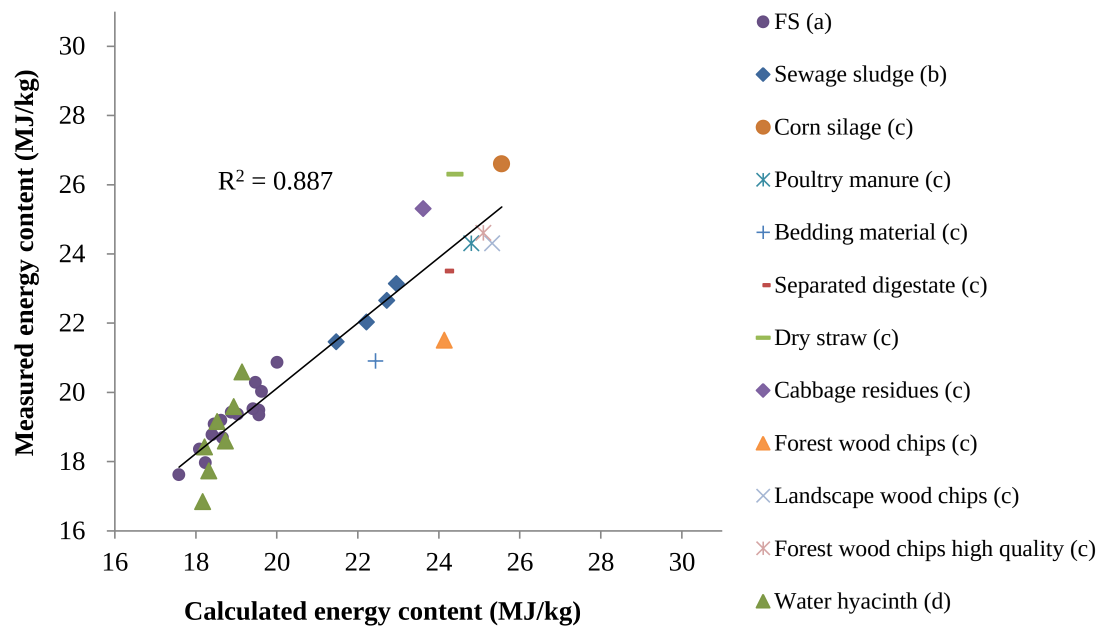
### 4.1.5 Modeling of HTC of FS

In order to develop a mathematical model which could estimate energy content of the produced hydrochar from the HTC of FS, a multiple linear regression analysis was conducted using the experimental data obtained from this study. The statistical analysis using Minitab-17 software showing a linear regression equation was

$$E_{hydrochar} = f\,(26.8 + 0.020T + 0.106t - 0.131W - 0.014VS) \qquad (4.1)$$

where $E_{hydrochar}$ is the energy content of the produced hydrochar (MJ/kg); $T$ is the temperature (°C); $t$ is the reaction time (h); $W$ is the moisture content of feedstock (%wt); $VS$ is the volatile solid concentration of feedstock (g/L); and $f$ is the correction factor for energy content of the dry initial feedstock ($E_{feedstock}$), which was found to be $0.07E_{feedstock}$. Analysis of variance (ANOVA) showed Equation (4.1) has the correlation coefficient ($R^2$) of 0.910 at the 95% confidence level.

Equation (4.1) was validated with 15 additional HTC experiments using FS with different HTC process conditions, and with literature data of HTC using other biomass as feedstock (Danso-Boateng et al., 2013; Gao et al., 2013; Oliveira et al., 2013). Figure 4.7 indicates that Equation (4.1) fits well with these data, having an $R^2$ value of 0.887. It should be noted that Equation (4.1) is applicable for predicting energy content of hydrochar produced by the HTC process operated within the conditions employed in this study. In addition, it could be useful for the HTC operators to adjust some operating parameters to achieve the desired energy content for the produced hydrochar. Further validations of Equation (4.1) with pilot- or full-scale HTC reactors treating FS or other biomass materials are recommended.



(a) Results of additional experiments, (b) Danso-Boateng et al. (2013), (c) Oliveira et al. (2013), (d) Gao et al. (2013)

**Figure 4.7 Comparison of calculated and measured energy contents of produced hydrochar from HTC of FS and other biomass**

## 4.2 Two-Stage HTC

In the experiments of two-stage HTC, effects of process parameters such as temperatures and reaction times of hydrolysis and carbonization stages on energy content of the produced hydrochar and hydrochar yield were investigated. The results of these experiments were also used to optimize the two-stage HTC process conditions and to provide mass and energy balances. Energy efficiency of the two-stage HTC was compared with other thermal conversion processes. The hydrochar formation pathway through two-stage HTC was proposed.

### 4.2.1 Effects of process parameters

Based on the experimental results according to RSM (Appendix C), surface and contour plots of the energy contents of the produced hydrochar vs. the process parameters were developed as shown in Figure 4.8. The ANOVA showed *p*-values of process parameters such as the hydrolysis temperature, hydrolysis reaction time, carbonization temperature, and carbonization reaction time to be 0.62, 0.01, 0.05, and 0.30, respectively, which indicated the significances of the hydrolysis reaction time and carbonization temperature on the energy content of the produced hydrochar. The effects of temperatures and reaction times in hydrolysis and carbonization stages on energy content of the produced hydrochar and optimum conditions of the two-stage HTC are discussed in the following sections.

#### 4.2.1.1 Hydrolysis stage

Process parameters of the hydrolysis stage in the two-stage HTC include temperature and reaction time. Figure 4.8(a) indicated that increasing the hydrolysis reaction time from 20 to 200 min resulted in the increased energy content of the produced hydrochar. The energy contents of the produced hydrochar were greater than 20 MJ/kg at hydrolysis temperatures and reaction times of 150-175 °C and 150-200 min, respectively. Analysis results of VM and FC contents in the produced hydrochar during the two-stage HTC operation, shown in Figure 4.9, indicated that the VM contents were reduced from 60% in the initial FS to about 50% in the produced hydrochar at the hydrolysis reaction times of ≥150 min, while the FC contents were relatively constant at all the hydrolysis reaction times.

At the hydrolysis temperature range of 150-180 °C, lignocellulosic biomass as VM content in FS was hydrolyzed. Operating the hydrolysis stage at reaction times longer than 150 min might allow more production of oligomers and glucose, which would be subsequently dehydrated and polymerized in the carbonization stage giving the products such as HMF, other soluble products and hydrochar (Sevilla and Fuertes, 2009).

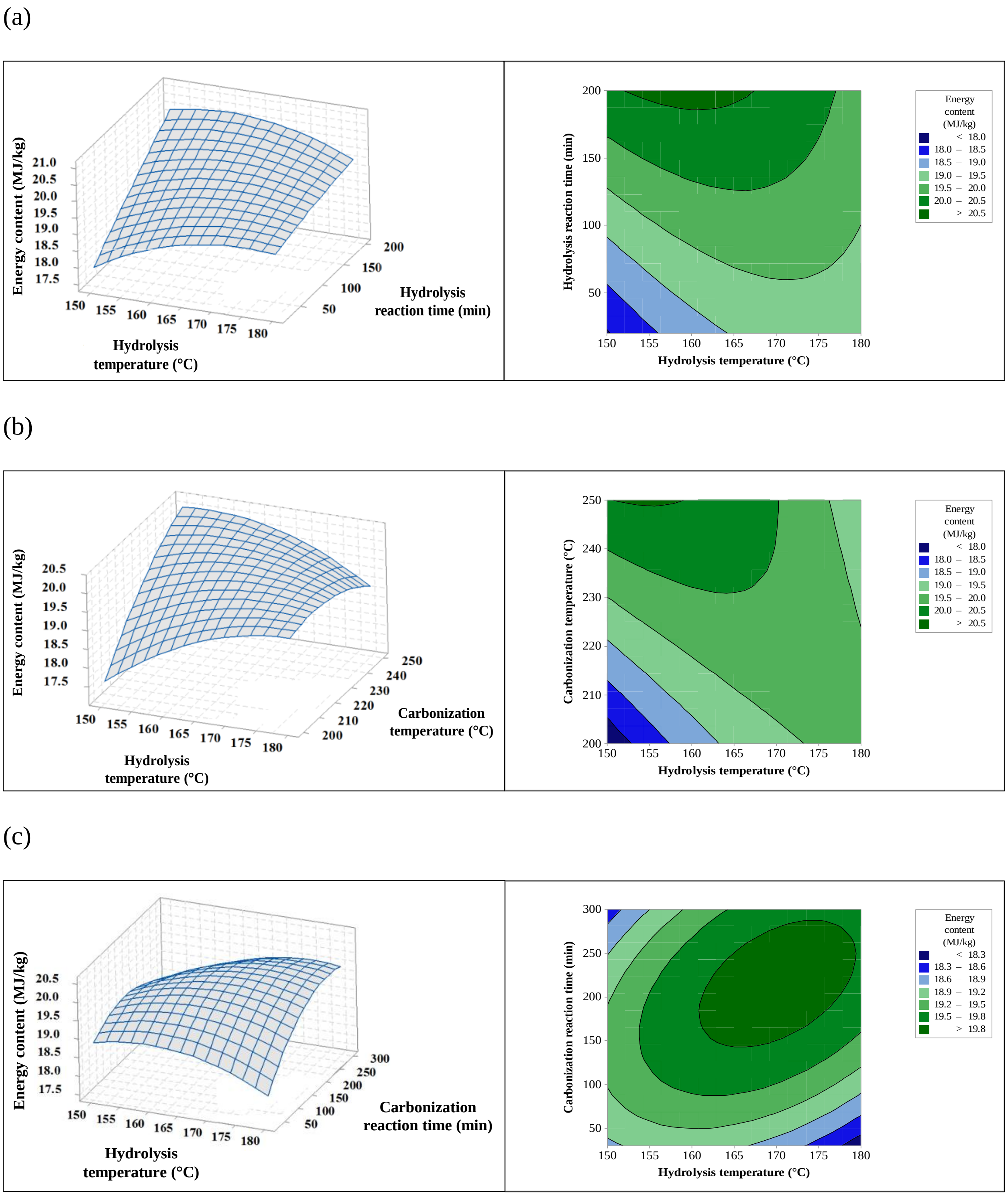


**Figure 4.8 Surface and contour plots of energy content vs. process parameters; hydrolysis temperature, hydrolysis reaction time, carbonization temperature, and carbonization reaction time**

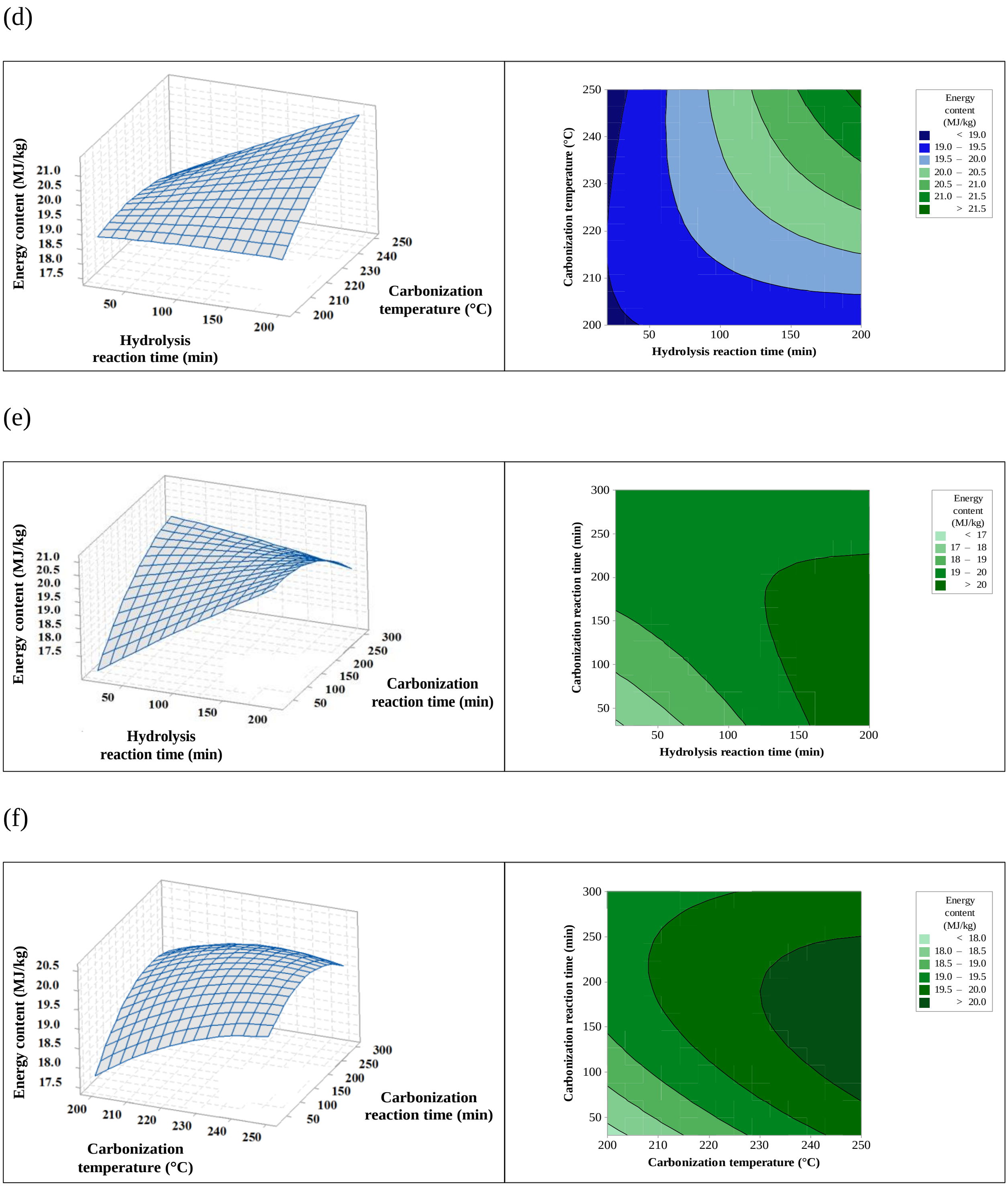


**Figure 4.8 Surface and contour plots of energy content vs. process parameters; hydrolysis temperature, hydrolysis reaction time, carbonization temperature, and carbonization reaction time (cont.)**

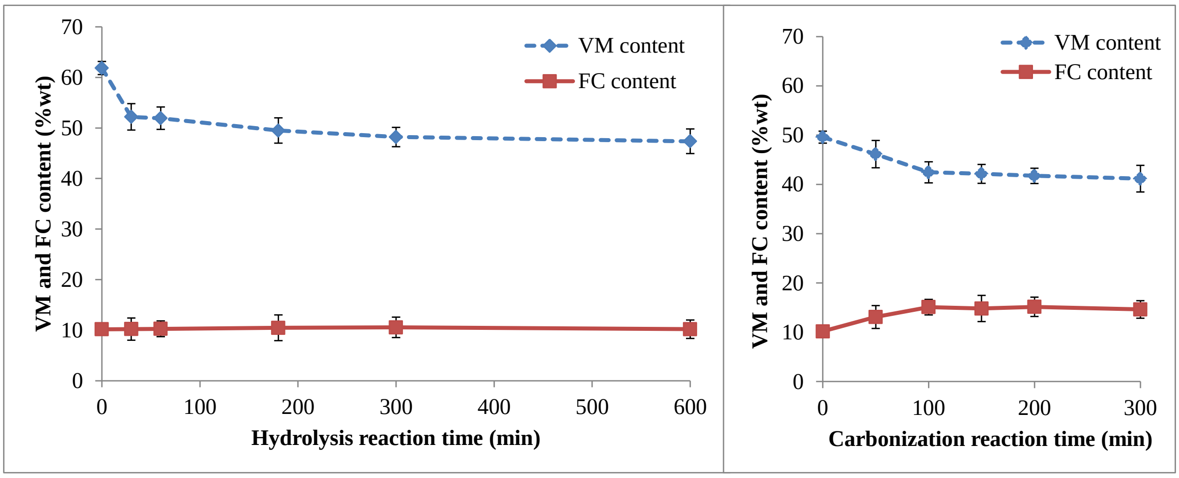


**Figure 4.9 VM and FC contents in hydrochar during two-stage HTC operated at hydrolysis and carbonization temperatures of 170 and 215 °C, respectively**

### 4.2.1.2 Carbonization stage

Effects of the carbonization temperature and reaction time on energy content of the produced hydrochar are shown in Figure 4.8(f). It can be seen that increasing the carbonization temperature from 200 to 250 °C resulted in the increased energy contents of the produced hydrochar. Figure 4.8(f) indicates the energy contents of the produced hydrochar to be greater than 20 MJ/kg at the carbonization temperature range of 230-250 °C. With respect to the carbonization reaction time, energy contents of the produced hydrochar tended to decrease with increasing the reaction time. If the energy contents of the produced hydrochar were expected to be greater than 20 MJ/kg, the carbonization reaction times should be 100-250 min.

At the carbonization stage, the VM contents were further degraded from 50% to about 40%, while the FC contents in the produced hydrochar were increased from 10% to about 15%, as showed in Figure 4.9, which were attributed to the carbonization of the hydrolyzed VM. It could be hypothesized that reduction of the VM was due to the hydrolysis reaction and the hydrolyzed products were subsequently dehydrated and polymerized to become hydrochar, soluble products and gases. The increase of FC and decrease of VM contents during the two-stage HTC could result in the increased energy content of the produced hydrochar.

### 4.2.2 Optimum conditions

In this study, the optimum conditions of the two-stage HTC were also based on the normalized energy yield. It could be deduced from the results in Figure 4.10 that optimum conditions to produce the highest normalized energy yields of 13.9 MJ/kg-FS were: hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C, and carbonization reaction time of 100 min. To verify these optimum conditions, 3 replicates of the two-stage HTC experiments using different FS samples were conducted. These experimental results showed energy contents of the produced hydrochar and hydrochar yield to be 19.7, 19.9 and 20.8 MJ/kg and 72.8, 70.7 and 71.2%, respectively, while the normalized energy yields of about 14.4 MJ/kg-FS were achieved. Further evaluations of these optimum conditions with pilot- or full-scale two-stage HTC reactors treating FS or other biomass materials are recommended.

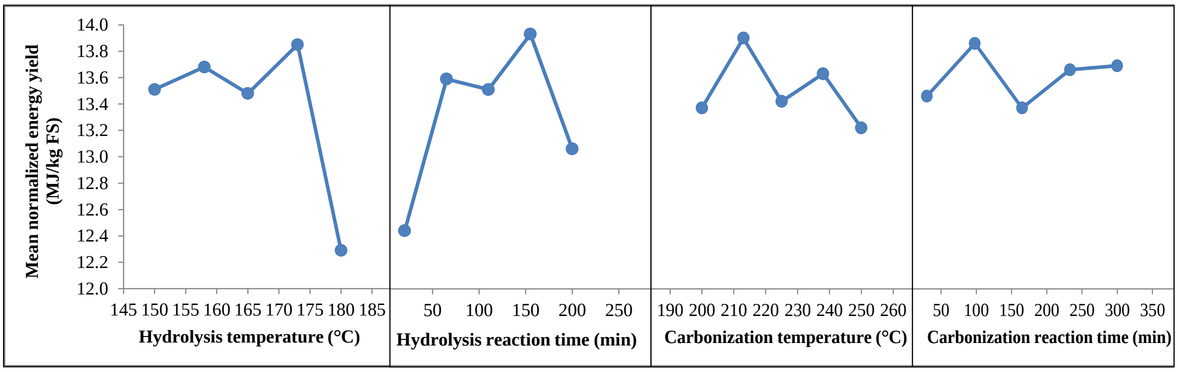


**Figure 4.10 Mean normalized energy yields at each process parameters of two-stage HTC of FS**

### 4.2.3 Mass balance and carbon distribution

Mass balance and carbon distribution of the two-stage HTC, shown in Figure 4.11, were carried out at the optimum conditions indicated in section 4.2.2. The carbon content of the initial FS was 38.1%wt and the other elements (e.g. hydrogen, nitrogen, oxygen, and sulfur) were 61.9%wt. The hydrothermally carbonized products, being hydrochar, liquid and gas, were found to be 72.8, 23.7 and 3.5%wt, respectively. The carbon distribution data indicated that 74.6% of carbon in the initial FS (38.1%wt) retained within the hydrochar (28.4%wt). The rest of the carbon was shifted into either the liquid or gaseous products. The carbon content in the liquid product was 7.8%wt of the initial FS which was calculated based on TOC concentrations. From the mass balance analysis, about 5.0% of carbon in the initial FS was transferred into gas products (1.9%wt). High carbon efficiency of the HTC process was obtained and discussed further in section 4.4.1.5.

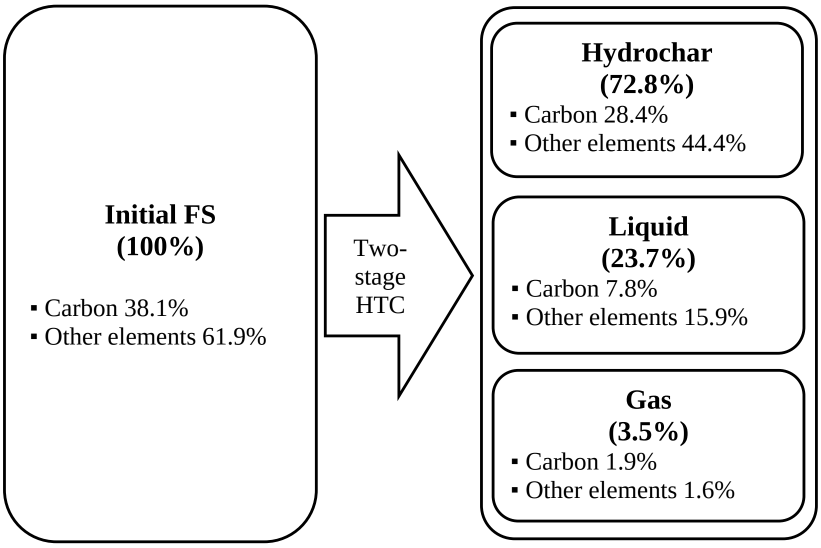


**Figure 4.11 Mass balance and carbon distribution for two-stage HTC of FS**

### 4.2.4 Energy balance

With respect to the energy balance of the two-stage HTC reactor, the results obtained from experiments and calculations (explained in section 3.7.3), illustrated in Figure 4.12 and compared with that of the conventional HTC in Table 4.1. It can be seen that only about 10% of energy input was used for the two-stage HTC operation while energy losses due to heat transferring to environments and heating reactor body were about 80% and 3% of energy inputs, respectively. To minimize these energy losses, insulation should be well installed and heating and cooling processes should be separated to reduce the quantity of heat that will be absorbed by the reactor body. Comparing with the conventional HTC process, the total energy input of the two-stage HTC was about 13% less than the conventional HTC. More comparisons of the two-stage HTC with conventional HTC and other thermal conversion processes were discussed in the section 4.2.6.

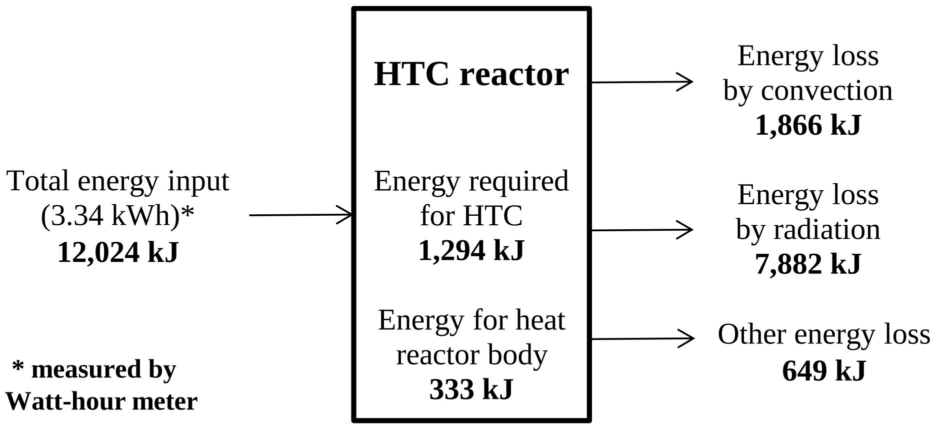


**Figure 4.12 Energy balance for two-stage HTC reactor**

**Table 4.1 Summary of Energy Balances for Conventional and Two-Stage HTC**

| System | Energy | Conventional HTC | Two-stage HTC |
|---|---|---|---|
| HTC reactor | *Energy input*<br>Measured by watt-hour meter | 13,788 kJ | 12,024 kJ |
| | *Energy for HTC operation* | 1,921 kJ | 1,294 kJ |
| | *Energy loss*<br>Energy for heating reactor body<br>Energy loss by convection<br>Energy loss by radiation<br>Other energy loss | 394 kJ<br>2,052 kJ<br>8,671 kJ<br>750 kJ | 333 kJ<br>1,866 kJ<br>7,882 kJ<br>649 kJ |

Note: Based on 1 kg/batch of FS feedstock

### 4.2.5 Hydrochar formation through two-stage HTC

Based on the experimental results obtained from this study and some literatures data on the hydrochar formation mechanisms, the concept of the two-stage HTC and hydrochar formation pathways during the two-stage HTC were proposed in Figure 4.13 and explained in the following section.

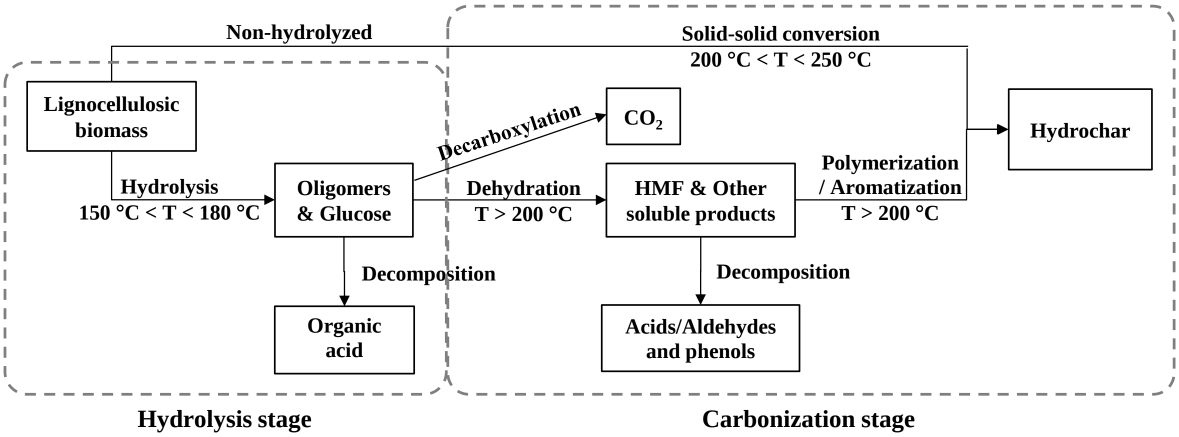


**Figure 4.13 Hydrochar formation mechanisms for two-stage HTC**

***Hydrolysis stage***

In the hydrolysis stage, a lignocellulosic biomass as VM in the FS is thermally hydrolyzed at temperatures of 150-180 °C giving low-molecular weight compounds such as oligosaccharides and glucose (or fructose) including organic acids (Funke and Ziegler, 2010; Sevilla and Fuertes, 2009) which could result in the decrease of pH from 6.8-7.2 in the FS feedstock to 5.5-6.0 in the hydrolyzed products. As earlier mentioned, at the hydrolysis stage, VM contents in the FS were reduced from 60% to about 50%, while the FC contents were relatively constant (Figure 4.9), indicating organic matters in FS were hydrolyzed and carbonization reactions were not occurred at low temperatures.

***Carbonization stage***

At high temperatures of 200-250 °C, the VM contents were further degraded from 50% to about 40% (Figure 4.9), and the carbonization stage takes place. The dehydration reaction of glucose or fructose generates HMF, soluble products (furfural-like compounds), organic acids, aldehydes and phenols (Qi and Xiuyang, 2008; Sevilla and Fuertes, 2009). The subsequent polymerization and aromatization reactions produce hydrochar (Sevilla and Fuertes, 2009). It could be hypothesized that reduction of the VM was due to the hydrolysis reaction and the hydrolyzed products were dehydrated and polymerized to become hydrochar indicated by decreasing hydrogen and oxygen content in the produced hydrochar from 5% to 4% and 19% to 9%, respectively, and increasing the FC contents from 10% to about 15% (Figure 4.9). Some remaining hydrolyzed and dehydrated products were detected in the liquid by-products which could be the organic matters (indicated as TOC and COD concentrations of 17-29 and 29-33 g/L, respectively), organic acids (indicated as VFA concentration of 5 g/L), and phenol (334 mg/L). Simultaneously, $CO_2$ gas (64.1%v) which is the main component in the produced gases could be generated by decarboxylation of the hydrolyzed products during the carbonization stage. In addition, at the carbonization stage, the hydrochar is also formed via the solid–solid conversion of the non-hydrolyzed lignocellulosic biomass (Falco et al., 2011). The SEM image in Figure 4.14 evidences that some lignocellusic biomass in the produced hydrochar were not disrupted and its structure was maintained intact.

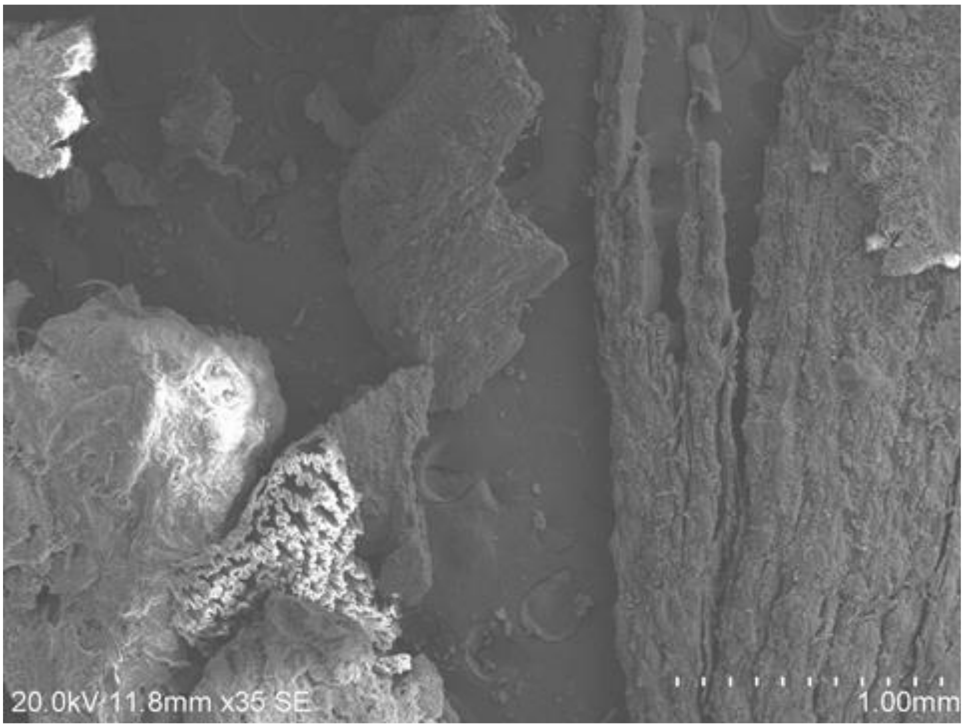


**Figure 4.14 SEM image of hydrochar produced from two-stage HTC of FS**

***Reaction kinetics***

To determine the degradation kinetics of VM in the FS, the first-order reaction and Arrhenius equation were employed, as defined in section 3.7.5. From the experimental results, the reaction rate constants ($k$) at various temperatures were obtained and shown in Figure 4.15. The high $R^2$ values indicated that the degradations of VM in FS were a good fit to the first-order reaction.

From the intercept and slope of the Arrhenius equation in Figure 4.16, $A$ and $Ea$ values were estimated to be 583 $h^{-1}$ and 37 kJ/mol, respectively, within the temperature range of 140-250 °C. A previous study by Reza et al. (2013) reported the *Ea* values of HTC for hemicelluloses and cellulose degradations to be 30 kJ/mol and 73 kJ/mol, respectively. The *Ea* of HTC of FS was comparable to hemicelluloses which could be slow biodegradable carbohydrates contained in the faeces (Lentner et al., 1981) and decomposed under hydrothermal conditions at temperature of 150-250 °C (Liu and Balasubramanian, 2012).

The Arrhenius equation of degradation of VM in the FS during the HTC process could be expressed as follow:

$$k = 583\, e^{-\frac{37}{RT}} \tag{4.2}$$

where $k$ is the reaction rate constant ($h^{-1}$), $T$ is the temperature (K), and $R$ is the gas constant (8.314 J/mol.K). The reaction rate constants of the hydrolysis stage ($k_1$) and carbonization stage ($k_2$) were 0.025 and 0.064 $h^{-1}$, respectively. Because of $k_1$ lower than $k_2$, the hydrolysis reaction time (155 min) was longer than the carbonization reaction time (100 min), at optimum conditions of two-stage HTC.

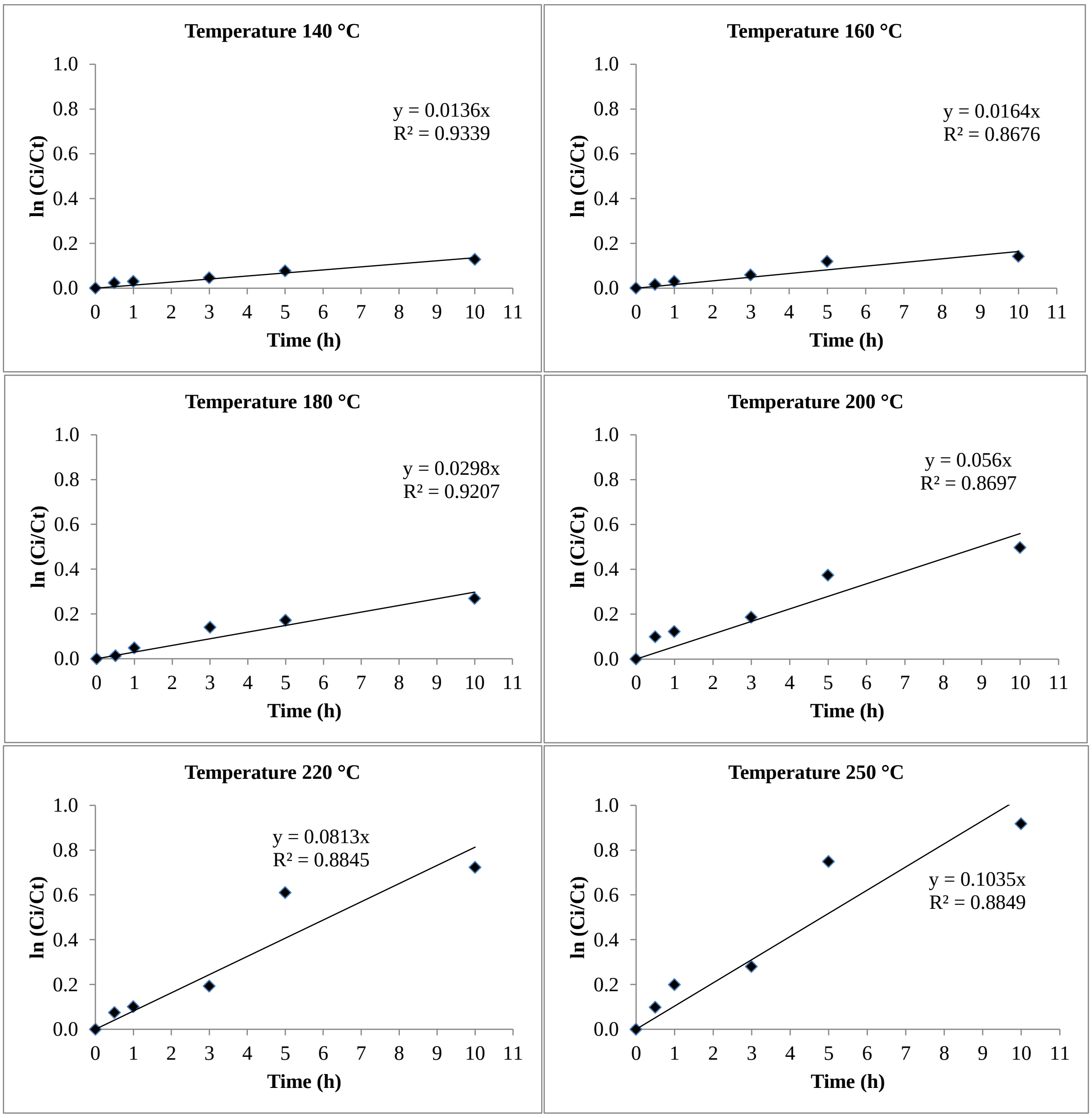


**Figure 4.15 Conversion of VM with reaction times at temperature of 140, 160, 180, 200, 220 and 250 °C**

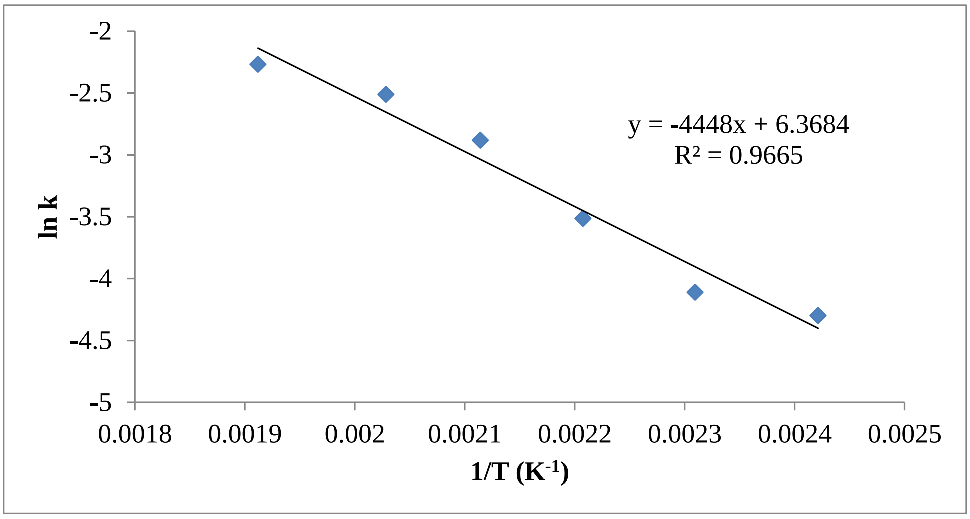


**Figure 4.16 Arrhenius plot of reaction rate constants with temperatures**

### 4.2.6 Comparison to conventional HTC and other thermal conversion processes

This comparison of the experimental results and available information from literatures focuses on the operating conditions and product distribution (Table 4.2), energy requirement (Table 4.3), as well as energy efficiency (Table 4.4) for the thermal conversion processes such as pyrolysis, gasification, conventional HTC and two-stage HTC, with the intent to examine the potential technology options for treating FS and producing valuable products. To more understand in the difference of conventional and two-stage HTC operations, the temperature profiles were displayed in Figure 4.17. It is obviously that the two-stage HTC was operated at lower temperatures and shorter times than conventional HTC.

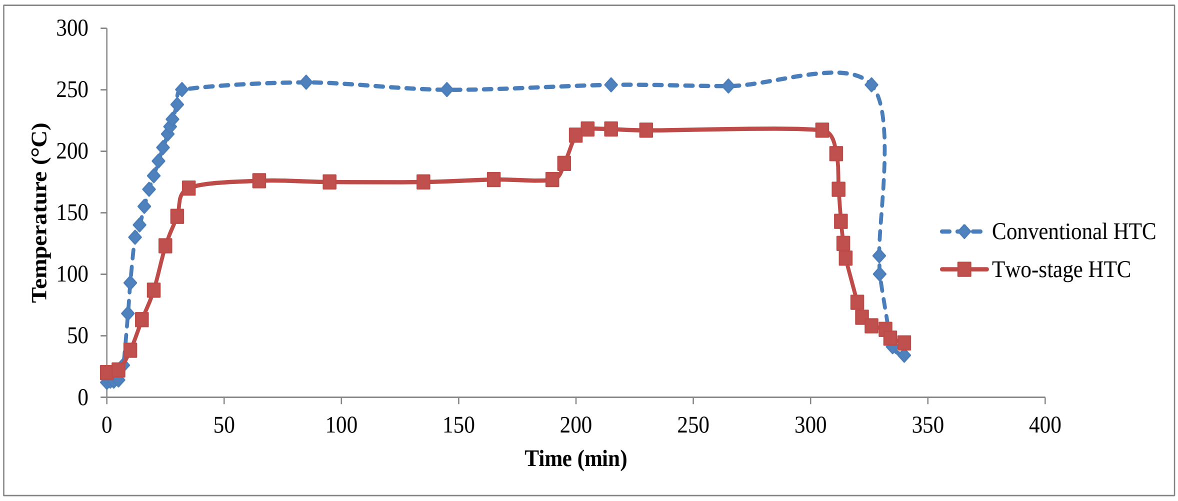


**Figure 4.17 Temperature profiles of conventional HTC operating at temperature of 250 °C and reaction time of 300 min, and two-stage HTC operating at hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C and carbonization reaction time of 100 min**

## Table 4.2 Comparison of Operating Condition, Energy Content and Product Distribution for Thermal Conversion Processes

| Process | Operation | | Feed stock | Product distribution | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Char | | Liquid | | Gas | |
| | | | | Dist. (%wt) | Energy (MJ/kg) | Dist. (%wt) | Energy (MJ/kg) | Dist. (%wt) | Energy (MJ/m$^3$) |
| | Temperature (°C) | Reaction time | | | | | | | |
| Pyrolysis [a,b,c] | 300 -500 | Sec -week | Dry | 12 -35 | 11 -35 | 30 -75 | 10 -35 | 13 -35 | 5 -30 |
| Gasification [b,c] | 800 -1400 | 10 -20 sec | Dry | 10 | NA | 5 | NA | 85 | 2 -20 |
| HTC [b,c] | 180 -250 | 1 -72 h | Wet | 50 -80 | 18 -36 | 5 -20 | NA | 2 -5 | NA |
| HTC of FS [d] | 250 | 300 min | Wet | 70 -73 | 19 -20 | 19 -21 | Not analyzed | 7 -9 | Not analyzed |
| Two-stage HTC of FS [d] | 170 and 215 | 155 and 100 min | Wet | 70 -73 | 20 -21 | 21 -23 | Not analyzed | 3 -7 | Not analyzed |

NA = not available

[a] Depends on process (slow, intermediate and fast)

[b] Libra et al. (2011)

[c] Lu et al. (2012)

[d] Data from this study

In general, the two-stage and conventional HTC processes could be operated at relatively lower temperatures and higher moisture contents of the feedstock than pyrolysis and gasification processes, but operating times of the HTC processes were relatively longer. The main advantage of the HTC processes is to produce hydrochar in the range of 50-80%wt while the pyrolysis yielded only 12-35%wt.

### *Energy content*

Energy contents of the char product from these thermal conversion processes were in the same range of 11-36 MJ/kg (Table 4.2) which were varied according to biomass feedstock and their process conditions. In comparison between the HTC processes, energy contents of the produced hydrochar from the two-stage HTC of FS were slightly higher than the conventional HTC, while hydrochar yields were not different.

### *Energy requirement*

From the experimental results and calculations (explained in section 3.7.3 and Appendix D), the energy balance of the conventional HTC process for treating FS feedstock of 1 kg/batch, operating at the optimum conditions, showed in Figure 4.18. Assuming without heat loss from HTC reactor, the energies required for the HTC operation, dewatering by vacuum filtration, and drying hydrochar were determined using Equations (3.5), (3.6), and (3.7), which were 1,921, 119, and 455 kJ, respectively. Considering 80% moisture content of FS as a feedstock, energy of the FS were 860 kJ. Therefore, total energy input were 3,355 kJ. Hydrochar, liquid and gas yields were found to be 72%, 20% and 8%, respectively. The produced hydrochar of 144 g with the energy content of about 19.5 MJ/kg could be obtained, resulting in the energy of 2,808 kJ, while the energies of liquid and gas products were estimated to be 556 and 69 kJ, respectively. The heat of HTC reaction is -1.6 MJ/kg-cellulose (exothermic reaction) (Libra et al., 2011), thus the energy released from the HTC process was about 192 kJ. Energy losses can be occurred due to heat transferring at the cooling process and heat losing with vapor generated at the drying process, which were found to be 841 and 369 kJ, respectively. The total energy output of about 4,835 kJ was relatively higher than the total energy input of the conventional HTC of FS.

The energy balance of the two-stage HTC process for treating FS feedstock of 1 kg/batch, operating at the optimum conditions, showed in Figure 4.19 and compared with that of the conventional HTC in Table 4.3. Assuming without energy loss from HTC reactor, the energies required for the two-stage HTC operations at hydrolysis and carbonization stages, dewatering at filtration process, and drying hydrochar were determined using Equations (3.5), (3.6), and (3.7), which were 765, 528, 119, and 455 kJ, respectively. Considering 80% moisture content of FS as a feedstock, energy of the FS were 860 kJ. Therefore, total energy input were 2,727 kJ. In the two-stage HTC process, hydrochar, liquid and gas yields were found to be 72%, 24% and 4%, respectively. The produced hydrochar of 144 g with the energy content of about 20.5 MJ/kg could be obtained, resulting in the energy of 2,952 kJ, while the energies of liquid and gas products were estimated to be 667 and 34 kJ, respectively. The energy released from the heat of HTC reaction and the energies lost from the cooling and drying processes were same values as calculated for the conventional HTC process, which were 192, 841 and 369 kJ, respectively. The total energy output of about 5,055 kJ was relatively higher than the total energy input of the two-stage HTC of FS.

Comparing with the conventional HTC, because of the two-stage HTC operating at lower temperatures and shorter reaction times than conventional HTC, the energy required for the two-stage HTC process was about 25% less than the conventional HTC.

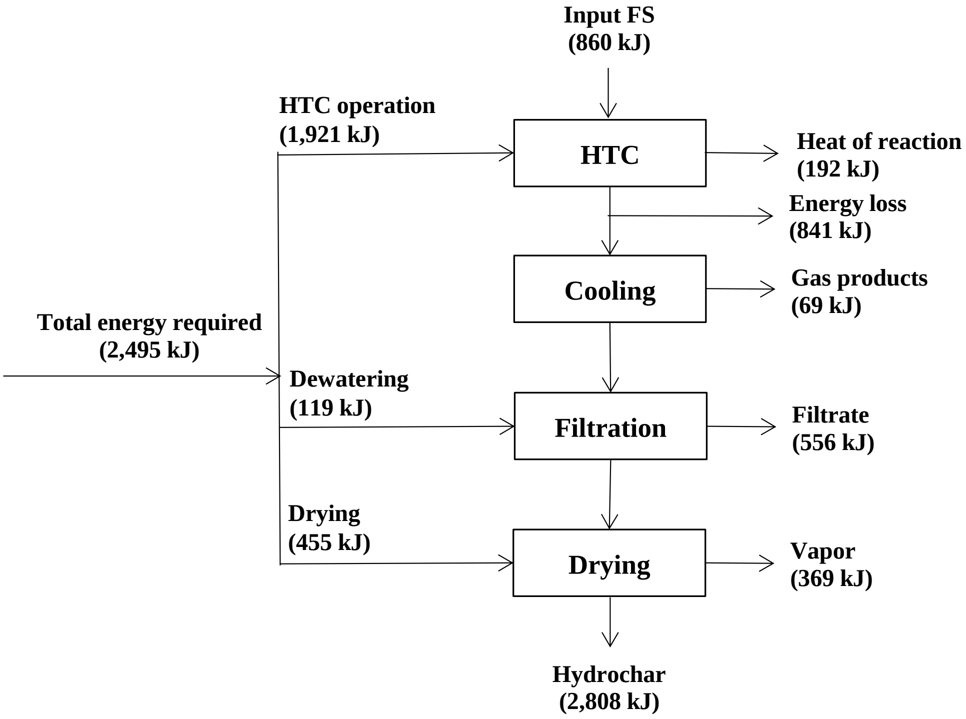


**Figure 4.18 Energy balance for conventional HTC process of FS**

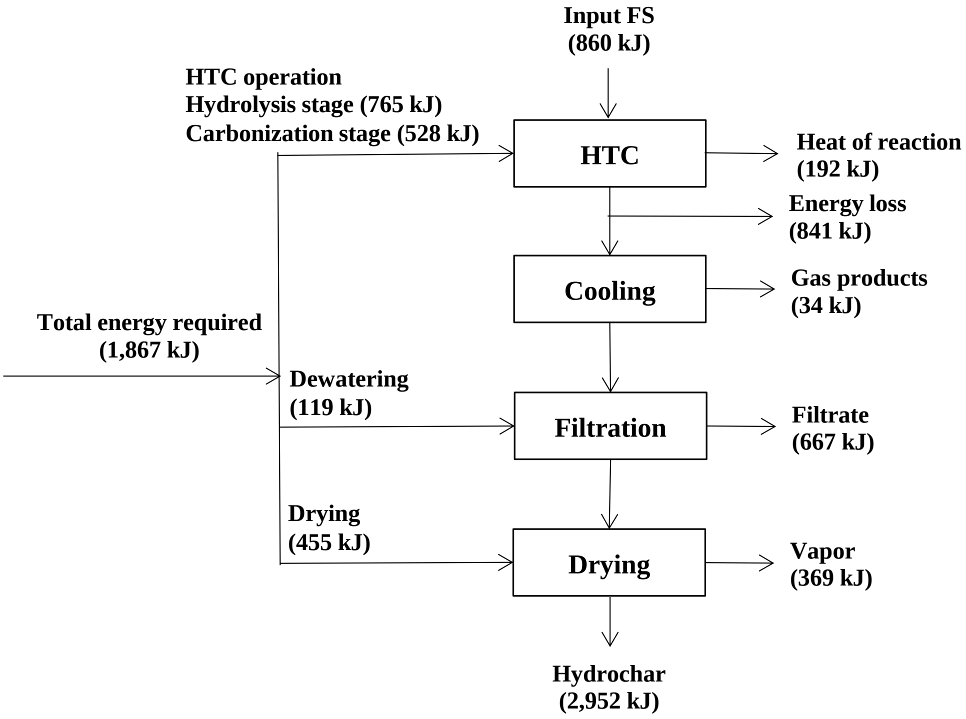


**Figure 4.19 Energy balance for two-stage HTC process of FS**

**Table 4.3 Summary of Energy Balance for Conventional and Two-Stage HTC Process**

| Energy | Conventional HTC | Two-stage HTC |
|---|---:|---:|
| *Energy input* | | |
| Energy required for HTC operation | 1,921 kJ | 1,293 kJ |
| Energy required for dewatering | 119 kJ | 119 kJ |
| Energy required for drying | 455 kJ | 455 kJ |
| Energy of FS | 860 kJ | 860 kJ |
| *Total energy required* | *2,495 kJ* | *1,867 kJ* |
| *Total energy input* | *3,355 kJ* | *2,727 kJ* |
| *Energy output* | | |
| Energy of hydrochar | 2,808 kJ | 2,952 kJ |
| Energy of filtrate | 556 kJ | 667 kJ |
| Energy of gas products | 69 kJ | 34 kJ |
| Heat of reaction | 192 kJ | 192 kJ |
| Energy loss from cooling | 841 kJ | 841 kJ |
| Energy loss from drying | 369 kJ | 369 kJ |
| *Total energy output* | *4,835 kJ* | *5,055 kJ* |

Note: Based on 1 kg/batch of FS feedstock

***Energy efficiency***

Energy efficiency is defined in the section 3.7.4. Considering the HTC, pyrolysis and gasification processes, the objective products are the produced hydrochar, liquid oil and char, and fuel gas, respectively, and the energy input is the energy required for these processes. The energy efficiency of the HTC process can be determined by:

$$Energy\ efficiency = \frac{energy\ content\ of\ hydrochar \times mass\ of hydrochar\ produced}{energy\ required} \tag{4.3}$$

Based on 1 kg of dewatered FS feedstock at 80% moisture content, the energy efficiencies of the HTC, pyrolysis and gasification processes were determined (Appendix D) and the results were compared in Table 4.4. Total energies required of pyrolysis and gasification (Table 4.4) were higher than the HTC processes because the operations of pyrolysis and gasification processes require the dried feedstock which utilizes high energy for drying wet FS (80% moisture content) during the pre-drying process. The highest energy efficiency of 1.58 could be observed at the two-stage HTC process which was higher than those for conventional HTC, pyrolysis and gasification processes. The experimental results obtained from this study proved the advantages of the two-stage HTC over the conventional HTC, pyrolysis and gasification, such as the relatively high hydrochar yield and low energy requirement (Table 4.4), which could result in lower operation cost.

**Table 4.4 Comparison of Energy Efficiency for Thermal Conversion Processes**

| Process | Energy required (MJ) | | | | Energy of product (MJ) | Energy efficiency |
|---|---|---|---|---|---|---|
| | Pre-drying | Operating | Post-drying | Total | | |
| Pyrolysis [a] | 2.13 | 1.07 | - | 3.20 | 3.38 | 1.06 |
| Gasification [b] | 2.13 | 1.45 | - | 3.58 | 3.18 | 0.89 |
| Conventional HTC [c] | - | 2.04 | 0.46 | 2.50 | 2.81 | 1.13 |
| Two-stage HTC [c] | - | 1.41 | 0.46 | 1.87 | 2.95 | 1.58 |

Note: Based on 1 kg of dewatered FS feedstock (80% moisture content)

[a] Data from Kim and Parker (2008); pyrolysis of digested sludge at 500 °C

[b] Data from Hamilton (2000); gasification of dried sewage sludge in a circulating fluidized bed at 850 °C

[c] Data from this study

## 4.3 Energy Content Improvement

Based on the experimental results obtained from Tajai (2015) and Pradeep (2015), acetic acid and cassava pulp were found to be the most effective catalyst and biomass, respectively, in increasing energy content of the hydrochar produced from the HTC of FS. The optimum conditions of HTC of the FS with acetic acid at the mixing ratio of 1:0.4 by weight were temperature of 220 °C and reaction time of 1 h, resulting in energy contents and yields of the produced hydrochar of 25.3 MJ/kg and 78.1%, respectively (Tajai, 2015). Likewise, the temperature of 250 °C and reaction time of 3 h were found to be the optimum conditions for the HTC treating the FS: cassava pulp mixture at the mixing ratio of 1:1 by weight. These optimum conditions would result in the energy content and yield of the produced hydrochar of 22.7 MJ/kg and 69.0%, respectively (Pradeep, 2015). The combination of acetic acid and cassava pulp was further investigated in this study. A mixture of FS, acetic acid and cassava pulp, at the ratio of 1:0.4:1 by weight was selected as an example and fed into the conventional and two-stage HTC reactors to determine energy contents of the produced hydrochar.

The results of conventional HTC experiments with the mixture of FS, acetic acid and cassava pulp at various temperatures and reaction times were shown in Figure 4.20 indicated that at the temperature of 220 °C, the higher energy contents of the produced hydrochar of 28.5 and 27.4 MJ/kg could be obtained at the reaction times of 0.5 and 1 h, respectively, which indicated the roles of acetic acid acting as a catalyst in accelerating the thermo-chemical reactions in HTC process. However, after 3-10 h of HTC process, these energy contents were reduced to about 20.1 MJ/kg, possibly due to acetic acid could accelerate the production of HMF in a relatively short reaction time. At the temperature of 250 °C, HTC could produce low energy contents of the produced hydrochar at any reaction times (Figure 4.20). This could indicate that increasing the temperature to 250 °C and long reaction time in HTC reactor with acetic acid could lead to the greater decomposition of HMF into organic acid such as levulinic acid (Li et al., 2009) and, consequently, resulting in lower energy contents of the produced hydrochar.

Based on the data of Figure 4.21, at the normalized energy yield of 19.9 MJ/kg-FS, the temperature of 220 °C and reaction time of 0.5 h were found to be the optimum conditions for the HTC treating the FS: acetic acid: cassava pulp mixture of 1:0.4:1. These optimum conditions would result in the energy contents and yields of the produced hydrochar of 28.5 MJ/kg and 70.5%, respectively.

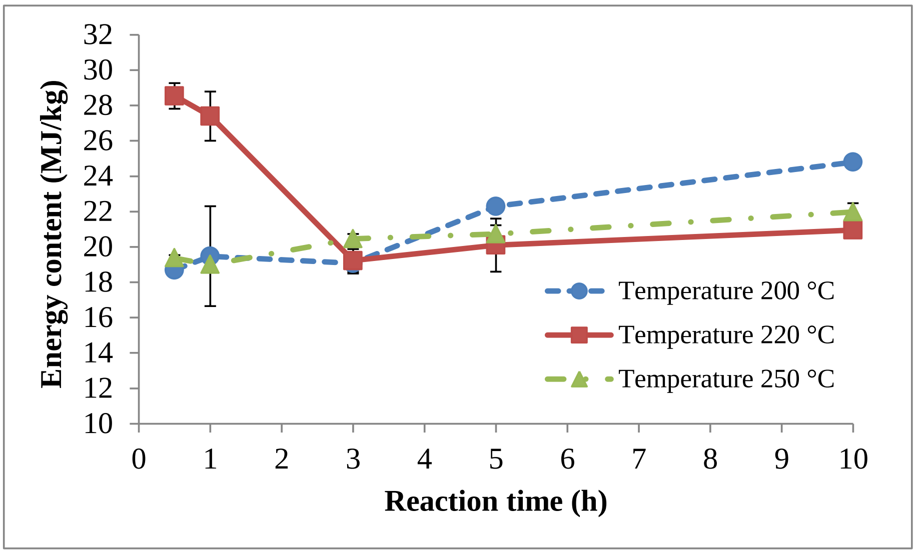


**Figure 4.20 Energy contents of hydrochar produced from HTC of mixture of FS, acetic acid and cassava pulp, at various temperatures and reaction times**

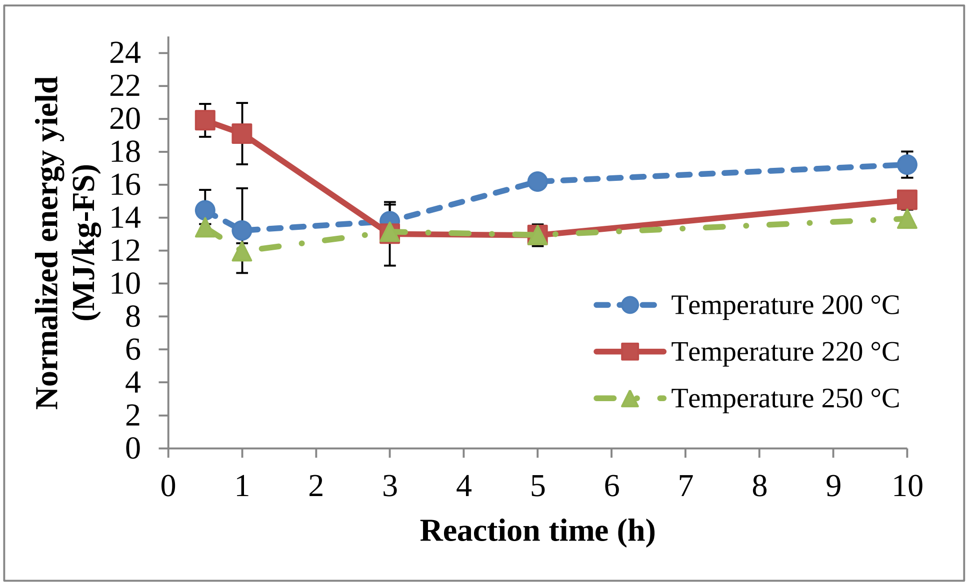


**Figure 4.21 Normalized energy yields of HTC of mixture of FS, acetic acid and cassava pulp, at various temperatures and reaction times**

Results of energy contents and hydrochar yields from the HTC of FS with different process conditions were illustrated in Figure 4.22. It is obvious that energy content of the produced hydrochar could be increased by adding either acetic acid or cassava pulp. Moreover, it could be further increased when using the FS: acetic acid: cassava pulp mixture as a feedstock.

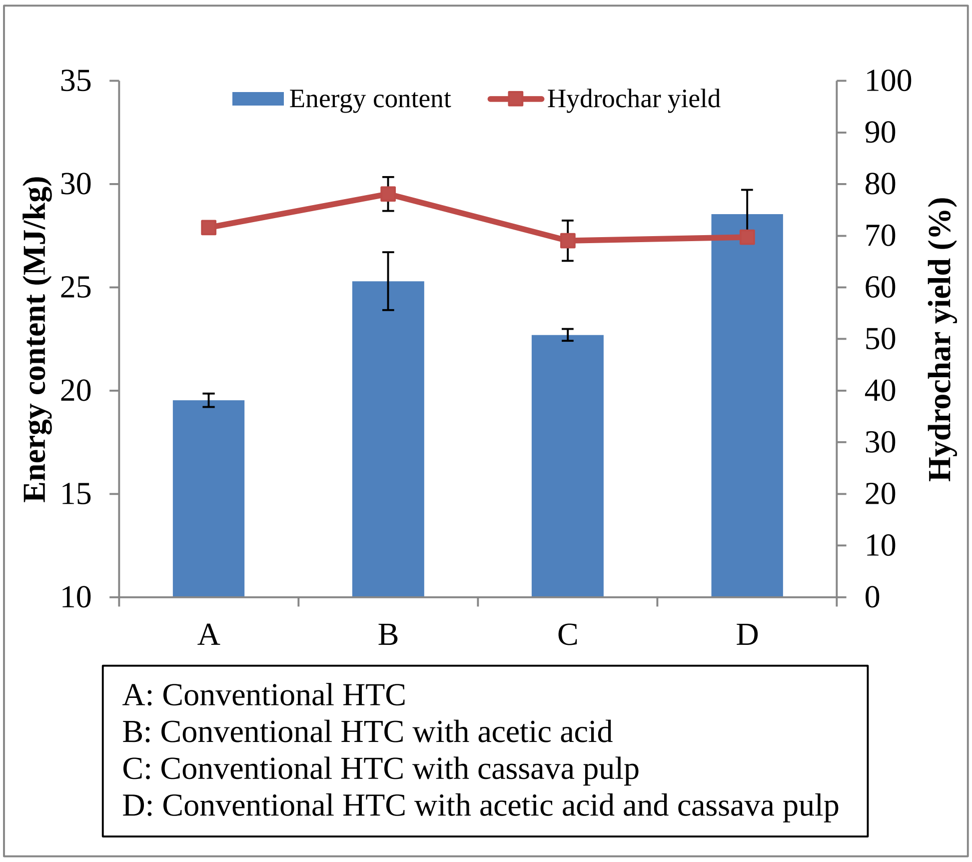


**Figure 4.22 Energy contents and hydrochar yields of HTC of FS with different process conditions**

Based on the experimental results obtained from the two-stage HTC of the mixtures of FS: acetic acid, FS: cassava pulp, and FS: acetic acid: cassava pulp, operated at optimum conditions of the two-stage HTC, average energy contents and yields of the produced hydrochar of 20.8, 20.4 and 21.8 MJ/kg and 66.5, 66.8, and 67.7%, respectively, were achieved. Energy contents of the produced hydrochar were not significantly increased, probably because the operating conditions were not optimum for these mixtures. To determine the optimum conditions of two-stage HTC of the mixtures of FS, acetic acid and cassava pulp, the RSM could be further conducted with various process conditions such as mixing ratio of FS: acetic acid: cassava pulp, temperatures and reaction times of hydrolysis and carbonization stages.

## 4.4 Characteristics of HTC Products

By HTC process, FS can be converted into the products, including solid (hydrochar), liquid and gas products. HTC product characteristics depending on process conditions were explained in the following sections.

### 4.4.1 Hydrochar

The appearance of the produced hydrochar and dried FS were shown in Appendix A. The produced hydrochar was a solid with brown color, insoluble in the water, and can be easily pulverized into powder. The SEM images (Figure 4.23) illustrated that the surface morphologies of dried FS and hydrochar produced from the HTC processes were clearly different and changed significantly by increasing the HTC temperatures. These images indicated that the conventional HTC of FS could be effective at temperature of about 250 °C which had the obvious destruction of surface into a porous appearance, while the two-stage HTC could be effective on that at relatively lower temperatures (hydrolysis and carbonization temperatures of 170 °C and 215 °C, respectively).

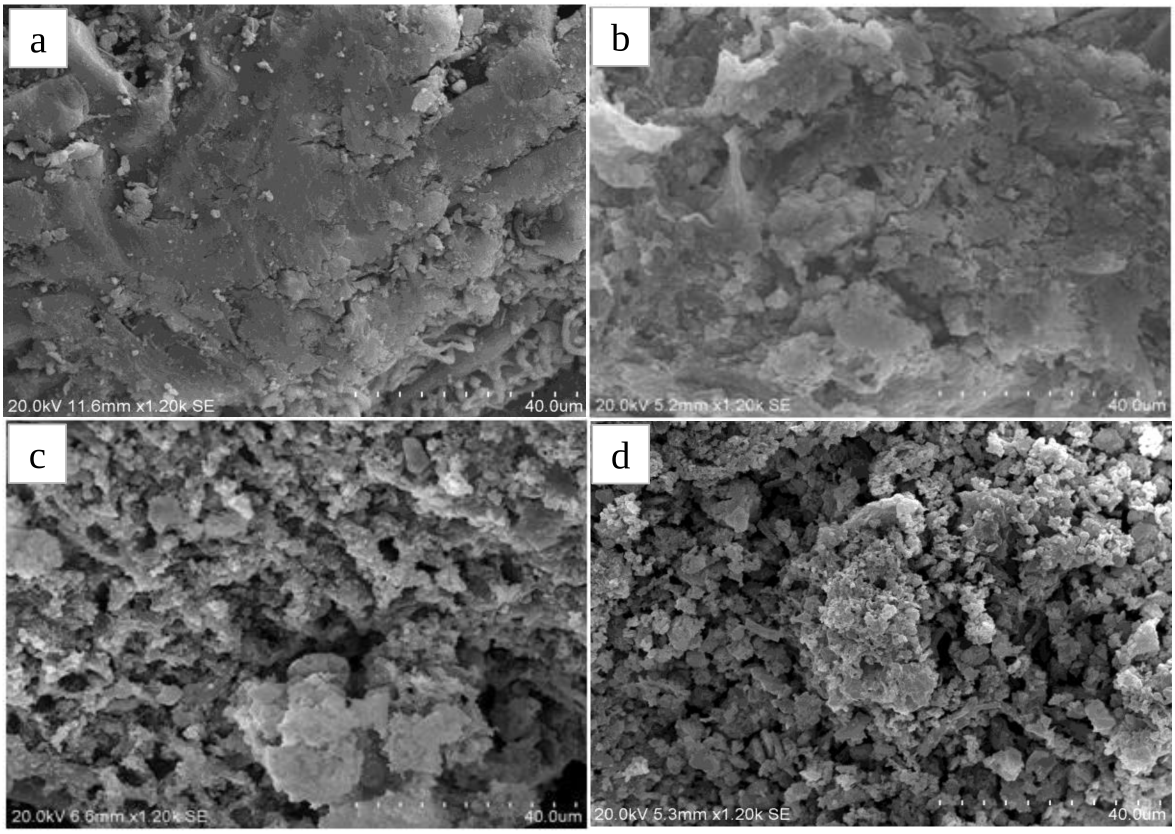


**Figure 4.23 SEM images of: (a) dried FS; (b) produced hydrochar at 220 °C; (c) produced hydrochar at 250 °C; (d) produced hydrochar from two-stage HTC (170 °C and 215 °C)**

Characteristics of the produced hydrochars from conventional and two-stage HTC of FS (at optimum HTC conditions) and dried initial FS were shown in Table 4.5. As a result of carbonization in the HTC processes, the FC contents of about 12.6 and 14.6 %wt in the produced hydrochars from conventional and two-stage HTC, respectively, increased compared with dried initial FS (9.7 %wt). On the other hand, the VM contents of about 43.7 and 39.8 %wt in the produced hydrochars from conventional and two-stage HTC, respectively, were relatively lower than that in the dried initial FS (57.0 %wt). These increased FC contents were probably due to the carbonization of VM during the HTC processes. However, considering the mass balance, the loss of VM contents in the FS rather than the increase of FC in the hydrochars, indicating the VM was also hydrolyzed, dehydrated and converted into other products in the form of soluble products (such as glucose, HMF and organic acids) and gases (such as $CO_2$). The increase of FC and decrease of VM in the produced hydrochar probably resulted in the increase of energy contents of the dried initial FS from about 13.5-14.1 MJ/kg to be about 19.3-19.9 and 19.7- 20.8 MJ/kg of the produced hydrochar from conventional and two-stage HTC, respectively.

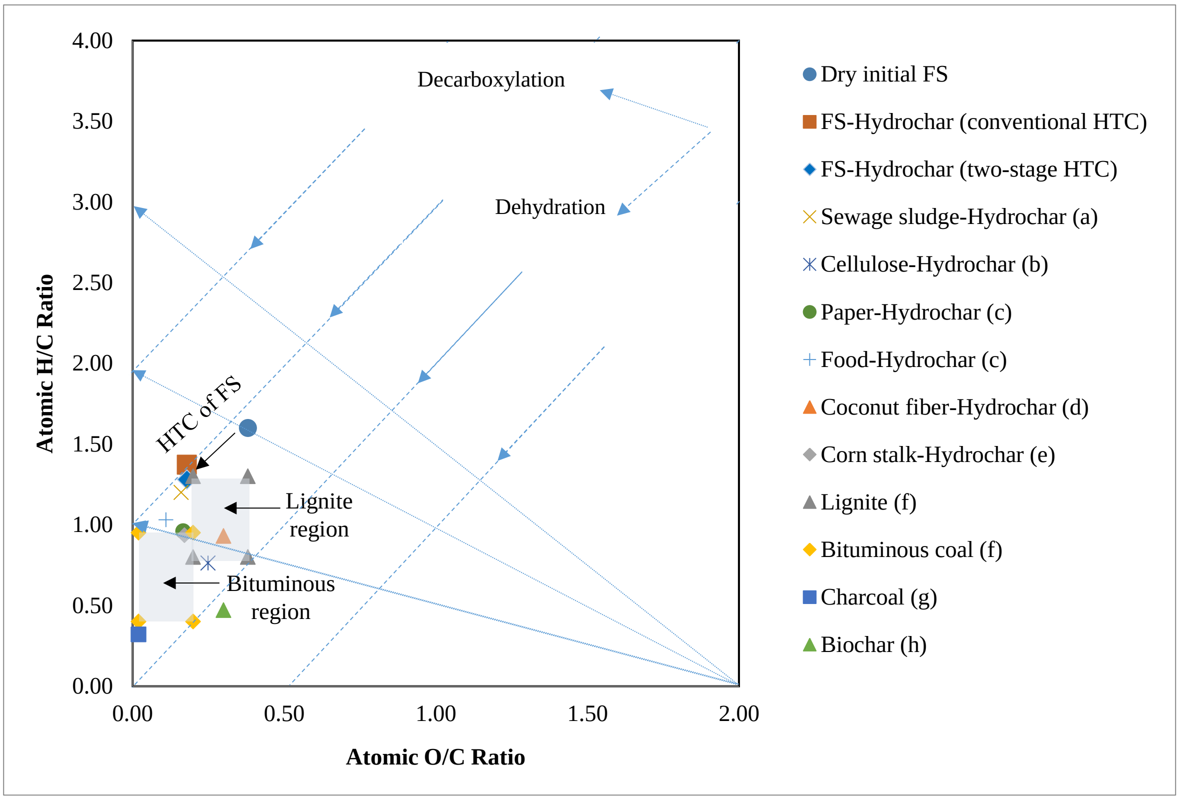
High values of ash content in the produced hydrochars were observed (Table 4.5), probably due to accumulation of inorganic matters and destruction of organic matters after carbonization in the HTC processes. These results were similar to that found in the produced hydrochar from sewage sludge (Danso-Boateng et al., 2013; He et al., 2013; Parshetti et al., 2013).

**Table 4.5 Characteristics of Hydrochars and Dried Initial FS**

| Parameters | Unit | Dried initial FS | Hydrochar | |
|---|---|---|---|---|
| | | | Conventional HTC | Two-stage HTC |
| *Proximate analysis* | | | | |
| Moisture | %wt | 1.0 | 0.8 | 0.8 |
| VM | %wt | 57.0 | 43.7 | 39.8 |
| Ash | %wt | 32.3 | 42.9 | 44.8 |
| FC | %wt | 9.7 | 12.6 | 14.6 |
| *Ultimate analysis* | | | | |
| Carbon | %wt | 38.1 | 39.7 | 38.8 |
| Hydrogen | %wt | 5.1 | 4.5 | 4.1 |
| Nitrogen | %wt | 3.5 | 2.0 | 1.9 |
| Sulfur | %wt | 1.6 | 1.3 | 1.2 |
| Oxygen | %wt | 19.40 | 9.56 | 9.13 |
| *Atomic ratio* | | | | |
| H:C | | 1.60 | 1.37 | 1.28 |
| O:C | | 0.38 | 0.18 | 0.18 |
| Energy content | MJ/kg | 13.5 – 14.1 | 19.3 – 19.9 | 19.7 – 20.8 |

The analysis results of elemental composition, as shown in Table 4.5, indicated that carbon contents in dried initial FS were increased from about 38.1 %wt to be about 39.7 and 38.8 %wt in the produced hydrochar from conventional and two-stage HTC, respectively. Oxygen and hydrogen contents in the produced hydrochar decreased compare with that of dried initial FS. Thus, the atomic ratios of H/C and O/C of dried initial FS decreased, resulting in lower values of atomic ratios of H/C and O/C of the produced hydrochars (Table 4.5).

Figure 4.24 compared the atomic ratios of H/C and O/C for dried initial FS, hydrochars produced from FS and other substances (i.e., cellulose, sewage sludge, paper, food, coconut fiber, and corn stalk), biochar and typical coals (i.e., lignite, bituminous and charcoal) plotting in Van Krevelen diagram. The atomic ratios of H/C and O/C of the produced hydrochars were decreased, which could be mainly due to the dehydration reactions during the HTC process. The produced hydrochars were in close proximity to lignite and bituminous coals, as shown in the diagram. In this regard, fuel characteristics the produced hydrochar were comparable to the natural coals, thus it could be considered to apply as solid fuel.



(a) Danso-Boateng et al., 2013; (b) Sevilla and Fuertes, 2009; (c) Berge et al., 2011; (d) Liu et al., 2013b; (e) Xiao et al., 2012; (f) Park and Jang, 2011; (g) Rose and Cooper, 1977; (h) Sukiran et al., 2011.

**Figure 4.24 Van Krevelen diagram of dried initial FS, hydrochars produced from FS and other biomasses (sewage sludge, cellulose, paper, food, coconut fiber and corn stalk), biochar and typical coals (lignite, bituminous and charcoal)**

## Applications of hydrochar

### 4.4.1.1 Solid fuel

Regarding to the characteristics of the produced hydrochar in this study, the ranges of energy content and H/C and O/C atomic ratios of the produced hydrochar (Table 4.5) were comparable to the lignite and bituminous coals (15.0 MJ/kg and 18.2 MJ/kg, respectively) (U.S. EPA, 2008). From ultimate analysis results, sulfur contents in the produced hydrochar of about 1 %wt were found. It indicated that combustion of the hydrochar could produce lower $SO_2$ gas than those of some lignite (sulfur contents of 0.5 - 3 %wt). In addition, the combustion performance of the hydrochar evaluated by He et al. (2013) indicates that hydrochar could result in more stable flame and longer combustion process. Thus, the produced hydrochar could be a significant substitute for natural coals in typical combustion process.

#### 4.4.1.2 Soil amendment

Analysis results found that bulk densities of the produced hydrochar and dried initial FS were 0.37 and 0.33 g/cm$^3$, respectively; indicating the HTC did not predominantly improve this property. Due to the lower operating temperature of HTC, the relatively higher bulk density of the produced hydrochar could result in a low surface area (4.4-5.6 m$^2$/g) compare to the biochar (10-500 m$^2$/g) (Gray et al, 2014; Kambo and Dutta, 2015). In addition, the hydrophobicity and acidity of the produced hydrochar were observed in this study. These properties could affect to the WHC of soil and the Al toxicity reduction in acidic soils. Moreover, the negative effect of applying hydrochar in soil on plant growth was observed by other researchers (Schimmelpfenning et al., 2014). Due to these physicochemical properties of the produced hydrochar, it is not recommended to use as a soil amendment for cropping and applying in acidic soil.

#### 4.4.1.3 Energy storage

One of the promising hydrochar applications is in the field of energy storage. The produced hydrochar from FS contained carbon about 40%wt which could be processed further to make it suitable for use as electrodes in batteries. The application of hydrochar as an anode in Li-ion battery was reported in some literatures. There are 2 main techniques to produce this specific hydrochar: (1) further carbonization of the produced hydrochar under argon at 1000 °C for 5 h (Wang et al., 2001) and, (2) hydrochar nanocomposite synthesis using the specific anode materials (such as Si nanoparticles, NiO, and $SnCl_4$) dispersed into biomass feedstock and subsequently treated by HTC to produce hydrochar nanocomposites (Cakan et al., 2008; Huang et al., 2007; Li et al., 2011). Most previous experiments were conducted with pure substrate (i.e., glucose) and experiments with complex organic matters such as FS have not yet been investigated.

#### 4.4.1.4 Adsorbent in water purification

The analysis results for the BET surface area and total pore volume of dried initial FS (about 1.07 m$^2$/g and 0.010 cm$^3$/g, respectively) and the produced hydrochar (4.4-5.6 m$^2$/g and 0.035-0.049 cm$^3$/g, respectively) indicated that the HTC process enhanced the BET surface area and total pore volume of the produced hydrochar. While the mean pore diameter of the produced hydrochar (31-34 nm) were found in the range of the mesopores which can adsorb the large size molecules such as sugar and heavy metals and small size molecules such as micropollutants (Inagaki et al., 2013; Liu et al., 2013a; Tamai et al., 1996). Therefore, the produced hydrochar could be able to use as an adsorbent for removing heavy metals and micropollutants in wastewater. However, further studied on the adsorption of the specific pollutants in the wastewater are recommended.

#### 4.4.1.5 $CO_2$ sequestration

According to carbon distribution during HTC processes (Figures 4.5 and 4.11), the majority of carbon in the FS retained within the hydrochar (about 75%) and transferred into liquid products (about 20%), resulting in high CE of 95%, and small amount of carbon shifted into gas phase (about 5%). It indicated that the HTC could be a most efficiency process for $CO_2$

sequestration compared to other processes such as fermentation (CE = 66%) and AD (CE = 50%) (Titirici and Antonietti, 2010). From the analysis result of gas composition, it showed $CO_2$ to be the main component (about 63%v). Gases produced from the HTC process were about 10 L-gas/kg-FS, therefore, $CO_2$ emission from the HTC process could be estimated to be 6.3 L-$CO_2$/kg-FS or 0.01 g-$CO_2$ equivalent/g-FS. The maximum $CO_2$ emission from the HTC process of 0.3 g-$CO_2$ equivalent/g-wet biomass is previously reported and it is lower than those expected from landfill, compost and incineration of the same biomass (Lu et al., 2012). Thus, the HTC process could substantially reduce GHG emissions from current treatment processes.

### 4.4.2 Liquid by-products

Liquid samples obtained from optimum conditions of the conventional and two-stage HTC processes were collected and analyzed for their physical and chemical characteristics (Table 4.6). Because the liquid samples were filtered with 1.2 µm filter paper, the total suspended solids concentrations were negligible, but the color was black (Appendix A). Liquid by-products still contained high concentrations of organic matter as indicated by TOC, COD and $BOD_5$, and relatively high nutrients of TN and TP (Table 4.6). These values were comparable to those reported in the literatures (Escala et al., 2013; Oliveira et al., 2013; Poerschmann et al., 2014). Due to the VFA generation from decomposition of the hydrolyzed products as earlier mentioned, the decrease of pH was observed for both conventional and two-stage HTC processes. Phenol was also found in the liquid by-products, which was produced by the decomposition of furfural-like compounds (Sevilla and Fuertes, 2009). It is apparent that these liquid by-products need to be further treated to minimize environmental pollution and produce valuable products. Applications and treatment options of these liquid by-products were discussed in the following section.

**Table 4.6 Characteristics of FS feedstock and HTC liquid by-products**

| Parameters | Unit | FS [a] | HTC liquid products | | |
|---|---|---|---|---|---|
| | | | Conventional HTC | Two-stage HTC | Literatures |
| TOC | g/L | 16-40 | 12-16 | 17-19 | 13-26 [b] |
| COD | g/L | 43-50 | 25-31 | 26-32 | 31-64 [c,d] |
| $BOD_5$ | g/L | 3-4 | 11-14 | 11-14 | 47-51 [d] |
| TN | g/L | 5-8 | 7-8 | 5-6 | 2-5 [c] |
| TP | mg/L | 10-15 | 5-10 | 5-10 | 14-160 [c] |
| pH | | 6.8-7.2 | 5.8-6.2 | 5.5-6.0 | 3-7 [b,c] |
| Phenol | mg/L | Not detected | 260 | 334 | 48-610 [e,f] |
| VFA | g/L | 1.0-1.1 | 5.2-5.4 | 5.2-5.3 | 3-10 [e,f] |

[a] FS at moisture content of 80%wt

[b] Oliveira et al. (2013)

[c] Escala et al. (2013)

[d] Poerschmann et al. (2014)

[e] Reza et al. (2014)

[f] Stemann et al. (2013)

### Applications and treatment options of HTC liquid by-product

#### 4.4.2.1 Recirculation of HTC liquid by-product

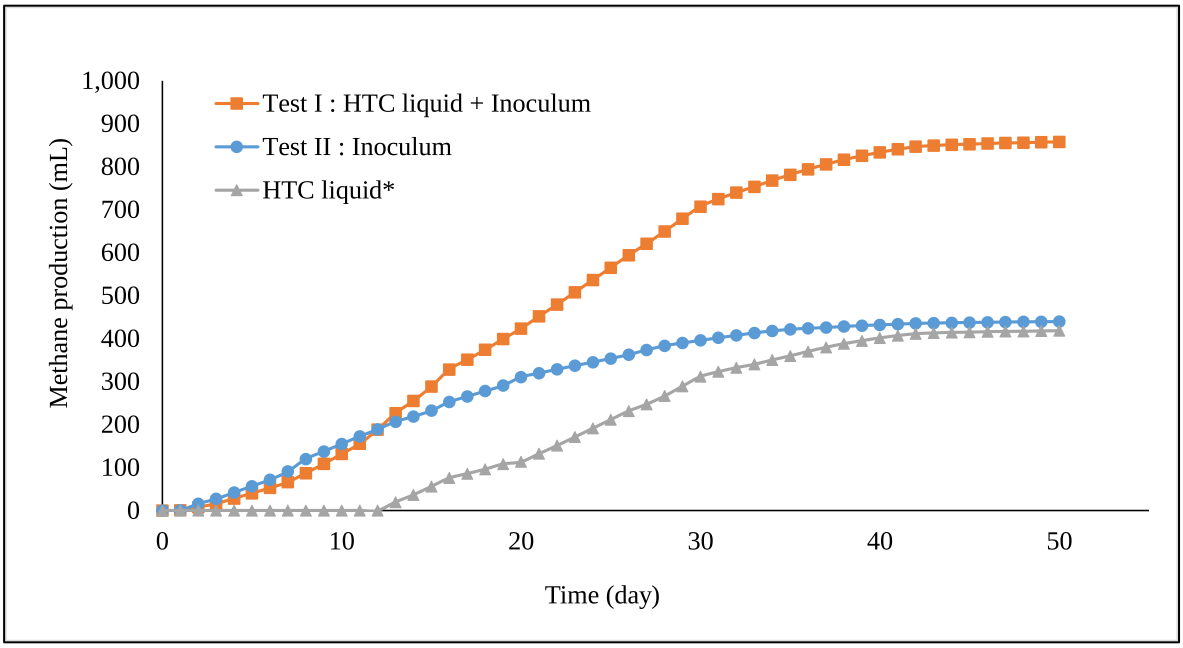
Due to the HTC liquid by-products still contained high concentrations of organic matters with acidic condition, they could be considered to reuse in the HTC process with many advantages:

1. Dissolved organic substances contained in the liquid by-product could be further polymerized by the HTC process, resulting in increased hydrochar yield and dewaterability (Stemann et al., 2013).
2. Remaining organic acids indicated as VFA of about 5 g/L in the liquid by-product could be served as a catalyst for dehydration reaction in HTC process, resulting in increased energy content of the produced hydrochar (Tajai, 2015).
3. Wastewater treatment costs could be reduced.

#### 4.4.2.2 Anaerobic digestion and biogas production

From the analysis results in Table 4.6, the COD/TOC and $BOD_5$/COD ratios were found to be about 1.6 and 0.4, respectively, and $BOD_5$ of liquid by-product were increased, probably due to lignocellulosic biomass were degraded to easy biodegradable molecules such as glucose and furfural-like compounds, which indicated that these HTC liquid by-products contained of oxidizable organic and could be treated by biological means such as AD (Lu et al., 2013; Tchobanoglous et al., 2003). To determine methane production from AD of the HTC liquid by-product, the BMP tests were conducted. The experimental results, as shown in Figure 4.25, showed that the cumulative methane produced from 150 g of the HTC liquid by-product was 418 mL-$CH_4$ or about 2.8 L-$CH_4$ per kg-HTC liquid by-product or 2.0 L-$CH_4$ per kg FS. While, Oliveira et al. (2013) reported that the methane productions from AD of liquid by-product from HTC of agriculture residues were 6-16 L-$CH_4$ per kg substrates.

To improve the methane production from AD of this HTC liquid by-product, the COD: N: P ratio of 300: 60: 1 and pH of 5.5 -6.2 should be adjusted to be 300: 5: 1 and 6.5 to 7.5, respectively, which are suitable conditions for AD and bacterial growth (Tchobanoglous et al., 2003). Organic biomass such as cassava pulp, MSW (food waste, green waste) would be added to the HTC liquid by-product to adjust COD: N: P prior feed into anaerobic digester. In addition, to reduce phenol contained in the liquid by-products, AD could be considered to operate under thermophilic conditions, which is suggested by Fang et al. (2006). The produced biogas from AD of the HTC liquid by-products could be used as a fuel gas for heating in the hydrochar drying process to remove remaining moisture, and/or other purposes such as pre-heating the feedstock, heating the HTC reactor, selling as fuel gas and cooking in households. However, the further experiments to investigate AD of the liquid by-product from HTC of FS are recommended.



∗ Methane production from HTC liquid = Methane production (Test I – Test II)

**Figure 4.25 Cumulative methane productions from BMP tests**

### 4.4.2.3 Liquid fertilizer

From the analysis results of nutrients in the liquid by-products, $NH_4$-N of 2000 mg/L, available phosphate ($P_2O_5$) of 10 mg/L and available potassium ($K_2O$) of 100 mg/L were found. Due to relatively high nutrient contents, the liquid by-products could be further processed to make it suitable to use as a liquid fertilizer in farmlands.

## 4.4.3 Gas by-products

Gases produced from the HTC process of about 3.5 L-gas/batch or 10 L-gas/kg-FS were analyzed to identify gas composition and in order to assess the environmental impacts. Analysis of the two-stage HTC gas samples showed $CO_2$ to be the main component (64.1%v), similar to the results of the conventional HTC of FS (61.9%v) and other literatures (Berge et al., 2011; and Funke et al., 2013), while there were trace amounts of $CH_4$, $O_2$, $N_2$, $H_2S$, CO, and VOC as shown in Table 4.7 and 4.8.

**Table 4.7 HTC Gas Composition**

| Gas composition | Gas amount (%v) | |
|---|---|---|
| | Conventional HTC | Two-stage HTC |
| $CO_2$ | 61.9 | 64.1 |
| $CH_4$ | 0.7 | Not detected |
| $O_2$ | 1.7 | 1.8 |
| $N_2$ | 21.5 | 20.1 |
| $H_2S$ | 2.0 | 2.2 |
| CO | 1.6 | 2.0 |
| Other | 10.6 | 9.8 |

To verify the environmental and health impacts, the total VOC was measured and specific VOCs were identified, as shown in Table 4.8. The VOCs were predominantly benzene, toluene, ethyl benzene, xylene, 2-butanone, and acetone. The management of these toxic gases released from HTC process needs to be considered. Treatment options for these gas by-products were discussed in the following section.

**Table 4.8 VOCs Composition**

| VOCs | Concentration (ppm) |
|---|---|
| Total VOC | 3.1* |
| Toluene | 79 |
| 2-Butanone | 46 |
| Acetone | 36 |
| Benzene | 15 |
| Ethyl benzene | 14 |
| Pentane | 12 |
| Xylene | 9 |
| Methyl isobutyl ketone | 5 |
| Hexane | 4 |
| Styrene | 4 |
| n-Butyl acetate | <0.01 |
| Carbon tetrachloride | <0.01 |
| Chloroform | <0.01 |
| Cyclohexanone | <0.01 |
| Diethyl ether | <0.01 |
| Ethylene dichloride | <0.01 |
| Ethyl acetate | <0.01 |
| Trichloroethylene | <0.01 |
| 1,1,1-Trichloroethane | <0.01 |
| Methylene chloride | <0.01 |
| Tetrachloroethylene | <0.01 |

*Unit: %v

**Treatment options of gas by-product**

Analytical results of the gas by-products obtained from the HTC indicate $CO_2$ to be the main component, and trace amounts VOCs, which were: benzene 15 ppm, toluene 79 ppm, ethyl benzene 14 ppm and xylene 9 ppm, 2-butanone 46 ppm, and acetone 36 ppm (Table 4.8). At present, air quality standards for VOCs are set up by several organizations. The standards of the world health organization (WHO), the pollution control department (PCD) and the ministry of natural resources and environment (MNRE) of Thailand are presented in Table 4.9. Exposure to VOCs can cause various health problems depending on the toxicity of compound, exposures level and length, and human health condition (PCD, 2009). To eliminate the toxic gases, odor and GHG emissions, the produced gases can be further treated, possibly by activated carbon adsorption or absorption with wet scrubber (Polprasert, 2007; Rackley, 2010; Rafson, 1998). Another possible option of the gas by-product management is the application of high temperature and high pressure stream generated during the HTC process for heating the FS feedstock before feed into HTC reactor and/or drying the wet hydrochar produced after filtration process.

**Table 4.9 VOCs Emission Standards**

| VOCs | Average ambient annual standard ($\mu g/m^3$) | | Industrial emission standard (ppm) |
|---|---|---|---|
| | WHO [a] | PCD [b] | MNRE |
| Benzene | 5-20 | 1.7 | 2 (7 $mg/m^3$) [c] |
| Toluene | 5-150 | - | - |
| Ethyl benzene | 1-100 | - | - |
| Xylene | 1-100 | - | 200 [d] |
| Acetone | 0.5-125 | - | - |
| Trichloroethylene | 1-10 | 23 | - |
| Vinyl Chloride | 0.1-10 | 10 | - |

Remark: Reference condition is 25 °C at 1 atm

[a] WHO (2000)

[b] PCD (2009)

[c] MNRE (2006)

[d] MNRE (2014)

## 4.5 Application of HTC for FS Treatment

Experimental results obtained from this study demonstrated the technical feasibility of applying the HTC process to treat and convert the FS to a valuable product such as hydrochar. However, it should be intensely focused on the investment and operation costs, including FS treatment plant design consideration.

### 4.5.1 Case study on HTC for FS treatment

A case study on the application of the HTC process to treat the FS of the Nontaburi municipality, Nontaburi province, a suburb of Bangkok city with a population of about 1,156,271 (DOPA, 2013) was conducted, and the capital and operating costs and revenues of the treatment plants were shown in Table 4.10. At present, about 9000 $m^3$/year of FS is being received by storage tanks and transferred to sand drying beds in which the dried sludge of about 150,000 kg/year is sold as soil conditioner. Capital and operating costs of this treatment plant are estimated to be 284,800 USD and 91,700 USD/year, respectively, while revenue earned from the soil conditioner selling is about 13,050 USD/year.

For simplification of the discussion, if the HTC process would be employed for treating same amount of the FS (9000 $m^3$/year), several assumptions may be adopted: (1) moisture content of the FS is originally 95%wt, the total input of the dried FS is to be 450,000 kg/year; (2) with a hydrochar yield of 75%, the total produced hydrochar is to be 337,500 kg/year; (3) collection and transportation costs may not be included. From these assumptions, the capital and operation costs for a typical 30 $m^3$/day HTC system are estimated to be 351,000 USD and 137,100 USD/year, respectively, while revenue to be earned from selling the produced hydrochar as a solid fuel is 31,725 USD/year. These economic analyses showed that FS treatment by the above systems still incurs deficit, but the intangible benefits such as pollution control and health risk minimization cannot be ruled out. To achieve an economic goal, the operation costs could be reduced by the HTC reactor design such as using stream or thermal oil heater, installing insulation and considering HTC plant design discussed in the section 4.5.2. Since the produced hydrochar is a pathogen-free and stable product without offensive odor, it should be more socially acceptable and user friendly than the soil conditioner generated from sand drying bed. However, it would be desirable to conduct cost-benefit analysis of full-scale HTC reactors treating FS.

**Table 4.10 Capital and Operation Costs and Revenue of Drying Bed and HTC Treatment Plants**

| Information | Treatment technology | |
|---|---|---|
| | Drying bed [a] | HTC |
| Capital cost [b] | 284,800 USD | 351,000 USD [c] |
| Operation cost | 91,700 USD/year | 137,100 USD/year [c] |
| FS amount | 9000 $m^3$/year | 9000 $m^3$/year |
| By-product | Bio-solid | Hydrochar |
| By-product amount | 150,000 kg/year | 337,500 kg/year |
| By-product price | 87 USD/1000 kg | 94 USD/1000 kg [d] |
| Revenue from selling by-product | 13,050 USD/year | 31,725 USD/year |

[a] Information from the interviewing of Nonthaburi municipality officer and including 30 units of FS storage tanks, each with a size of 30 $m^3$

[b] Not including land cost

[c] Derived from EVI (2013)

[d] Based on coal price (PPAD, 2014)

### 4.5.2 HTC plant design consideration

With the concept of HTC plant for FS treatment as illustrated in Figure 4.26, there are several key issues need to be considered for the design of HTC plant to reduce the operating cost and sustainable in the FSM.

#### *Feedstock*

Feedstock is the important factor for designing a treatment plant. Because of the low VM and high moisture content in raw FS and its fluctuating characteristics as compared with other biomass materials, pre-treatments of FS are necessary.

- To adjust the moisture content of FS to be 80-85 %wt, original FS (about 95% moisture content) could be pre-dewatered before feeding into the reactors by sedimentation, thickening, or drying bed.
- As previously mentioned on the improvement of energy content by adding biomass, other available organic wastes such as cassava pulp, MSW (food waste, green waste, paper), agriculture residues (manure, rice husk) and sewage sludge could be added to the FS feedstock to increase the VM prior feed into HTC reactor, which could result in increased energy content of the produced hydrochar.
- To reduce the energy required for heating such feedstock in the HTC reactor, pre-heating of FS is necessary. Hot water used in HTC reactor is recommended to recirculate for heating FS feedstock before feeding in to HTC reactor.

### *HTC reactor and scale-up effects*

With respect to scale-up, an increase in volume or capacity of production is usually an increasing investment cost but decreasing operation cost. In case of the HTC reactor, increase in size or volume of the reactor may affect heat transfer efficiency which might require longer operation time to complete the reactions. To avoid these scale-up effects on the HTC reactor, the following recommendations could be considered:

- Applying numbering-up (increasing number of reactors, not size of reactor) (Titirici, 2013) is a way to increase hydrochar production and avoid the effects of large-scale reactor.
- Determining the optimal heating rate for the HTC operation, because fast too heating could lead to a high difference of temperatures inside the reactor.
- Mixing of the reactor content to make the uniform heat distribution.
- Heating the reactor from inside could be applied in the large-scale reactor for improving the heat transfer and reducing heat loss.

### *Energy conservation*

Main energy consumptions in the HTC process are the energy required to heat the HTC reactor to achieve desired temperatures and the energy required to dry the wet hydrochar after filtration process. In general, energy conservation of HTC process could be achieved by the designing HTC reactor and using internal heat sources as efficiently as possible through the recirculation and reuse of the cooling water, liquid and gas by-products, the following recommendations could be considered:

- For the design of HTC reactor, applying semi-continuous reactors could be more efficient heat transfer and better energy conservation (Stemann and Ziegler, 2011).
- To minimize the energy losses, insulation should be well installed and heating and cooling processes should be separated to reduce the quantity of heat that will be absorbed by the reactor body.
- Recirculation of the hot water from HTC reactor for pre-heating the FS feedstock could reduce external energy consumption at HTC reactor and could be an efficient method of heat recovery.
- Hot stream generated from HTC reactor could be considered to use as a heat source for drying wet hydrochar produced after filtration process.
- Solar energy could be used in a drying bed technology for reducing the moisture content in feedstock prior feeding into HTC reactor and drying wet hydrochar produced after filtration process.

### *Treatment of waste streams*

One final consideration in the design of HTC plant is the treatment unit of waste streams (liquid from filtration process and gases by-product). In order to minimize the environmental impacts and recover any valuable materials from the liquid by-products, the combination of HTC and AD are recommended, as previously discussed in section 4.4.2.2. This is similar to that proposed by Oliveira et al. (2013) and Poerschmann et al. (2014). In addition, the digested sludge generated from anaerobic digester could be mixed with FS feedstock to reduce the waste disposal and increase organic substrates for producing hydrochar. For gaseous waste, it could be treated by activated carbon adsorption or absorption with wet scrubber.

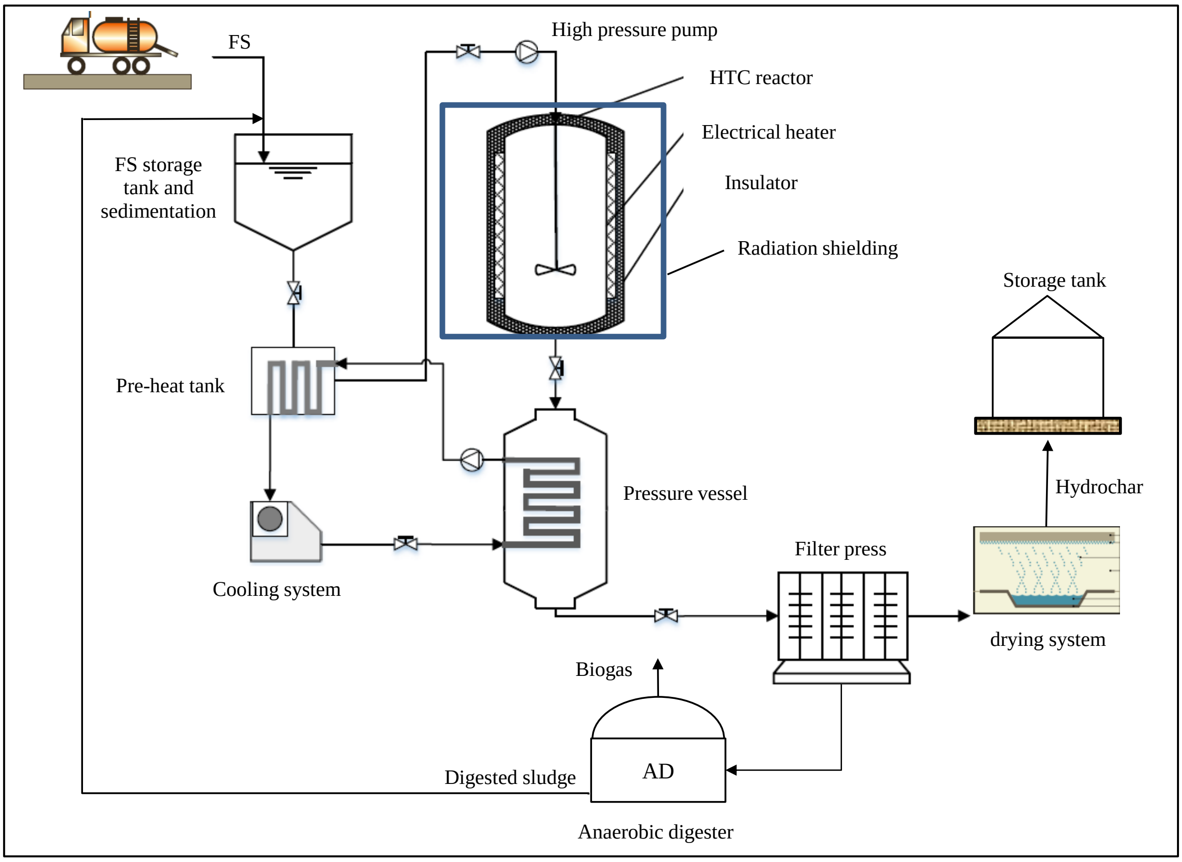


Figure 4.26 Concept of HTC for FS treatment

# Chapter 5

# Conclusions and recommendations

## 5.1 Conclusions

Based on the results obtained from these experiments, FS can be converted to the hydrochar using HTC processes. For the conventional HTC of FS, optimum conditions to produce the highest normalized energy yield were found to be: moisture content 80%, reaction time 5 h and temperature 250 °C. In these conditions, the energy content and hydrochar yield were 19-20 MJ/kg and 70-73%, respectively. A linear regression model was developed which could estimate energy content of the produced hydrochar at various operating conditions. This model was validated with some literature data satisfactorily.

The experimental results obtained from the two-stage HTC of FS indicated that optimum conditions were: hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C, and carbonization reaction time of 100 min. At these conditions, experimental results showed energy content and hydrochar yield to be 20-21 MJ/kg and 70-73%, respectively. The energy required for the two-stage HTC was about 25% less than the conventional HTC. The energy efficiency of the two-stage HTC using FS as feedstock was higher than those of conventional HTC, pyrolysis and gasification processes. The results of this study proved the advantages of the two-stage HTC over the conventional HTC, pyrolysis and gasification, such as the relatively high hydrochar yield and low energy requirement. Therefore, the two-stage HTC could be considered as a potential technology for treating FS and producing hydrochar for using as solid fuels and other value-added products.

Characteristics of HTC products included hydrochar, liquid and gas products were identified. Energy content, H/C and O/C atomic ratios of the produced hydrochar were comparable to natural coals. Thus, it could be considered to apply as solid fuel in the typical combustion processes. The HTC liquid by-products need to be further treated to minimize environmental pollution and producing valuable products, for example, applying AD to produce useful biogas, reusing in the HTC process, using as a liquid fertilizer in farmlands. To eliminate the toxic gases, odor and GHG emissions, the produced gases can be further treated, possibly by activated carbon adsorption or absorption with wet scrubber.

Although FS treatment by the HTC system still incurs deficits, the intangible benefits such as pollution control and health risk minimization should be considered. As HTC is a relatively new technology shift from laboratory to pilot- or full-scale productions such as the FS treatment plant, opportunities and challenges related to HTC of FS still exist. However, there is potential for FS to be converted to valuable product as the hydrochar through the HTC process.

## 5.2 Recommendations

The results of this study mainly obtained from lab-scale 1 L HTC reactors fed with raw FS samples and performed in batch experiments. Due to the limitations of these experiments and to achieve the ultimate goal of this research area, the following recommendations are required for further studies.

1. Further evaluation of the optimum conditions of conventional and two-stage HTC with pilot- or full-scale reactors treating FS or other biomass materials
2. Further validation of Equation (4.2) with pilot- or full-scale HTC reactors treating FS or other biomass materials
3. Analysis of the hydrochar characteristics such as surface functional groups, surface charge, and thermal behavior to identify their properties and further make it as value-added products
4. Investigation of application of the produced hydrochar as an adsorbent for heavy metal and phosphorous removal in water and wastewater treatment.
5. Investigation of improvement techniques to make the produced hydrochar from FS suitable for use as electrodes in Li-ion battery
6. Evaluation of using the produced hydrochar as a soil amendment in agriculture to improve crop growth
7. Further evaluation of the application and treatment options for the HTC liquid and gas by-products
8. Further study on energy conversation of the HTC process such as insulation, reactor design and HTC process design to minimize the energy consumption and heat losses.

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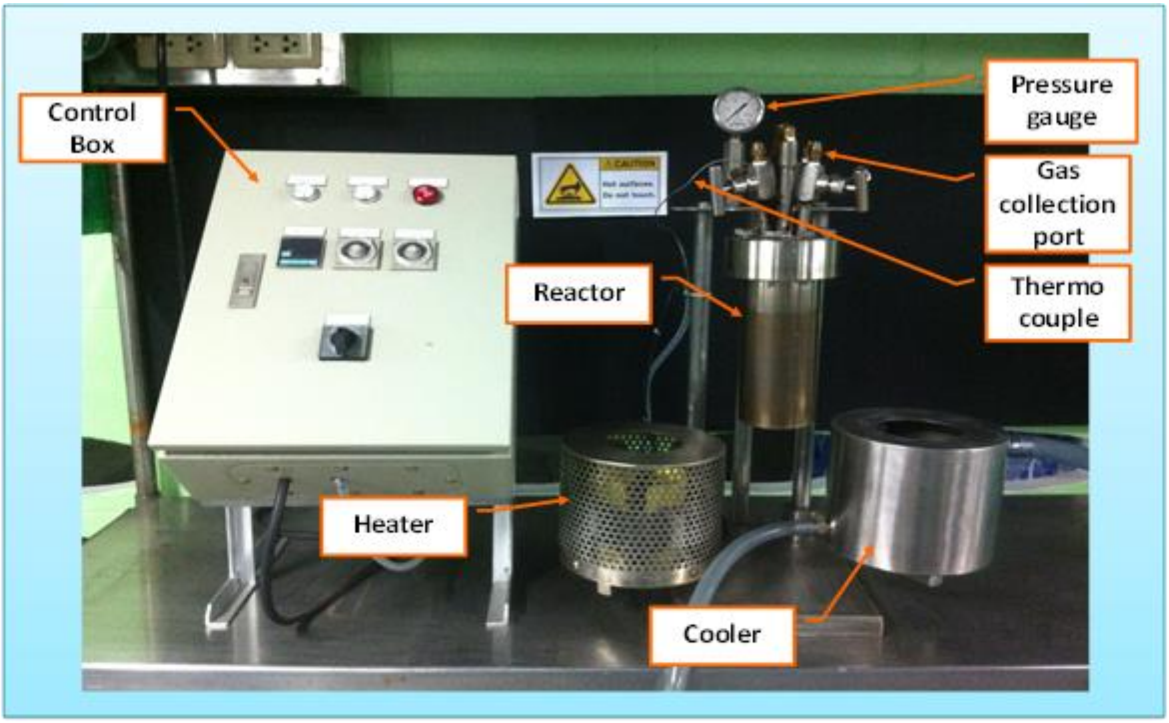
# Appendix A

## Photographs of HTC Experiments



**Appendix A-1**: HTC components

**Appendix A-2:** Left - Dried FS, and Right - Hydrochar

# Appendix B

## Results of HTC Experiments

## Appendix B-1: Energy Content and Yield of Produced Hydrochar from Conventional HTC of FS at Various Process Conditions.

| No. | Process parameters | | | Energy content (MJ/kg) | | | Yield (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Moisture content (%wt) | Temperature (°C) | Reaction time (h) | #1 | #2 | #3 | #1 | #2 | #3 |
| 1 | 95 | 220 | 5 | 18.42 | 18.34 | 17.42 | 72.72 | 68.53 | 65.70 |
| 2 | 90 | 220 | 5 | 18.80 | 19.13 | 19.03 | 73.38 | 68.55 | 66.11 |
| 3 | 80 | 220 | 5 | 18.96 | 19.35 | 19.12 | 73.02 | 68.77 | 67.82 |
| 4 | 70 | 220 | 5 | 17.92 | 17.24 | 17.68 | 80.01 | 71.32 | 74.46 |
| 5 | 80 | 180 | 0.5 | 17.42 | 16.23 | 16.99 | 78.97 | 79.70 | 80.57 |
| 6 | 80 | 180 | 1 | 17.00 | 17.73 | 17.83 | 76.40 | 75.29 | 77.69 |
| 7 | 80 | 180 | 5 | 17.92 | 17.57 | 17.24 | 74.03 | 75.52 | 77.23 |
| 8 | 80 | 180 | 10 | 17.99 | 17.67 | 17.12 | 70.05 | 73.65 | 71.49 |
| 9 | 80 | 220 | 0.5 | 16.93 | 17.70 | 17.92 | 76.19 | 77.94 | 79.79 |
| 10 | 80 | 220 | 1 | 18.77 | 18.86 | 18.69 | 74.64 | 73.40 | 72.24 |
| 11 | 80 | 220 | 5 | 18.96 | 19.35 | 19.12 | 69.15 | 70.47 | 71.95 |
| 12 | 80 | 220 | 10 | 19.79 | 19.84 | 18.83 | 64.13 | 63.19 | 66.63 |
| 13 | 80 | 250 | 0.5 | 17.68 | 18.45 | 18.59 | 75.55 | 73.71 | 77.39 |
| 14 | 80 | 250 | 1 | 18.01 | 18.69 | 19.91 | 71.80 | 73.47 | 75.00 |
| 15 | 80 | 250 | 5 | 20.82 | 19.14 | 19.09 | 68.65 | 70.93 | 71.53 |
| 16 | 80 | 250 | 10 | 19.86 | 20.12 | 20.86 | 61.48 | 64.68 | 63.45 |

## Appendix B-2: Validation Data Obtained from Conventional HTC of FS (Results from This Study)

| No. | Feedstock type | Moisture content (%wt) | Temperature (°C) | Reaction time (h) | TVS (g/L) | Energy content (MJ/kg) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Measured | Calculated |
| 1 | Faecal sludge | 70 | 220 | 5 | 340 | 17.62 | 17.59 |
| 2 | Faecal sludge | 80 | 180 | 5 | 150 | 17.97 | 18.24 |
| 3 | Faecal sludge | 80 | 220 | 5 | 150 | 19.37 | 19.03 |
| 4 | Faecal sludge | 80 | 220 | 10 | 150 | 19.49 | 19.56 |
| 5 | Faecal sludge | 80 | 220 | 10 | 150 | 19.35 | 19.56 |
| 6 | Faecal sludge | 80 | 250 | 5 | 150 | 20.03 | 19.63 |
| 7 | Faecal sludge | 90 | 180 | 5 | 70 | 18.36 | 18.09 |
| 8 | Faecal sludge | 90 | 180 | 10 | 70 | 19.20 | 18.62 |
| 9 | Faecal sludge | 90 | 220 | 0.5 | 70 | 18.78 | 18.40 |
| 10 | Faecal sludge | 90 | 220 | 1 | 70 | 19.09 | 18.46 |
| 11 | Faecal sludge | 90 | 220 | 5 | 70 | 19.42 | 18.88 |
| 12 | Faecal sludge | 90 | 220 | 10 | 70 | 19.52 | 19.41 |
| 13 | Faecal sludge | 90 | 250 | 5 | 70 | 20.29 | 19.48 |
| 14 | Faecal sludge | 90 | 250 | 10 | 70 | 20.86 | 20.01 |
| 15 | Faecal sludge | 95 | 220 | 5 | 40 | 18.69 | 18.66 |

**Note:**

Energy content calculation based on Equation (4.1):

$$E_{hydrochar} = f(26.8 + 0.020T + 0.106t - 0.131M - 0.014VS) \qquad (4.1)$$

and $f = 0.07E_{feedstock}$

Using No. 1 is an example of energy content calculation. $E_{feedstock}$ of FS is 14.28 MJ/kg, thus:

$$E_{hydrochar} = (0.07\text{x}14.28)(26.8 + 0.020(220) + 0.106(5) - 0.131(70) - 0.014(340))$$
$$E_{hydrochar} = 17.59 \text{ MJ/kg}$$

## Appendix B-3: Validation Data of HTC of Various Biomass Obtained from Literatures

| No. | Feedstock | | Moisture content (%wt) | Temperature (°C) | Reaction time (h) | TVS (g/L) | Energy content (MJ/kg) | |
|---|---|---|---|---|---|---|---|---|
| | Name | Energy content (MJ/kg) | | | | | Measured | Calculated |
| 1 | Sewage sludge | 18.01 | 96 | 140 | 4 | 27 | 21.45 | 21.47 |
| 2 | Sewage sludge | 18.01 | 96 | 170 | 4 | 27 | 22.02 | 22.21 |
| 3 | Sewage sludge | 18.01 | 96 | 190 | 4 | 27 | 22.65 | 22.72 |
| 4 | Sewage sludge | 18.01 | 96 | 200 | 4 | 27 | 23.13 | 22.96 |
| 5 | Corn silage | 19.6 | 85 | 220 | 4 | 125 | 26.60 | 25.55 |
| 6 | Poultry manure | 18.8 | 85 | 220 | 4 | 110 | 24.30 | 24.80 |
| 7 | Bedding material | 16.9 | 85 | 220 | 4 | 102 | 20.90 | 22.44 |
| 8 | Separated digestate | 18.4 | 85 | 220 | 4 | 116 | 23.50 | 24.17 |
| 9 | Dry straw | 18.7 | 85 | 220 | 4 | 124 | 26.30 | 24.40 |
| 10 | Cabbage residues | 18.0 | 85 | 220 | 4 | 117 | 25.30 | 23.62 |
| 11 | Forest wood chips | 18.4 | 85 | 220 | 4 | 127 | 21.50 | 24.14 |
| 12 | Landscape wood chips | 19.4 | 85 | 220 | 4 | 118 | 24.30 | 25.32 |
| 13 | Forest wood chips high quality | 19.3 | 85 | 220 | 4 | 124 | 24.60 | 25.10 |
| 14 | Water Hyacinth | 13.78 | 94 | 240 | 0.5 | 129 | 16.83 | 18.17 |
| 15 | Water Hyacinth | 13.78 | 94 | 240 | 1 | 28 | 18.41 | 18.22 |
| 16 | Water Hyacinth | 13.78 | 94 | 240 | 2 | 28 | 17.72 | 18.32 |
| 17 | Water Hyacinth | 13.78 | 94 | 240 | 4 | 28 | 19.15 | 18.53 |
| 18 | Water Hyacinth | 13.78 | 94 | 240 | 6 | 28 | 18.58 | 18.73 |
| 19 | Water Hyacinth | 13.78 | 94 | 240 | 8 | 28 | 19.58 | 18.94 |
| 20 | Water Hyacinth | 13.78 | 94 | 240 | 10 | 28 | 20.58 | 19.14 |

Note: No. 1-4, data from Danso-Boateng et al. (2013)
No. 5-13, data from Oliveira et al. (2013)
No. 14-20, data from Gao et al. (2013)

## Appendix B-4: Experimental Results of RSM for Two-Stage HTC of FS

| Experiment no. | Hydrolysis | | Carbonization | | Energy content (MJ/kg) | Hydrochar yield (%) |
|---|---|---|---|---|---|---|
| | Temperature (°C) | Reaction time (min) | Temperature (°C) | Reaction time (min) | | |
| 1 | 150 | 110 | 225 | 165 | 19.82 | 68.19 |
| 2 | 158 | 65 | 213 | 98 | 18.24 | 74.07 |
| 3 | 158 | 65 | 213 | 233 | 18.58 | 71.57 |
| 4 | 158 | 65 | 238 | 98 | 18.39 | 69.71 |
| 5 | 158 | 65 | 238 | 233 | 19.46 | 71.33 |
| 6 | 158 | 155 | 213 | 98 | 19.86 | 73.36 |
| 7 | 158 | 155 | 213 | 233 | 18.69 | 73.40 |
| 8 | 158 | 155 | 238 | 98 | 21.13 | 65.90 |
| 9 | 158 | 155 | 238 | 233 | 20.14 | 68.04 |
| 10 | 165 | 20 | 225 | 165 | 19.05 | 65.33 |
| 11 | 165 | 110 | 200 | 165 | 19.05 | 70.19 |
| 12 | 165 | 110 | 225 | 30 | 18.47 | 72.90 |
| 13 | 165 | 110 | 225 | 165 | 20.34 | 66.47 |
| 14 | 165 | 110 | 225 | 165 | 18.84 | 69.21 |
| 15 | 165 | 110 | 225 | 165 | 19.53 | 69.79 |
| 16 | 165 | 110 | 225 | 165 | 20.21 | 69.17 |
| 17 | 165 | 110 | 225 | 165 | 20.77 | 72.21 |
| 18 | 165 | 110 | 225 | 165 | 19.59 | 68.49 |
| 19 | 165 | 110 | 225 | 300 | 19.96 | 68.57 |
| 20 | 165 | 110 | 250 | 165 | 19.91 | 66.43 |
| 21 | 165 | 200 | 225 | 165 | 20.00 | 65.33 |
| 22 | 173 | 65 | 213 | 98 | 18.52 | 74.93 |
| 23 | 173 | 65 | 213 | 233 | 20.29 | 71.03 |
| 24 | 173 | 65 | 238 | 98 | 19.44 | 73.91 |
| 25 | 173 | 65 | 238 | 233 | 19.05 | 65.87 |
| 26 | 173 | 155 | 213 | 98 | 19.94 | 70.26 |
| 27 | 173 | 155 | 213 | 233 | 19.95 | 69.17 |
| 28 | 173 | 155 | 238 | 98 | 20.30 | 68.19 |
| 29 | 173 | 155 | 238 | 233 | 20.24 | 68.74 |
| 30 | 180 | 110 | 225 | 165 | 18.83 | 65.27 |

## Appendix B-5: Experimental Results of Determination of VM and FC During Two-Stage HTC

| Stage | Moisture content (%wt) | Temperature (°C) | Reaction time (min) | VM (%wt) | | FC (%wt) | |
|---|---|---|---|---|---|---|---|
| | | | | #1 | #2 | #1 | #2 |
| Hydrolysis | 80 | 170 | 0 | 63.16 | 60.58 | 11.29 | 9.07 |
| | 80 | 170 | 30 | 54.80 | 49.58 | 12.42 | 8.00 |
| | 80 | 170 | 60 | 49.72 | 54.14 | 8.70 | 11.84 |
| | 80 | 170 | 180 | 46.99 | 51.99 | 7.91 | 13.03 |
| | 80 | 170 | 300 | 50.13 | 46.29 | 12.56 | 8.56 |
| | 80 | 170 | 600 | 44.94 | 49.80 | 8.37 | 12.03 |
| Carbonization | 80 | 215 | 0 | 50.82 | 48.38 | 11.29 | 9.07 |
| | 80 | 215 | 50 | 48.89 | 43.39 | 15.43 | 10.79 |
| | 80 | 215 | 100 | 40.33 | 44.59 | 13.55 | 16.69 |
| | 80 | 215 | 150 | 40.24 | 44.04 | 12.18 | 17.48 |
| | 80 | 215 | 200 | 43.29 | 40.19 | 17.11 | 13.19 |
| | 80 | 215 | 300 | 38.46 | 43.88 | 12.86 | 16.42 |

## Appendix B-6: Experimental Results of Determination of Reaction Kinetics

| No. | Moisture content (%wt) | Temperature (°C) | Reaction time (h) | Initial FS (g) | VM in FS (%) | Ci | Hydrochar (g) | VM in hydrochar (%) | Ct | ln Ci/Ct |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 80 | 140 | 0.5 | 39.61 | 55.05 | 35.10 | 36.51 | 54.14 | 34.28 | 0.02 |
| 2 | 80 | 140 | 1 | 40.51 | 54.32 | 33.64 | 35.78 | 50.41 | 32.67 | 0.03 |
| 3 | 80 | 140 | 3 | 41.15 | 54.64 | 37.12 | 34.37 | 49.44 | 35.45 | 0.05 |
| 4 | 80 | 140 | 5 | 43.18 | 58.05 | 34.98 | 25.70 | 46.14 | 32.41 | 0.08 |
| 5 | 80 | 140 | 10 | 43.59 | 58.53 | 34.65 | 19.25 | 42.63 | 30.48 | 0.13 |
| 6 | 80 | 160 | 0.5 | 41.15 | 53.34 | 32.57 | 38.72 | 52.62 | 32.03 | 0.02 |
| 7 | 80 | 160 | 1 | 39.38 | 50.82 | 40.59 | 35.89 | 50.40 | 39.40 | 0.03 |
| 8 | 80 | 160 | 3 | 40.13 | 52.28 | 36.74 | 34.93 | 49.51 | 34.65 | 0.06 |
| 9 | 80 | 160 | 5 | 42.70 | 58.77 | 39.16 | 28.40 | 48.02 | 34.78 | 0.12 |
| 10 | 80 | 160 | 10 | 45.13 | 59.37 | 34.61 | 24.24 | 45.40 | 30.04 | 0.14 |
| 11 | 80 | 180 | 0.5 | 55.96 | 55.43 | 31.02 | 44.86 | 47.47 | 21.30 | 0.38 |
| 12 | 80 | 180 | 1 | 56.26 | 53.51 | 30.11 | 43.40 | 44.73 | 19.41 | 0.44 |
| 13 | 80 | 180 | 3 | 60.13 | 43.48 | 26.15 | 50.19 | 32.70 | 16.41 | 0.47 |
| 14 | 80 | 180 | 5 | 55.88 | 44.56 | 24.90 | 49.92 | 28.37 | 14.16 | 0.56 |
| 15 | 80 | 180 | 10 | 56.79 | 45.29 | 25.72 | 49.87 | 26.15 | 13.04 | 0.68 |
| 16 | 80 | 200 | 0.5 | 60.24 | 62.96 | 37.93 | 51.25 | 60.26 | 30.89 | 0.21 |
| 17 | 80 | 200 | 1 | 59.65 | 63.65 | 37.97 | 50.98 | 57.33 | 29.23 | 0.26 |
| 18 | 80 | 200 | 3 | 56.32 | 48.79 | 27.48 | 46.88 | 41.02 | 19.23 | 0.36 |
| 19 | 80 | 200 | 5 | 58.27 | 44.87 | 26.15 | 47.84 | 31.40 | 15.02 | 0.55 |
| 20 | 80 | 200 | 10 | 56.27 | 48.70 | 27.40 | 45.96 | 29.10 | 13.37 | 0.72 |
| 21 | 80 | 220 | 0.5 | 41.15 | 53.34 | 21.95 | 38.72 | 52.62 | 20.38 | 0.07 |
| 22 | 80 | 220 | 1 | 39.38 | 50.82 | 20.01 | 35.89 | 50.40 | 18.09 | 0.10 |
| 23 | 80 | 220 | 3 | 40.13 | 52.28 | 20.98 | 34.93 | 49.51 | 17.30 | 0.19 |
| 24 | 80 | 220 | 5 | 42.70 | 58.77 | 25.10 | 28.40 | 48.02 | 13.64 | 0.61 |
| 25 | 80 | 220 | 10 | 45.13 | 59.37 | 26.79 | 24.24 | 45.40 | 13.01 | 0.72 |
| 26 | 80 | 250 | 0.5 | 39.61 | 55.05 | 21.81 | 36.51 | 54.14 | 19.77 | 0.10 |
| 27 | 80 | 250 | 1 | 40.51 | 54.32 | 22.00 | 35.78 | 50.41 | 18.04 | 0.20 |
| 28 | 80 | 250 | 3 | 41.15 | 54.64 | 22.48 | 34.37 | 49.44 | 16.99 | 0.28 |
| 29 | 80 | 250 | 5 | 43.18 | 58.05 | 25.06 | 25.70 | 46.14 | 11.86 | 0.75 |
| 30 | 80 | 250 | 10 | 43.59 | 58.53 | 25.52 | 19.25 | 42.63 | 10.20 | 0.92 |

## Appendix B-7: Reaction Rate Constants of Various HTC Temperatures

| Temperature (°C) | k ($h^{-1}$) | Equation | $R^2$ |
|---|---|---|---|
| 140 | 0.0136 | $y = 0.0136x$ | 0.9339 |
| 160 | 0.0164 | $y = 0.0164x$ | 0.8676 |
| 180 | 0.0298 | $y = 0.0298x$ | 0.9207 |
| 200 | 0.0560 | $y = 0.0560x$ | 0.8697 |
| 220 | 0.0813 | $y = 0.0813X$ | 0.8845 |
| 250 | 0.1035 | $y = 0.1035x$ | 0.8849 |

## Appendix B-8: Changing of Temperature and Pressure During Conventional and Two-Stage HTC Operations

| Conventional HTC | | | | Two-stage HTC | | | |
|---|---|---|---|---|---|---|---|
| Process | Operation time (min) | Temperature (°C) | Pressure (bar) | Process | Operation time (min) | Temperature (°C) | Pressure (bar) |
| Heating | 0 | 12 | 1 | Heating | 0 | 20 | 1 |
| | 1.5 | 13 | 1 | | 5 | 22 | 1 |
| | 3 | 13 | 1 | | 10 | 38 | 6 |
| | 5 | 14 | 1 | | 15 | 63 | 16 |
| | 7 | 26 | 1 | | 20 | 87 | 30 |
| | 9 | 68 | 3.5 | | 25 | 123 | 30 |
| | 10 | 93 | 5 | | 30 | 147 | 33 |
| | 12 | 130 | 7 | Hydrolysis | 35 | 170 | 30 |
| | 14 | 140 | 9.5 | | 65 | 176 | 23 |
| | 16 | 155 | 12.5 | | 95 | 175 | 15 |
| | 18 | 169 | 16.5 | | 135 | 175 | 15 |
| | 20 | 180 | 21 | | 165 | 177 | 14 |
| | 22 | 192 | 23 | Heating | 190 | 177 | 15 |
| | 24 | 203 | 25 | | 195 | 190 | 23 |
| | 26 | 214 | 23 | Carbonization | 200 | 213 | 40 |
| | 27 | 220 | 25 | | 205 | 218 | 45 |
| | 28 | 226 | 24 | | 215 | 218 | 40 |
| | 30 | 238 | 24 | | 230 | 217 | 40 |
| HTC | 32 | 250 | 23 | | 305 | 217 | 39 |
| | 85 | 256 | 23 | Cooling | 311 | 198 | 15 |
| | 145 | 250 | 23.5 | | 312 | 169 | 12 |
| | 215 | 254 | 24.5 | | 313 | 143 | 10 |
| | 265 | 253 | 22 | | 314 | 125 | 8 |
| | 326 | 254 | 22 | | 315 | 113 | 7 |
| Cooling | 329 | 115 | 7 | | 320 | 77 | 6 |
| | 330 | 100 | 6 | | 322 | 65 | 5 |
| | 335 | 41 | 4 | | 326 | 58 | 5 |
| | 340 | 34 | 3 | | 332 | 55 | 5 |
| | - | - | - | | 334 | 48 | 5 |
| | - | - | - | | 340 | 44 | 5 |

## Appendix B-9: Experimental Results of HTC of Mixture of FS Mixed With Acetic Acid and Cassava Pulp

| No. | Mixing ratio FS:acetic acid:cassava pulp (by weight) | Temperature (°C) | Reaction time (h) | Energy content (MJ/kg) | | Hydrochar yield (%) | |
|---|---|---|---|---|---|---|---|
| | | | | #1 | #2 | #1 | #2 |
| 1 | 1 : 0.4 : 1 | 200 | 0.5 | 18.70 | 18.65 | 75.93 | 78.45 |
| 2 | 1 : 0.4 : 1 | 200 | 1 | 19.48 | 19.47 | 65.29 | 70.44 |
| 3 | 1 : 0.4 : 1 | 200 | 3 | 18.97 | 19.18 | 73.28 | 71.27 |
| 4 | 1 : 0.4 : 1 | 200 | 5 | 22.15 | 22.45 | 72.20 | 72.95 |
| 5 | 1 : 0.4 : 1 | 200 | 10 | 24.45 | 25.14 | 70.21 | 68.63 |
| 6 | 1 : 0.4 : 1 | 220 | 0.5 | 27.71 | 29.38 | 68.74 | 70.73 |
| 7 | 1 : 0.4 : 1 | 220 | 1 | 27.15 | 27.66 | 67.85 | 71.58 |
| 8 | 1 : 0.4 : 1 | 220 | 3 | 19.23 | 19.22 | 69.66 | 65.78 |
| 9 | 1 : 0.4 : 1 | 220 | 5 | 20.13 | 20.08 | 65.00 | 63.68 |
| 10 | 1 : 0.4 : 1 | 220 | 10 | 20.82 | 21.12 | 64.92 | 65.43 |
| 11 | 1 : 0.4 : 1 | 250 | 0.5 | 19.34 | 19.41 | 68.96 | 69.38 |
| 12 | 1 : 0.4 : 1 | 250 | 1 | 18.75 | 19.25 | 62.44 | 63.42 |
| 13 | 1 : 0.4 : 1 | 250 | 3 | 20.46 | 20.50 | 64.64 | 63.82 |
| 14 | 1 : 0.4 : 1 | 250 | 5 | 20.73 | 20.61 | 62.18 | 62.81 |
| 15 | 1 : 0.4 : 1 | 250 | 10 | 21.97 | 21.07 | 63.98 | 62.89 |

## Appendix B-10: Experimental Results of BMP Tests

| Day | Biogas (mL) | | | | | | | | Methane (%v) | | | | | | Methane production (mL) | | Cumulative methane production (mL) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Test I | | | | Test II | | | | Test I | | | Test II | | | Test I | Test II | Test I | Test II | HTC liquid |
| | #1 | #2 | #3 | Avg. | #1 | #2 | #3 | Avg. | #1 | #2 | #3 | #1 | #2 | #3 | Avg. | Avg. | Avg. | Avg. | Avg. |
| 1 | 2 | 1 | 2 | 1.67 | 3 | 3 | 1 | 2.33 | - | - | - | - | - | - | 0.50 | 0.75 | 0.50 | 0.75 | 0.00 |
| 2 | 24 | 25 | 24 | 24.33 | 47 | 50 | 40 | 45.67 | - | - | - | - | - | - | 7.32 | 14.70 | 7.83 | 15.45 | 0.00 |
| 3 | 27 | 25 | 27 | 26.33 | 36 | 36 | 35 | 35.67 | - | - | - | - | - | - | 7.93 | 11.48 | 15.75 | 26.93 | 0.00 |
| 4 | 40 | 42 | 40 | 40.67 | 43 | 42 | 53 | 46.00 | - | - | - | - | - | - | 12.24 | 14.81 | 27.99 | 41.74 | 0.00 |
| 5 | 41 | 40 | 40 | 40.33 | 43 | 42 | 53 | 46.00 | - | - | - | - | - | - | 12.14 | 14.81 | 40.13 | 56.55 | 0.00 |
| 6 | 41 | 40 | 42 | 41.00 | 43 | 43 | 53 | 46.33 | - | - | - | - | - | - | 12.34 | 14.91 | 52.47 | 71.46 | 0.00 |
| 7 | 44 | 45 | 45 | 44.67 | 60 | 60 | 60 | 60.00 | 29.52 | 28.58 | 32.19 | 20.43 | 37.23 | 38.91 | 13.44 | 19.31 | 65.92 | 90.78 | 0.00 |
| 8 | 35 | 35 | 35 | 35.00 | 60 | 61 | 60 | 60.33 | - | - | - | - | - | - | 21.02 | 29.01 | 86.94 | 119.79 | 0.00 |
| 9 | 36 | 36 | 36 | 36.00 | 36 | 36 | 37 | 36.33 | - | - | - | - | - | - | 21.62 | 17.47 | 108.55 | 137.26 | 0.00 |
| 10 | 46 | 33 | 36 | 38.33 | 36 | 37 | 37 | 36.67 | - | - | - | - | - | - | 23.02 | 17.63 | 131.57 | 154.90 | 0.00 |
| 11 | 46 | 36 | 36 | 39.33 | 36 | 36 | 37 | 36.33 | - | - | - | - | - | - | 23.62 | 17.47 | 155.19 | 172.37 | 0.00 |
| 12 | 47 | 59 | 59 | 55.00 | 36 | 36 | 30 | 34.00 | - | - | - | - | - | - | 33.03 | 16.35 | 188.22 | 188.72 | 0.00 |
| 13 | 62 | 62 | 66 | 63.33 | 38 | 38 | 36 | 37.33 | - | - | - | - | - | - | 38.03 | 17.95 | 226.25 | 206.67 | 19.58 |
| 14 | 50 | 50 | 44 | 48.00 | 25 | 25 | 25 | 25.00 | 57.85 | 60.09 | 62.22 | 45.68 | 49.74 | 48.84 | 28.82 | 12.02 | 255.08 | 218.70 | 36.38 |
| 15 | 51 | 50 | 45 | 48.67 | 25 | 26 | 25 | 25.33 | - | - | - | - | - | - | 33.26 | 13.65 | 288.34 | 232.34 | 56.00 |
| 16 | 63 | 63 | 48 | 58.00 | 37 | 37 | 38 | 37.33 | - | - | - | - | - | - | 39.64 | 20.11 | 327.98 | 252.45 | 75.53 |
| 17 | 39 | 39 | 23 | 33.67 | 24 | 24 | 23 | 23.67 | - | - | - | - | - | - | 23.01 | 12.75 | 350.99 | 265.20 | 85.79 |
| 18 | 39 | 39 | 23 | 33.67 | 24 | 24 | 23 | 23.67 | - | - | - | - | - | - | 23.01 | 12.75 | 374.01 | 277.95 | 96.05 |
| 19 | 47 | 39 | 24 | 36.67 | 24 | 24 | 24 | 24.00 | - | - | - | - | - | - | 25.06 | 12.93 | 399.07 | 290.88 | 108.19 |
| 20 | 32 | 35 | 40 | 35.67 | 36 | 36 | 36 | 36.00 | - | - | - | - | - | - | 24.38 | 19.39 | 423.45 | 310.27 | 113.17 |

**Table B-10: Experimental Results of BMP Tests (cont.)**

| Day | Biogas (mL) | | | | | | | | Methane (%v) | | | | | | Methane production (mL) | | Cumulative methane production (mL) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Test I | | | | Test II | | | | Test I | | | Test II | | | Test I | Test II | Test I | Test II | HTC liquid |
| | #1 | #2 | #3 | Avg. | #1 | #2 | #3 | Avg. | #1 | #2 | #3 | #1 | #2 | #3 | Avg. | Avg. | Avg. | Avg. | Avg. |
| 21 | 37 | 45 | 42 | 41.33 | 17 | 17 | 18 | 17.33 | 68.35 | 68.42 | 68.28 | 53.36 | 53.34 | 54.91 | 28.25 | 9.34 | 451.70 | 319.61 | 132.09 |
| 22 | 44 | 43 | 43 | 43.33 | 17 | 18 | 19 | 18.00 | - | - | - | - | - | - | 27.47 | 8.69 | 479.17 | 328.31 | 150.86 |
| 23 | 48 | 44 | 44 | 45.33 | 18 | 17 | 19 | 18.00 | - | - | - | - | - | - | 28.74 | 8.69 | 507.91 | 337.00 | 170.91 |
| 24 | 45 | 45 | 45 | 45.00 | 16 | 16 | 19 | 17.00 | - | - | - | - | - | - | 28.53 | 8.21 | 536.44 | 345.21 | 191.23 |
| 25 | 45 | 45 | 46 | 45.33 | 16 | 17 | 20 | 17.67 | - | - | - | - | - | - | 28.74 | 8.53 | 565.18 | 353.74 | 211.44 |
| 26 | 44 | 45 | 48 | 45.67 | 18 | 17 | 20 | 18.33 | - | - | - | - | - | - | 28.95 | 8.86 | 594.14 | 362.60 | 231.54 |
| 27 | 42 | 45 | 40 | 42.33 | 24 | 24 | 21 | 23.00 | - | - | - | - | - | - | 26.84 | 11.11 | 620.97 | 373.71 | 247.27 |
| 28 | 41 | 47 | 47 | 45.00 | 22 | 22 | 15 | 19.67 | 65.06 | 63.35 | 61.97 | 48.77 | 48.58 | 47.56 | 28.53 | 9.50 | 649.50 | 383.21 | 266.30 |
| 29 | 45 | 47 | 48 | 46.67 | 14 | 19 | 14 | 15.67 | - | - | - | - | - | - | 29.63 | 6.67 | 679.14 | 389.88 | 289.26 |
| 30 | 45 | 45 | 43 | 44.33 | 9 | 16 | 16 | 13.67 | - | - | - | - | - | - | 28.15 | 5.82 | 707.29 | 395.70 | 311.59 |
| 31 | 30 | 28 | 25 | 27.67 | 14 | 16 | 14 | 14.67 | - | - | - | - | - | - | 17.57 | 6.25 | 724.86 | 401.95 | 322.91 |
| 32 | 25 | 20 | 25 | 23.33 | 10 | 12 | 16 | 12.67 | - | - | - | - | - | - | 14.82 | 5.40 | 739.67 | 407.35 | 332.33 |
| 33 | 25 | 20 | 20 | 21.67 | 10 | 15 | 17 | 14.00 | - | - | - | - | - | - | 13.76 | 5.96 | 753.43 | 413.31 | 340.12 |
| 34 | 24 | 22 | 23 | 23.00 | 8 | 9 | 14 | 10.33 | - | - | - | - | - | - | 14.61 | 4.40 | 768.04 | 417.71 | 350.33 |
| 35 | 20 | 20 | 23 | 21.00 | 8 | 12 | 7 | 9.00 | 64.97 | 65.55 | 60.05 | 46.03 | 46.23 | 35.55 | 13.34 | 3.83 | 781.37 | 421.55 | 359.83 |
| 36 | 24 | 20 | 23 | 22.33 | 8 | 8 | 7 | 7.67 | - | - | - | - | - | - | 12.74 | 2.42 | 794.11 | 423.97 | 370.14 |
| 37 | 22 | 18 | 20 | 20.00 | 5 | 5 | 7 | 5.67 | - | - | - | - | - | - | 11.41 | 1.79 | 805.52 | 425.76 | 379.76 |
| 38 | 18 | 20 | 19 | 19.00 | 8 | 5 | 10 | 7.67 | - | - | - | - | - | - | 10.84 | 2.42 | 816.36 | 428.18 | 388.18 |
| 39 | 14 | 18 | 15 | 15.67 | 5 | 7 | 8 | 6.67 | - | - | - | - | - | - | 8.94 | 2.11 | 825.30 | 430.29 | 395.01 |
| 40 | 10 | 15 | 18 | 14.33 | 5 | 5 | 5 | 5.00 | - | - | - | - | - | - | 8.18 | 1.58 | 833.48 | 431.87 | 401.61 |

## Appendix B-10: Experimental Results of BMP Tests (cont.)

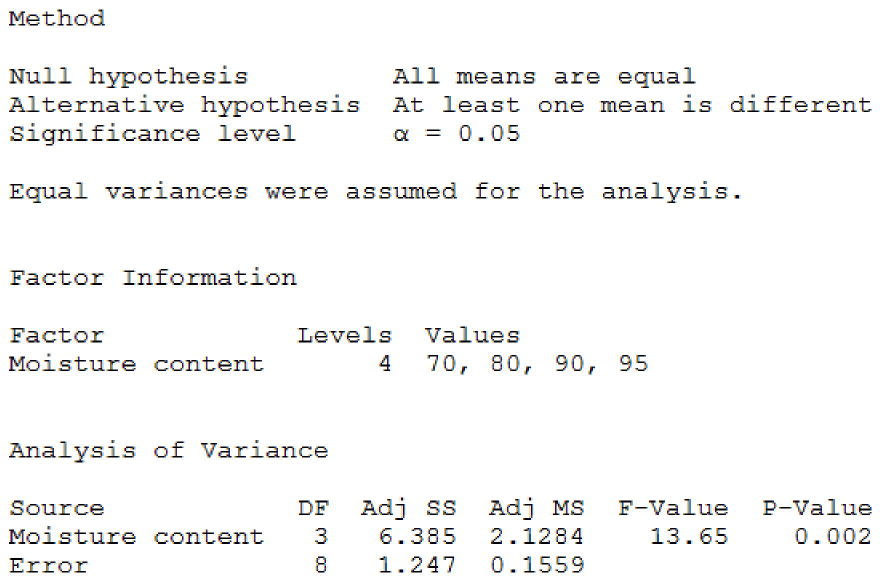
| Day | Biogas (mL) | | | | | | | | Methane (%v) | | | | | | Methane production (mL) | | Cumulative methane production (mL) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Test I | | | | Test II | | | | Test I | | | Test II | | | Test I | Test II | Test I | Test II | HTC liquid |
| | #1 | #2 | #3 | Avg. | #1 | #2 | #3 | Avg. | #1 | #2 | #3 | #1 | #2 | #3 | Avg. | Avg. | Avg. | Avg. | Avg. |
| 41 | 12 | 10 | 15 | 12.33 | 6 | 5 | 5 | 5.33 | - | - | - | - | - | - | 7.04 | 1.69 | 840.51 | 433.55 | 406.96 |
| 42 | 8 | 10 | 14 | 10.67 | 7 | 4 | 5 | 5.33 | 59.73 | 54.37 | 57.06 | 37.37 | 35.19 | 22.23 | 6.09 | 1.69 | 846.60 | 435.24 | 411.36 |
| 43 | 5 | 10 | 10 | 8.33 | 5 | 4 | 5 | 4.67 | - | - | - | - | - | - | 2.63 | 0.91 | 849.23 | 436.15 | 413.08 |
| 44 | 6 | 6 | 8 | 6.67 | 2 | 4 | 5 | 3.67 | - | - | - | - | - | - | 2.10 | 0.72 | 851.33 | 436.87 | 414.46 |
| 45 | 2 | 4 | 5 | 3.67 | 4 | 4 | 3 | 3.67 | - | - | - | - | - | - | 1.16 | 0.72 | 852.48 | 437.58 | 414.90 |
| 46 | 5 | 4 | 5 | 4.67 | 1 | 2 | 2 | 1.67 | - | - | - | - | - | - | 1.47 | 0.33 | 853.95 | 437.91 | 416.05 |
| 47 | 2 | 4 | 7 | 4.33 | 3 | 5 | 2 | 3.33 | - | - | - | - | - | - | 1.37 | 0.65 | 855.32 | 438.56 | 416.76 |
| 48 | 1 | 2 | 2 | 1.67 | 1 | 3 | 2 | 2.00 | - | - | - | - | - | - | 0.53 | 0.39 | 855.84 | 438.95 | 416.90 |
| 49 | 5 | 5 | 2 | 4.00 | 2 | 2 | 1 | 1.67 | - | - | - | - | - | - | 1.26 | 0.33 | 857.10 | 439.27 | 417.83 |
| 50 | 2 | 2 | 2 | 2.00 | 2 | 1 | 1 | 1.33 | 28.76 | 28.15 | 37.64 | 21.92 | 17.83 | 18.76 | 0.63 | 0.26 | 857.73 | 439.53 | 418.20 |

# Appendix C

## Statistical analysis

## Appendix C-1: One-way ANOVA of energy content vs. moisture content

At temperature of 220 °C and reaction time of 5 h



```
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
Moisture content       4  70, 80, 90, 95


Analysis of Variance

Source            DF  Adj SS  Adj MS  F-Value  P-Value
Moisture content   3   6.385  2.1284    13.65    0.002
Error              8   1.247  0.1559
```

## Appendix C-2: One-way ANOVA of energy content vs. 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       3  180, 220, 250


Analysis of Variance
```

At moisture content of 80%wt and reaction time of 0.5 h

```
Source       DF  Adj SS  Adj MS  F-Value  P-Value
Temperature   2   2.772  1.3858     4.75    0.058
Error         6   1.750  0.2916
Total         8   4.521
```

At moisture content of 80%wt and reaction time of 1 h

```
Source       DF  Adj SS  Adj MS  F-Value  P-Value
Temperature   2   3.403  1.7017     4.47    0.065
Error         6   2.283  0.3805
Total         8   5.686
```

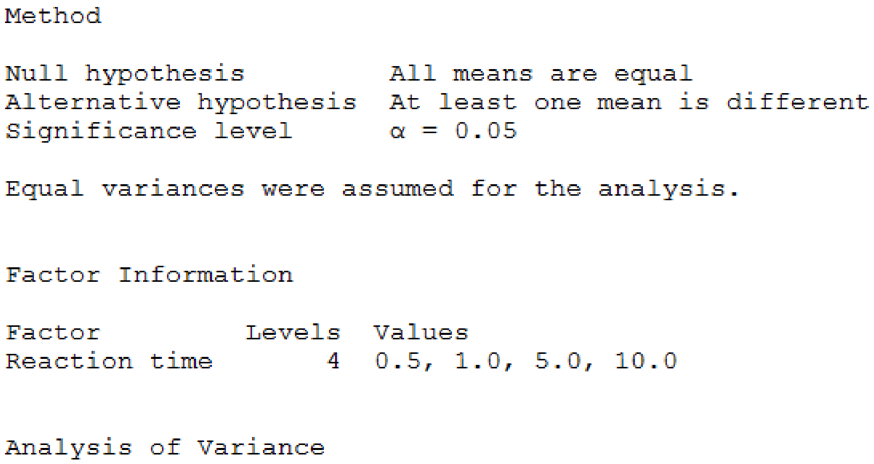
At moisture content of 80%wt and reaction time of 5 h

```
Source       DF  Adj SS  Adj MS  F-Value  P-Value
Temperature   2   7.204  3.6021     9.60    0.013
Error         6   2.251  0.3751
Total         8   9.455
```

At moisture content of 80%wt and reaction time of 10 h

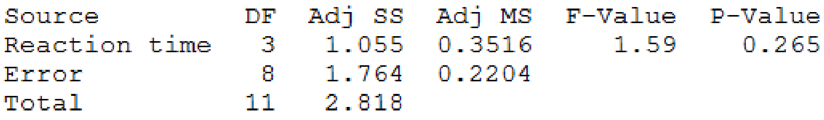
```
Source       DF  Adj SS  Adj MS  F-Value  P-Value
Temperature   2  11.423  5.7117    21.78    0.002
Error         6   1.574  0.2623
Total         8  12.997
```

## Appendix C-3: One-way ANOVA of energy content vs. reaction time



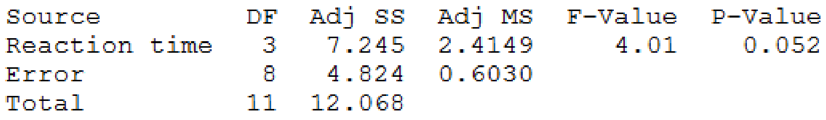
```
Method

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
Reaction time       4  0.5, 1.0, 5.0, 10.0


Analysis of Variance
```

At moisture content of 80%wt and temperature of 180 °C



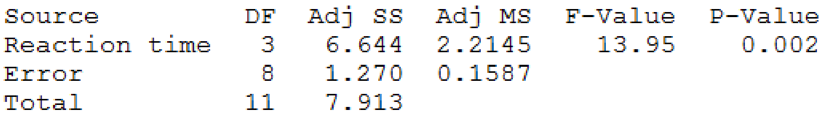
```
Source         DF  Adj SS  Adj MS  F-Value  P-Value
Reaction time   3   1.055  0.3516     1.59    0.265
Error           8   1.764  0.2204
Total          11   2.818
```

At moisture content of 80%wt and temperature of 220 °C



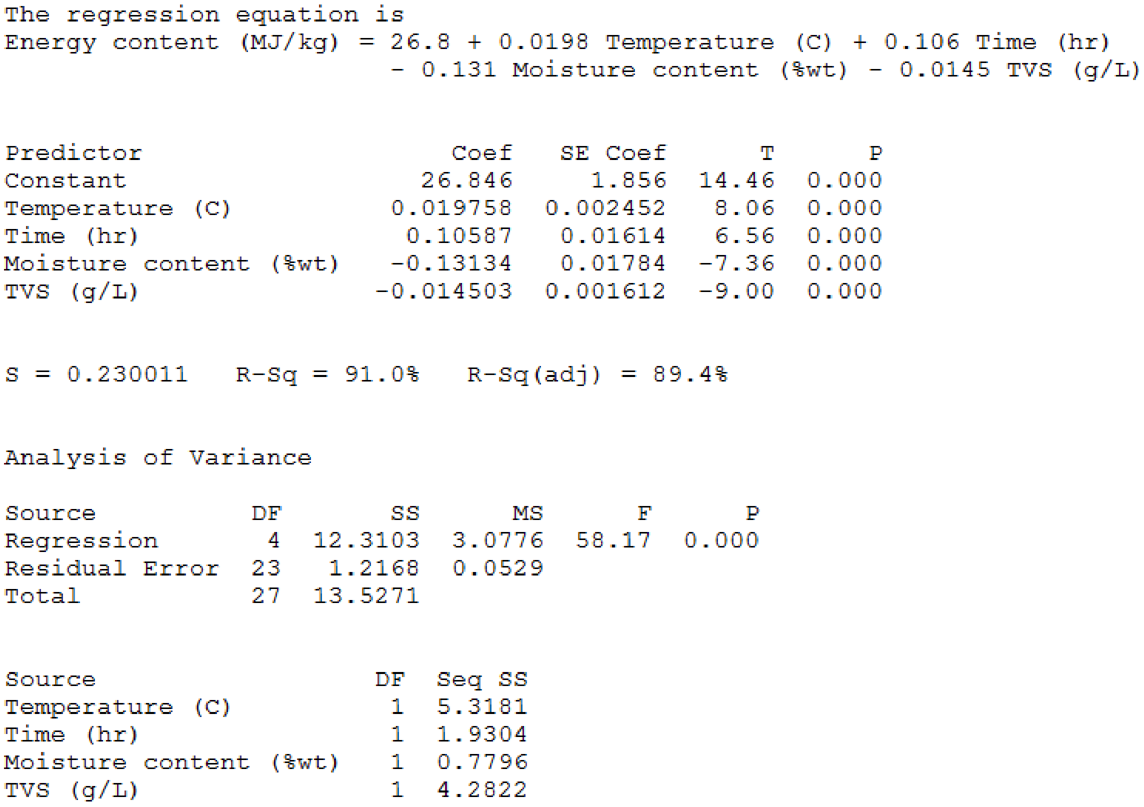
```
Source         DF  Adj SS  Adj MS  F-Value  P-Value
Reaction time   3   7.245  2.4149     4.01    0.052
Error           8   4.824  0.6030
Total          11  12.068
```

At moisture content of 80%wt and temperature of 250 °C



```
Source         DF  Adj SS  Adj MS  F-Value  P-Value
Reaction time   3   6.644  2.2145    13.95    0.002
Error           8   1.270  0.1587
Total          11   7.913
```

## Appendix C-4: Regression analysis: energy content vs. temperature, reaction time, moisture content and VS concentration



```
The regression equation is
Energy content (MJ/kg) = 26.8 + 0.0198 Temperature (C) + 0.106 Time (hr)
                         - 0.131 Moisture content (%wt) - 0.0145 TVS (g/L)


Predictor                     Coef    SE Coef      T      P
Constant                    26.846      1.856  14.46  0.000
Temperature (C)           0.019758   0.002452   8.06  0.000
Time (hr)                  0.10587    0.01614   6.56  0.000
Moisture content (%wt)    -0.13134    0.01784  -7.36  0.000
TVS (g/L)                -0.014503   0.001612  -9.00  0.000


S = 0.230011   R-Sq = 91.0%   R-Sq(adj) = 89.4%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       4  12.3103  3.0776  58.17  0.000
Residual Error  23   1.2168  0.0529
Total           27  13.5271


Source                  DF  Seq SS
Temperature (C)          1  5.3181
Time (hr)                1  1.9304
Moisture content (%wt)   1  0.7796
TVS (g/L)                1  4.2822
```

## Appendix C-5: ANOVA: energy content vs. temperature and reaction time of hydrolysis and carbonization in two-stage HTC

```
Analysis of Variance

Source                                DF   Adj SS   Adj MS  F-Value  P-Value
Model                                  4   5.9999  1.49999     3.39    0.024
  Linear                               4   5.9999  1.49999     3.39    0.024
    Hydrolysis temperature (˚C)        1   0.0572  0.05724     0.13    0.722
    Hydrolysis reaction time (min)     1   3.5057  3.50567     7.93    0.009
    Carbonization temperature (˚C)     1   1.9070  1.90696     4.31    0.048
    Carbonizati reaction time (min)    1   0.5293  0.52929     1.20    0.284
Error                                 25  11.0585  0.44234
  Lack-of-Fit                         20   8.6662  0.43331     0.91    0.611
  Pure Error                           5   2.3922  0.47845
Total                                 29  17.0584
```

# Appendix D

# Calculations

## Appendix D-1: Mass balance and carbon distribution for conventional HTC of FS

### Analysis data and assumptions for 1 batch operation

| | |
|---|---|
| ***Input-materials*** | |
| FS sample | 350 mL |
| Dried FS | 62.74 g |
| Carbon in dried FS | 38.45 %wt |
| Water | 300 mL |
| ***Output-products*** | |
| Hydrochar | 43.83 g |
| Carbon in hydrochar | 41.04 %wt |
| Filtrate | 275 mL |
| TOC of filtrate | 15.845 g/L |
| Water as vapor | 38 g (~38 mL) |
| Gas volume | 3.5 L |
| $CO_2$ content in gas | 61.9 %v |

### Mass balance

Hydrochar yield = 43.83 g x 100/62.74 g = 69.86 %
Mass of liquid product = (275 mL + 38 mL) – 300 mL = 13 mL (~13 g)
Liquid product yield = 13 g x 100/62.74 g = 20.72 %
Gas product yield = 100 – 69.86 – 20.72 = 9.42 %

### Carbon balance

Mass of carbon in hydrochar = 41.04 %wt x 43.83 g = 17.99 g
Carbon distribution into hydrochar = 17.99 g x 100/62.74 g = 28.67 %wt

Mass of carbon in liquid product = 275 mL x 15.845 g/L/1000 = 4.36 g
Carbon distribution into liquid product = 4.36 g x 100/62.74 g = 6.94 %wt

Carbon distribution into gas product = 38.45 – 28.67 – 6.94 = 2.84 %
Mass of carbon in gas product = 62.74 g x 2.84% = 1.78 g

### Balance confirmation of carbon in gas product

Based on $CO_2$ gas which is the main component of gas products

$CO_2$ content in gas product = 3.5 L x 61.9 %v = 2.17 L
According to the ideal gas law:

$$PV = nRT$$

Where, $P$ = the pressure of the gas (atm)
$V$ = the volume of the gas (L)
$n$ = the amount of substance of gas (mole = g/g-molecular weight)
$R$ = the gas constant (0.08206 $L.atm.mole^{-1}.K^{-1}$)
$T$ = the temperature of the gas (K)

Mass of $CO_2$ content in gas (g) = $\frac{(1\ \text{atm})(2.17\ \text{L})(44\ \text{g-molecular weight})}{(0.08206\ \text{L.atm.mole}^{-1}.\text{K}^{-1})(298\ \text{K})}$

= 3.90 g

Mass of carbon content in gas = 12/44 x 3.90 g = 1.06 g ∗

Carbon distribution into gas product = 1.06*100/62.74 = 1.69 %

∗ Because this value is based on mass of carbon in the $CO_2$ gas, it was slightly lower than the mass of the carbon calculated from the carbon balance (1.78 g). The rest of the carbon of about 1.15 % was converted into other hydrocarbon gases such as $CH_4$ and VOCs.

## Appendix D-2: Energy balance for conventional HTC process

HTC process

*Energy required for HTC operation* (Eq. 3.3) + *Energy required for dewatering* + *Energy required for drying* + *Energy of FS*
= *Energy of products* + *Heat of reaction* + *Energy losses* (3.4)

Energy inputs to the HTC process, including energy required for HTC operation, dewatering by vacuum filtration, drying hydrochar and energy of FS, were determined using Equations (3.5), (3.6), (3.7) and (3.8), respectively. Energy outputs included the energies of the products (hydrochar, filtrate and gas) and heat of HTC reaction can be calculated using Equation (3.8) and (3.9), respectively, while energy losses occurred during the cooling and drying processes were determined using Equation (3.5) and (3.7), respectively.

Equations:

$$E_{required,\,HTC} = M \times W \times (C_{p,W} \times \Delta T) + [M \times (1-W)] \times C_{p,M} \times \Delta T + [E_{com} \times t] \tag{3.5}$$

$$E_{dewater} = P \times t \tag{3.6}$$

$$E_{dry} = M \times W \times [(C_{p,W} \times \Delta T) + \Delta H_{vap}] + [M \times (1-W)] \times C_{p,M} \times \Delta T \tag{3.7}$$

$$E_{substrate} = E_{content} \times M_{substrate} \tag{3.8}$$

$$E_{reaction} = E_{heat} \times M_{VM} \tag{3.9}$$

### Analysis data and assumptions

***HTC operation***

| | | |
|---|---|---|
| $M$ | is the mass of initial FS | 1 kg |
| $W$ | is the moisture content in FS (80 %wt) | 0.8 kg |
| $M_{VM}$ | is the mass of volatile matter content in FS (volatile matter content of about 60 %wt) | 1 x 0.6 x 0.2 = 0.12 kg |
| $C_{p,W}$ | is the heat capacity of water | 4.186 kJ/kg/°C |
| $C_{p,M}$ | is heat capacity of solids in FS | 1.95 kJ/kg/°C |
| $E_{com}$ | is the energy consumption rate at 250 °C | 36 kJ/min |
| $t$ | is operating time | 300 min |

HTC operating temperature of 250 °C
Hydrochar, liquid and gas yield of 72%, 20% and 8%
HTC reactor has efficiency of 10%

***Vacuum filtration***

| | | |
|---|---|---|
| $P$ | is the power of vacuum pump | 0.4 kW |
| $t$ | is operating time | 5 min |

***Drying of hydrochar***

| | | |
|---|---|---|
| $M$ | is the mass of wet produced hydrochar | 0.363 kg |
| $W$ | is the moisture content in wet produced hydrochar | 45 % |
| $\Delta H_{vap}$ | is the latent heat for vaporization of water | 2,260 kJ/kg |

Drying temperature of 105 °C

***Raw FS***

| | | |
|---|---|---|
| $E_{substrate,1}$ | is the energy content of dried FS | 13.5 MJ/kg |
| $M_{substrate,1}$ | is the mass of dried FS | 200 g |
| $E_{substrate,\ 2}$ | is the heat of evaporation of water | 2.3 MJ/kg [a] |
| $M_{substrate,2}$ | is the mass of water | 800 g |

***Produced hydrochar***

| | | |
|---|---|---|
| $E_{substrate}$ | is the energy content of the produced hydrochar | 19.5 MJ/kg |
| $M_{substrate}$ | is the mass of the produced hydrochar | 144 g |

***Produced liquid (filtrate)***

| | | |
|---|---|---|
| $E_{product}$ | is the energy content of the TS in filtrate | 13.9 MJ/kg [b] |
| $M_{product}$ | is the mass of the TS in filtrate | 40 g |

***Produced gas***

| | | |
|---|---|---|
| $E_{product}$ | is the energy content of the produced gas | 4.3 MJ/kg [c] |
| $M_{product}$ | is the mass of the produced gas | 16 g |

***Heat of HTC reaction***

| | | |
|---|---|---|
| $E_{heat}$ | is the heat of HTC reaction (exothermic reaction) | -1.6 MJ/kg [d] |
| $M_{VM}$ | is the mass of volatile matter content in FS (volatile matter content of about 60 %wt) | 1 x 0.6 x 0.2 = 0.12 kg |

[a] Source: https://en.wikipedia.org/wiki/Enthalpy_of_vaporization

[b] estimated from Equation given by Parikh et al. (2005)

$$HHV = 0.3536(\%FC) + 0.1559(\%VM) - 0.0078(\%Ash)$$

From analysis results; %FC of solid in filtrate = 1.00
%VM of solid in filtrate = 87.66
%Ash of solid in filtrate = 11.34

$$\begin{aligned} HHV &= 0.3536(1) + 0.1559(87.66) - 0.0078(11.34) \\ &= 13.9\ \text{MJ/kg} \end{aligned}$$

[c] estimated from: http://www.unitrove.com/engineering/tools/gas/natural-gas-calorific-value

[d] Based on the heat of HTC reaction of cellulose (Libra et al, 2011)

## Energy balance

Energy required for HTC operation = [(0.80 x 1 kg)(4.186 kJ/kg°C)(250-25 °C)] + [(0.20 x 1 kg)(1.95 kJ/kg°C)(250-25 °C)] + [36 kJ/min x 300 min x 0.1]
= 1,921 kJ

Energy required for vacuum filtration = 0.4 kW x 5/60 h
= 0.033 kWh
= 119 kJ

Energy required for drying hydrochar = [(0.45 x 0.363 kg)(4.186 kJ/kg°C)(105-25 °C) + [(0.45 x 0.363 kg)(2,260 kJ/kg)] + [(0.55 x 0.363 kg)(1.95 kJ/kg. °C)(105-25 C)]
= 455 kJ

Energy of FS = (13.5 MJ/kg x 200 g) – (2.3 MJ/kg x 800 g)
= 860 kJ
**Total energy input = 3,355 kJ**

Energy of hydrochar = 19.5 MJ/kg x 144 g
= 2,808 kJ
Energy of liquid product = 13.9 MJ/kg x 40 g
= 556 kJ
Energy of gas product = 4.3 MJ/kg x 16 g
= 69 kJ
Heat of reaction = 1.6 MJ/kg x 0.12 kg
= 192 kJ
Energy loss in cooling process = [(0.80 x 1 kg)(4.186 kJ/kg°C)(250-25 °C)] + [(0.20 x 1 kg)(1.95 kJ/kg°C)(250-25 °C)]
= 841 kJ
Energy loss in vapor (drying process) = (0.45 x 0.363 kg)(2,260 kJ/kg)
= 369 kJ
**Total energy output = 4,835 kJ**

**Energy efficiency**

$$Energy\ efficiency = \frac{energy\ content\ of\ hydrochar \times mass\ of hydrochar}{energy\ required} \tag{4.3}$$

*Energy efficiency* = 2,808/2,495
= 1.13

## Appendix D-3: Energy balance for conventional HTC reactor

Energy balance of the HTC reactor can be determined by:

*Energy input from electricity heating* = *Energy required for HTC operation* + *Energy losses* (3.3)

### Energy input

Energy input during the HTC operation measured by a watt-hour meter = 3.83 kWh
= 13,788 kJ

### Energy required for HTC

Energy required for HTC operation = 1,921 kJ (from Appendix D-2)

### Energy loss

Energy losses for heating reactor body and heat transferring to environments (convection and radiation) were calculated using Equation (3.10), (3.11), and (3.12).

Equations:

$$E_{convection} = h \times s \times (T_s - T_a) \tag{3.10}$$
$$E_{radiation} = \sigma \times s \times \varepsilon \cdot (T_s^{\,4} - T_a^{\,4}) \tag{3.11}$$
$$E_{loss,\,reactor} = M_{reactor} \times C_{p,reactor} \times \Delta T \tag{3.12}$$

**Analysis data and assumptions**

| | | |
|---|---|---|
| $M_{reactor}$ | is the mass of HTC reactor body | 3.5 kg |
| $C_{p,reactor}$ | is the heat capacity of reactor body | stainless steel = 0.5 kJ/kg°C |
| $\Delta T$ | is temperature difference | (250-25) °C |
| $h$ | is the convection coefficient | calculated through the Nusselt number |
| $s$ | is heater surface | 4 heater bars, size 0.12 x 0.06 $m^2$ each |
| $T_a$ | is the air temperature | 303 K |
| $T_s$ | is the heater bar temperature | 995 K |
| $\varepsilon$ | is the emissivity of the surface | ceramic = 0.69 |
| $\sigma$ | is the Stefan-Boltzman constant | $5.67 \times 10^{-8}$ W/$m^2$ $K^4$ |

Heater bar operating time = 2.2 h

The Nusselt number is "the ratio between the convection and conductive heat transfer":

$$Nu = (h \times L)/k$$

where $Nu$ is the Nusselt number, $L$ is the characteristic length, and $k$ is the air thermal conductivity (0.026 W/mK). "The Nusselt number depends on the geometrical shape of the sink and air flow".

Laminar flow: $Nu = 0.59 \times Ra^{0.25}$
Turbulent flow: $Nu = 0.14 \times Ra^{0.33}$

where Ra is the Rayleigh number, which defined as following:

$$Ra = Gr \text{ x } Pr$$

*Gr* is the Grashof number, is defined as following:

$$Gr = g \text{ x } L^3 \text{ x } \beta \text{ x } (Tp - Ta)/\eta^2$$

where $g$ is the acceleration of gravity, $L$ is the longer side of the heater bar (0.12 m), $\beta$ is the air thermal expansion coefficient (1/303), $Tp$ is the heater bar temperature (722 °C), $Ta$ is the air temperature (30 °C) and $\eta$ is the air kinetic viscosity ($1.6^{-5}$ m$^2$/s at 30 °C)

$$Gr = (9.81 \text{ m/s}^2) \text{ x } (0.12 \text{ m})^3 \text{ x } (1/303) \text{ x } (722 - 30) / (1.6\text{x}10^{-5} \text{ m}^2\text{/s})^2$$
$$Gr = 1.5 \text{ x } 10^8$$

Pr is the Prandtl number, is defined as following:

$$Pr = \mu \text{ x } c_p / k$$

where $\mu$ is the air dynamic viscosity ($1.86\text{x}10^{-5}$ kg/m at 30 °C) and $c_p$ is the air specific heat (1005 J/kg K).

$$Pr = (1.86\text{x}10^{-5} \text{ kg/m}) \text{ x } (1005 \text{ J/kg K}) / (0.026 \text{ W/mK})$$
$$Pr = 0.72$$

Then, $Ra = 1.5 \text{ x } 10^8 \text{ x } 0.72 = 1.08 \text{ x } 10^8$

*Ra* is less than $10^9$, the heat flow is laminar.

$$Nu = 0.59 \text{ x } (1.08 \text{ x } 10^8)^{0.25} = 60$$

Then, $h = Nu \text{ x } k / L$

$$= 60 \text{ x } (0.026 \text{ W/mK})/(0.12 \text{ m})$$
$$= 13 \text{ W/m}^2\text{K}$$

**Energy losses for heating reactor body** = (3.5 kg) x (0.5 kJ/kg°C) x (250-25 °C)
= 394 kJ

**Energy loss by convention** = (13 W/m$^2$K) x (4 x 0.12 x 0.06 m$^2$) x (995-303 K)
= 259 W (or 933 kJ/h)
= 2,052 kJ (for 2.2 h)

**Energy loss by radiation** = ($5.67 \times 10^{-8}$ W/m$^2$ K$^4$) x (4 x 0.12 x 0.06 m$^2$) x 0.69 x ($995^4$ - $303^4$ K$^4$)
= 1095 W (or 3941 kJ/h)
= 8,671 kJ (for 2.2 h)

## Appendix D-4: Mass balance and carbon distribution for two-stage HTC of FS

### Analysis data and assumptions

| | |
|---|---|
| ***Input-materials*** | |
| FS sample | 350 mL |
| Dried FS | 76.01 g |
| Carbon in dried FS | 38.10 %wt |
| Water | 300 mL |
| ***Output-products*** | |
| Hydrochar | 55.34 g |
| Carbon in hydrochar | 39.04 %wt |
| Filtrate | 200 mL |
| TOC of filtrate | 29.450 g/L |
| Water as vapor | 118 g (~118 mL) |
| Gas volume | 3.5 L |
| $CO_2$ content in gas | 64.1 %v |

### Mass balance

Hydrochar yield = 55.34 g x 100/76.01 g = 72.82 %
Mass of liquid product = (200 mL + 118 mL) – 300 mL = 18 mL (~18 g)
Liquid product yield = 18 g x 100/76.01 g = 23.68 %
Gas product yield = 100 – 72.82 – 23.68 = 3.50 %

### Carbon balance

Mass of carbon in hydrochar = 39.04 %wt x 55.34 g = 21.60 g
Carbon distribution into hydrochar = 21.60 g x 100/76.01 g = 28.42 %wt

Mass of carbon in liquid product = 200 mL x 29.45 g/L/1000 = 5.89 g
Carbon distribution into liquid product = 5.89 g x 100/76.01 g = 7.75 %wt

Carbon distribution into gas product = 38.10 – 28.42 – 7.75 = 1.93 %
Mass of carbon in gas product = 76.01 g x 1.93 % = 1.47 g

### Confirm balance of carbon in gas product

Based on $CO_2$ gas which is the main component of gas products

$CO_2$ content in gas product = 3.5 L x 64.1 %v = 2.24 L
According to the ideal gas law (Appendix D-1)

$$\text{Mass of } CO_2 \text{ content in gas (g)} = \frac{(1\ \text{atm})(2.24\ \text{L})(44\ \text{g-molecular weight})}{(0.08206\ \text{L.atm.mole}^{-1}.\text{K}^{-1})(298\ \text{K})} = 4.03\ \text{g}$$

Mass of carbon content in gas = 12/44 x 4.03 g = 1.10 g ∗
Carbon distribution into gas product = 1.10*100/76.01 = 1.45 %

∗ Because this value is based on mass of carbon in the $CO_2$ gas, it was slightly lower than the mass of the carbon calculated from the carbon balance (1.47 g). The rest of the carbon of about 0.48 % was converted into other hydrocarbon gases such as $CH_4$ and VOCs.

## Appendix D-5: Energy balance for two-stage HTC process

HTC process

*Energy required for HTC operation* (Eq. 3.3) + *Energy required for dewatering* + *Energy required for drying* + *Energy of FS*
= *Energy of products* + *Heat of reaction* + *Energy losses* (3.4)

Energy inputs to the two-stage HTC process, including energy required for HTC operation, dewatering by vacuum filtration, drying hydrochar and energy of FS, were determined using Equations (3.5), (3.6), (3.7) and (3.8), respectively. Energy outputs included the energies of the products (hydrochar, filtrate and gas) and heat of HTC reaction can be calculated using Equation (3.8) and (3.9), respectively, while energy losses occurred during the cooling and drying processes were determined using Equation (3.5) and (3.7), respectively.

Equations:

$$E_{required,\,HTC} = M \text{ x } W \text{ x } (C_{p,W} \text{ x } \Delta T) + [M \text{ x } (1-W)] \text{ x } C_{p,M} \text{ x } \Delta T + [E_{com} \text{ x } t] \tag{3.5}$$

$$E_{dewater} = P \text{ x } t \tag{3.6}$$

$$E_{dry} = M \text{ x } W \text{ x } [(C_{p,W} \text{ x } \Delta T) + \Delta H_{vap}] + [M \text{ x } (1-W)] \text{ x } C_{p,M} \text{ x } \Delta T \tag{3.7}$$

$$E_{substrate} = E_{content} \text{ x } M_{substrate} \tag{3.8}$$

$$E_{reaction} = E_{heat} \text{ x } M_{VM} \tag{3.9}$$

### Analysis data and assumptions

#### *HTC operation*

| | | |
|---|---|---|
| $M$ | is the mass of initial FS | 1 kg |
| $M_{VM}$ | is the mass of volatile matter content in FS (volatile matter content of about 60 %wt) | 1 x 0.6 x 0.2 = 0.12 kg |
| $W$ | is the moisture content in FS | 80 % |
| $E_{com}$ | is the energy consumption rate at 170 °C | 14.4 kJ/min |
| | and the energy consumption rate at 215 °C | 36 kJ/min |

Hydrolysis temperature of 170 °C and reaction time of 155 min
Carbonization temperature of 215 °C and reaction time of 100 min
Hydrochar, liquid and gas yield of 72%, 24% and 4%
HTC reactor has efficiency of 10%

#### *Vacuum filtration*

| | | |
|---|---|---|
| $P$ | is the power of vacuum pump | 0.4 kW |
| $t$ | is operating time | 5 min |

#### *Drying of hydrochar*

| | | |
|---|---|---|
| $M$ | is the mass of wet produced hydrochar | 0.363 kg |
| $W$ | is the moisture content in wet produced hydrochar | 45 % |

Drying temperature of 105 °C

***Raw FS***

| | | |
|---|---|---|
| $E_{substrate,1}$ | is the energy content of dried FS | 13.5 MJ/kg |
| $M_{substrate,1}$ | is the mass of dried FS | 200 g |
| $E_{substrate,2}$ | is the heat of evaporation of water | 2.3 MJ/kg [a] |
| $M_{substrate,2}$ | is the mass of water | 800 g |

***Produced hydrochar***

| | | |
|---|---|---|
| $E_{product}$ | is the energy content of the objective product | 20.5 MJ/kg |
| $M_{product}$ | is the mass of the objective product | 144 g |

***Produced liquid (filtrate)***

| | | |
|---|---|---|
| $E_{product}$ | is the energy content of the TS in filtrate | 13.9 MJ/kg [b] |
| $M_{product}$ | is the mass of the TS in filtrate | 48 g |

***Produced gas***

| | | |
|---|---|---|
| $E_{product}$ | is the energy content of the produced gas | 4.3 MJ/kg [c] |
| $M_{product}$ | is the mass of the produced gas | 8 g |

***Heat of HTC reaction***

| | | |
|---|---|---|
| $E_{heat}$ | is the heat of HTC reaction (exothermic reaction) | -1.6 MJ/kg [d] |
| $M_{VM}$ | is the mass of volatile matter content in FS (volatile matter content of about 60 %wt) | 1 x 0.6 x 0.2 = 0.12 kg |

[a, b, c, d] Refer to Appendix D-2

**Energy balance**

| | | |
|---|---|---|
| Energy required for hydrolysis stage of HTC | = | [(0.80 x 1 kg)(4.186 kJ/kg°C)(170-25 °C)] +<br>[(0.20 x 1 kg)(1.95 kJ/kg°C)(170-25 °C)] +<br>[14.4 kJ/min x 155 min x 0.1] |
| | = | 765 kJ |
| Energy required for carbonization stage of HTC | = | [(0.80 x 1 kg)(4.186 kJ/kg°C)(215-170 °C)] +<br>[(0.20 x 1 kg)(1.95 kJ/kg°C)(215-170 °C)] +<br>[36 kJ/min x 100 min x 0.1] |
| | = | 528 kJ |
| Energy required for vacuum filtration | = | 0.4 kW x 5/60 h |
| | = | 0.033 kWh |
| | = | 119 kJ |
| Energy required for drying hydrochar | = | [(0.45 x 0.363 kg)(4.186 kJ/kg°C)(105-25 °C) +<br>[(0.45 x 0.363 kg)(2,260 kJ/kg)] +<br>[(0.55 x 0.363 kg)(1.95 kJ/kg. °C)(105-25 C)] |
| | = | 455 kJ |
| Energy of FS | = | (13.5 MJ/kg x 200 g) – (2.3 MJ/kg x 800 g) |
| | = | 860 kJ |
| **Total energy input** | **=** | **2,727 kJ** |

Energy of hydrochar = 20.5 MJ/kg x 144 g
= 2,952 kJ
Energy of liquid product = 13.9 MJ/kg x 48 g
= 667 kJ
Energy of gas product = 4.3 MJ/kg x 8 g
= 34 kJ
Heat of reaction = 1.6 MJ/kg x 0.12 kg
= 192 kJ
Energy loss in cooling process = [(0.80 x 1 kg)(4.186 kJ/kg°C)(250-25 °C)] + [(0.20 x 1 kg)(1.95 kJ/kg°C)(250-25 °C)]
= 841 kJ
Energy loss in vapor (drying process) = (0.45 x 0.363 kg)(2,260 kJ/kg)
= 369 kJ
**Total energy output = 5,055 kJ**

**Energy efficiency**

$$Energy\ efficiency = \frac{energy\ content\ of\ hydrochar \times mass\ of hydrochar}{energy\ required} \tag{4.3}$$

*Energy efficiency* = 2,952/1,867
= 1.58

## Appendix D-6: Energy balance for two-stage HTC reactor

Energy balance of the two-stage HTC reactor can be determined by:

*Energy input from electricity heating = Energy required for HTC operation + Energy losses* (3.3)

### Energy input

Energy input during the HTC operation measured by a watt-hour meter = 3.34 kWh
= 12,024 kJ

### Energy required for HTC

Energy required for HTC operation = 1,294 kJ (from Appendix D-5)

### Energy loss

Energy losses for heating reactor body and heat transferring to environments (convection and radiation) were calculated using Equation (3.10), (3.11) and (3.12).

Equations:

$$E_{convection} = h \times s \times (T_s - T_a) \tag{3.10}$$

$$E_{radiation} = \sigma \times s \times \varepsilon \cdot (T_s^{\,4} - T_a^{\,4}) \tag{3.11}$$

$$E_{loss,\,reactor} = M_{reactor} \times C_{p,reactor} \times \Delta T \tag{3.12}$$

**Analysis data and assumptions**

| | | |
|---|---|---|
| $M_{reactor}$ | is the mass of HTC reactor body | 3.5 kg |
| $C_{p,reactor}$ | is the heat capacity of reactor body | stainless steel = 0.5 kJ/kg°C |
| $\Delta T$ | is temperature difference | (215-25) °C |
| $h$ | is the convection coefficient | 13 W/m$^2$K (Appendix D-5) |
| $s$ | is heater surface | 4 heater bars, size 0.12 x 0.06 m$^2$ each |
| $T_a$ | is the air temperature | 303 K |
| $T_s$ | is the heater bar temperature | 995 K |
| $\varepsilon$ | is the emissivity of the surface | ceramic = 0.69 |
| $\sigma$ | is the Stefan-Boltzman constant | 5.67 ×10$^{-8}$ W/m$^2$ K$^4$ |

Heater bar operating time = 2.0 h

**Energy losses for heating reactor body** = (3.5 kg) x (0.5 kJ/kg°C) x (215-25 °C)
= 333 kJ

**Energy loss by convention** = (13 W/m$^2$K) x (4 x 0.12 x 0.06 m$^2$) x (995-303 K)
= 259 W (or 933 kJ/h)
= 1,866 kJ (for 2.0 h)

**Energy loss by radiation** = (5.67 ×10$^{-8}$ W/m$^2$ K$^4$) x (4 x 0.12 x 0.06 m$^2$) x 0.69 x (995$^4$ - 303$^4$ K$^4$)
= 1095 W (or 3941 kJ/h)
= 7,882 kJ (for 2.0 h)

## Appendix D-7: Energy efficiency for pyrolysis process

Energy requirements include energy for pre-drying FS and operating pyrolysis process.

Equations:

$$E_{dry} = M \times W \times [(C_{p,W} \times \Delta T) + \Delta H_{vap}] + [M \times (1-W)] \times C_{p,M} \times \Delta T \quad (3.5)$$

$$E_{output} = E_{product} \times M_{product} \quad (3.6)$$

### Analysis data and assumptions

***Pre-drying***

| | | |
|---|---|---|
| $M$ | is the mass of initial FS | 1 kg |
| $W$ | is the moisture content in FS | 80 % |

***Pyrolysis operation****

Pyrolysis temperature of 500 °C
Energy required during operation = 300 kJ/kg-input

***Products****

| | |
|---|---|
| Oil | Energy content = 38.5 MJ/kg-oil<br>Yield = 0.26 kg-oil/kg-dried sludge |
| Char | Energy content = 13 MJ/kg-char<br>Yield = 0.53 kg-char/kg- dried sludge |

∗ Based on data of Kim and Parker, (2008)

### Energy requirement

| | | |
|---|---|---|
| Energy required for pre-drying | = | [(0.80 x 1 kg)(4.186 kJ/kg°C)(105-25 °C)] + [(0.80 x 1 kg)(2,260 kJ/kg)] + [(0.20 x 1 kg)(1.95 kJ/kg°C)(105-25 °C)] |
| | = | 2,131 kJ |
| Energy required for heating to 500°C | = | (1 kg)(1.95 kJ/kg°C)(500-105 °C) |
| | = | 770 kJ |
| Energy required during operation | = | 300 kJ |
| Total energy required | = | 3,201 kJ |
| **Energy of products** | = | [(38.5 MJ/kg-oil) x (0.26 kg-oil/kg-ds) + (13 MJ/kg-ds) x (0.53 kg-ds/kg-ds)] x (0.2 kg-ds/kg-FS) |
| | = | 3,380 kJ |

### Energy efficiency

$$\text{Energy efficiency} = \frac{(\text{energy content of oil} \times \text{mass of oil}) + (\text{energy content of char} \times \text{mass of char})}{\text{energy required}}$$

| | | |
|---|---|---|
| *Energy efficiency* | = | 3,380/3,201 |
| | = | 1.06 |

## Appendix D-8: Energy efficiency for gasification process

Energy requirements include energy for pre-drying of FS and operating gasification process.

Equations:

$$E_{dry} = M \times W \times [(C_{p,W} \times \Delta T) + \Delta H_{vap}] + [M \times (1-W)] \times C_{p,M} \times \Delta T \quad (3.5)$$

$$E_{output} = E_{product} \times M_{product} \quad (3.6)$$

**Analysis data and assumptions**

***Pre-drying***

| | | |
|---|---|---|
| $M$ | is the mass of initial FS | 1 kg |
| $W$ | is the moisture content in FS | 80 % |

***Gasification operation****

Pyrolysis temperature of 850 °C

***Products****

Fuel gas Energy content = 15.89 MJ/kg-dried sludge

∗ Based on data of Hamilton (1998)

**Energy requirement**

Energy required for pre-drying = [(0.80 x 1 kg)(4.186 kJ/kg°C)(105-25 °C)] + [(0.80 x 1 kg)(2,260 kJ/kg)] + [(0.20 x 1 kg)(1.95 kJ/kg°C)(105-25 °C)]
= 2,131 kJ

Energy required for heating to 850°C = (1 kg)(1.95 kJ/kg°C)(850-105 °C)
= 1,453 kJ

Total energy required = 3,584 kJ

**Energy of product** = (15.89 MJ/kg-ds) x (0.2 kg-ds/kg-FS)
= 3,178 kJ

**Energy efficiency**

$$Energy\ efficiency = \frac{energy\ content\ of\ fuel\ gas \times mass\ of fule\ gas\ produced}{energy\ required}$$

*Energy efficiency* = 3,178/3,584
= 0.89