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FACOLTA’ DI INGEGNERIA

DIPARTIMENTO DI INGEGNERIA CIVILE ED ARCHITETTURA

CORSO DI LAUREA MAGISTRALE IN INGEGNERIA
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TESI DI LAUREA

HYDROTHERMAL CARBONIZATION (HTC) OF FOOD WASTE – TESTING OF A HTC PROTOTYPE RESEARCH UNIT FOR DEVELOPING COUNTRIES

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AI MIEI GENITORI

RIASSUNTO

Alle soglie del 2014, ancora un terzo della popolazione mondiale, principalmente collocata in quei Paesi normalmente indicati come Paesi in via di sviluppo (PVS), oltre a non avere accesso all'acqua potabile, non è in grado di soddisfare i propri bisogni energetici mediante quelle fonti energetiche che, nei Paesi industrializzati, vengono considerate "tradizionali" (energia elettrica e metano). Per soddisfare dunque le esigenze più basilari, come la cottura dei cibi, l'illuminazione e il riscaldamento degli ambienti, vengono utilizzate biomasse quali carbonella, letame, paglia, residui colturali ma, principalmente, legna da ardere. Essa è reperita tagliando, in modo del tutto incontrollato, gli alberi; ciò ha ripercussioni decisamente negative sia sull'ambiente (aumento delle alluvioni, frane, dissesti, diminuzione della biodiversità, variazioni climatiche, ecc.) che sull'economia locale in quanto la deforestazione causa una progressiva perdita della sostanza organica presente nel terreno, comportando una successiva infertilità del suolo e scarsa produttività dei raccolti.

Oltre a quanto sopra esposto, nelle zone rurali ed urbane dei Paesi a medio e basso reddito, vi è un inadeguato sistema di raccolta e gestione dei rifiuti che causa sia un inquinamento delle già scarse risorse idriche (acque superficiali e profonde) sia un inquinamento dell'aria dovuto all'emissione di gas serra (tra tutti si cita il metano, originato dalla decomposizione dei rifiuti stessi). Per di più, la gestione incontrollata dei rifiuti, espone la popolazione a gravi rischi igienico-sanitari. Infatti, lo smaltimento inadeguato di quest'ultimi crea le condizioni ideali per la proliferazione di insetti e roditori che costituiscono i vettori principali per la diffusione di malattie virali quali: salmonella, tifo, colera, malaria, febbre dengue, febbre gialla, e così via. A tutto ciò va aggiunto il fatto che, solitamente, vi è un inappropriato, inesistente o mal gestito servizio igienico-sanitario e questo peggiora ulteriormente le condizioni di salute degli abitanti a causa della diffusione di malattie (come dissenteria e infezioni respiratorie acute), che si rivelano molto spesso mortali per bambini ed anziani.

Al fine di risolvere o ridurre i problemi legati alla mal gestione dei rifiuti si è deciso di progettare e costruire, presso l'*Eawag-Sandec* (uno dei più importanti internazionali centri di ricerca per le acque, situato in Svizzera), un reattore sperimentale di ***carbonizzazione idrotermale (HTC)***. Tale processo, scoperto nel 1913 da Friedrich Bergius e recentemente riportato alla luce da Markus Antonietti, è un trattamento termochimico che sottopone, per

diverse ore (1-72 ore), la matrice organica in fase acquosa a severe condizioni di temperatura (180-220°C) e pressione (20-35 bar). In tal modo, la biomassa è convertita in un materiale caratterizzato da un elevato contenuto di carbonio e simile al carbone naturale.

Uno dei grossi vantaggi legati all'utilizzo di questa tecnologia è quello di poter trattare matrici ad elevato contenuto di umidità (75-90%), senza subire pre-trattamenti particolari, quasi sempre necessari negli altri processi termici (incenerimento e pirolisi). Matrici caratterizzate da elevato contenuto di umidità sono, appunto, il letame, i residui agricoli, le acque reflue, i fanghi di depurazione e i rifiuti solidi urbani.

L'HTC, sebbene sia ad oggi impiegata nei Paesi industrializzati (specialmente in Germania e in Svizzera) a causa degli elevati costi di investimento/gestionali, potrebbe comunque essere interessante da applicare nei Paesi in via di sviluppo in quanto consente, non solo di risolvere il problema della gestione dei rifiuti, ma anche di ottenere un residuo solido sterile. Tenendo inoltre presente che il composto solido finale della reazione è del tutto paragonabile al tradizionale carbone, questo può essere impiegato come **combustibile**, andando così a sostituire la biomassa legnosa e risolvendo parte dei problemi sopra esposti; **ammendante** oltre ad altre applicazioni ambientali, elettrochimiche e catalitiche (ad esempio può essere impiegato come carbone attivo, atto alla rimozione di inquinati presenti nelle acque oppure come cattura e sequestro del carbonio).

Proprio per tutte queste interessanti proprietà ed impieghi che può avere il carbone, derivante dalla carbonizzazione idrotermale, si è pensato di utilizzare questa tecnologia per il trattamento dei rifiuti organici.

Al fine di investigare l'applicabilità e la sostenibilità del processo HTC, si è utilizzato un reattore cilindrico in acciaio inox, funzionante in discontinuo, con un volume utile di 21.8 L; tale volume consente di trattare circa 10 kg di biomassa organica. L'intervallo di temperatura al quale il prototipo è in grado di lavorare è compreso tra 5°C e 280°C e la pressione massima ammissibile è pari a 30 bar.

A causa dell'iniziale endotermia del processo di ossidazione, si è scelto di riscaldare il reattore mediante un mantello elettrico, ossia una sorta di "coperta" che, sfruttando l'effetto Joule, fornisce il calore necessario alla reazione (funzione, ovviamente, della tipologia di matrice alimentata).

Durante i test è possibile monitorare in continuo sia la temperatura che la pressione interna al reattore oltre alla temperatura del mantello elettrico. All'inizio e alla fine delle prove sono state effettuate delle analisi di laboratorio sia sul residuo solido (carbone) che su quello liquido. Sul composto solido sono stati determinati i solidi totali, il potere calorifico superiore, il contenuto di carbonio, di ossigeno, di azoto e di idrogeno (analisi elementare) mentre, su quello liquido, sono stati misurati il pH, l'elettroconduttività (EC) ed il carbonio organico totale (TOC).

Al fine di verificare il corretto funzionamento dell'impianto pilota, sono stati eseguiti tre test: il primo eseguito con sola acqua ed i successivi con riso crudo (nei due test è stato utilizzato un differente contenuto di solidi totali (2.6% e 5.2% rispettivamente).

Dopo questa prima fase di verifica, si è passati a testare la frazione organica proveniente dalla mensa "Aqua" del centro di ricerca Eawag.

In totale, sono stati eseguiti **10 test** nei quali si è andati ad investigare l'influenza del contenuto dei solidi totali iniziali (test da 1 a 6) e l'effetto della temperatura sul residuo solido finale (test da 7 a 10). Infatti, scopo di queste prove era quello di massimizzare il contenuto di carbonio nel residuo solido finale col più basso dispendio energetico.

Nei test da 1 a 6 si è variato il contenuto dei solidi totali in ingresso (2.5%; 4.9%; 7.4%; 9.4%; 12.8%; 15.2%) e mantenuto costante il tempo totale di residenza (10 h) nonché la temperatura interna (fissata pari a 200°C). Nei test da 7 a 10, invece, si è modificata la temperatura interna di reazione (200°C; 190°C; 180°C; 170°C) e tenuto costante il tempo di reazione (4 h) una volta raggiunta, all'interno del reattore, quella determinata condizione termica.

Dalla sperimentazione effettuata ed in particolare dalla serie degli ultimi 4 test, è emerso che, per ottenere un prodotto solido con elevato contenuto di carbonio, utilizzando come biomassa questo tipo di frazione organica alimentare, è necessario mantenere una temperatura interna intorno ai 200°C (il più possibile stabile), per un tempo totale di 10 ore, (avendo cura di verificare che la biomassa sia mantenuta a 180°C per circa 6 ore).

Queste condizioni sono per lo più da considerarsi delle linee guida; innanzitutto perché il sistema è totalmente manuale (accensione, variazione temperatura esterna del mantello e spegnimento) ma, soprattutto, perché va tenuto conto della grande variabilità qualitativa della frazione organica (funzione soprattutto del reddito pro-capite della popolazione).

Tutti i residui solidi finali sono risultati però simili fra loro, evidenziando la limitata influenza delle condizioni operative sulla qualità del residuo solido finale. Tutti i carboni infatti presentano un contenuto di carbonio del tutto confrontabile con quello della lignite naturale (67% e 70%, rispettivamente) e un valore di potere calorifico superiore paragonabile a quello del carbone bituminoso (29 MJ/kg e 30 MJ/kg, rispettivamente), rendendo quindi molto interessante il suo possibile impiego, quale combustibile alternativo alla legna da ardere.

In merito al bilancio energetico si è visto che, come atteso, il consumo di energia elettrica è funzione della durata complessiva delle prove e del contenuto dei solidi totali in ingresso. Il consumo medio registrato è risultato pari a 11.4 kWh mentre il bilancio finale energetico positivo si è ottenuto alimentando un rifiuto organico con un contenuto iniziale di solidi totali pari al 15.2%. In questo caso, infatti, a fronte dei 9.97 kWh consumati per il riscaldamento del reattore è stato ottenuto un residuo solido con un potere calorifico superiore pari a 29.2 MJ/kg che, se bruciato, consente di ottenere 11.3 kWh.

Nella parte finale del presente lavoro sono riportate alcune considerazioni in merito alle problematiche che questa tecnologia può ad oggi incontrare nei Paesi in via di sviluppo e i possibili sviluppi futuri della sperimentazione, in particolar modo riguardanti l’ottimizzazione del processo da un punto di vista energetico e la sua probabile applicazione, in via sperimentale, in Tanzania.

TABLE OF CONTENTS

ABBREVIATIONS

AD	Anaerobic Digestion
BOD_5	Biological Oxygen Demand in 5
CE	Carbon Efficiency
COD	Chemical Oxygen Demand
DCs	Developing Countries
DM	Dry Matter
DW	Dry Weight
EAWAG	Swiss Federal Institute of Aquatic Science and Technology
EC	Electrical Conductivity
FS	Faecal Sludge
FSM	Faecal Sludge Management
FW	Food Waste
GHG	Greenhouse Gas Emission
GNI	Gross National Income
HHV	Higher Heating Value
HTC	Hydrothermal Carbonization
IEA	International Energy Agency
ISWM	Integrated Solid Waste Management
MSW	Municipal Solid Waste
MSWM	Municipal Solid Waste Management
OSS	On-Site Sanitation
SANDEC	Department of Water and Sanitation in Developing Countries
SOM	Soil Organic Matter
SW	Solid Waste
SWM	Solid Waste Management
TOC	Total Organic Carbon
TS	Total Solids
WHO	World Health Organization
WW	Wet Weight
ZHAW	Zurich University of Applied Sciences

INTRODUCTION

Worldwide, more than two billion people in developing countries depend on traditional solid fuels (wood, animal dung and agricultural residues) to meet their basic energy needs. In fact, biomass is still the most important energy source in several low-income countries and it is used mainly for cooking, heating water and domestic space heating. More precisely, the daily demand for cooking fuel is globally estimated to be more than two million tonnes of biomass. Therefore, in these poor areas where lands are ecologically degradable (characterized by low water and nutrient retention capacity, poor texture, hardening and so on) and firewood is in short supply, the continuous cutting of live trees for household energy leads to soil erosion, soil degradation and desertification, causing as a result low crop yield and inevitably malnutrition of people, which become more and more susceptible to diseases, as well as to contribute the global greenhouse warming.

On this subject, only in the last decade, the *hydrothermal carbonization (HTC)*, that is a promising thermal conversion process able to convert biomass into a coal-like material with a higher carbon content, has regained considerable interest, after its discovery in 1913 by Friedrich Bergius, which also won the Nobel Prize in Chemistry to have explained and described, for the first time, the HTC-process as a method for simulating natural coalification of organic matter in the laboratory. This renewed interest for this particular thermo-chemical process is firstly due to the need for efficient biomass technologies and secondly to its particularities and advantages compared to other conversion processes (e.g. dry pyrolysis).

Specifically, hydrothermal carbonization is realized in a pressure vessel (reactor) by applying high temperatures (generally between 180-220°C) and high pressures (approximately 20-35 bar) to biomass in aqueous phase, that is in presence of water under saturated pressure, for several hours (usually about 4-12 h). Under these carbonization conditions, initial biomass waste with a low calorific value and high moisture content is mainly transformed through a series of complicated reactions (hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization) into a solid product, called hydrochar or HTC-coal, with similar characteristics to natural coal in regard to elemental composition (C, H, O and N) and higher heating value (HHV), increasing thus the energetic use of the biowaste. HTC-process, also known as wet pyrolysis, has a great advantage, compared to other usual thermo-chemical treatments, to convert wet input substrate (i.e. with high water content) into a carbonaceous solids without the need for an energy-intensive drying before or during the HTC-reaction, extending, in this way, the potential feedstock, such as wet animal manure, human waste, sewage sludge, municipal solid waste, aquaculture and algal residues. Therefore, HTC is seen as a promising technology for conversion of any kind of organic waste with high water contents (typically around 75-90%) and also for treatment of problematic biomass streams like biowaste, sewage sludge or industrial waste, where, especially in developing countries, they represent a serious issue for both environmental level and human well-being.

Moreover, the final HTC-coal obtained from biowaste after hydrothermal carbonization is a stable and sterile product and it has various interesting applications, thanks to its valuable properties, such as renewable energy carrier, soil amendment, carbon sequestration, activated carbon adsorbents and finally other electrochemical and catalytic uses.

This novel thermal conversion process is recently developed especially in Germany, where the world’s first industrial size HTC production plant, designed to use biowaste mainly from breweries, has already been put in operation in 2010. In these years, different experimental HTC-reactors with various technologies, volume and degree of complexity, have been constructed in Europe (especially Germany and Switzerland) in order to well understand the complex reaction mechanisms during the hydrothermal carbonization, depending on types of feedstock and process parameters (temperature, pressure and residence time).

Even though, to date, the implementation of this technology seems to be restricted to high cost and high-tech solutions suitable only for industrialized countries, the wide field of applications and potential benefits of HTC-coal are attractive for its use also in developing countries; since, through HTC process, food waste and faecal sludge (main problems in low and middle income countries) can be transformed in a valuable energy carrier (substituting traditional firewood and avoiding thus deforestation) allowing to improve, at the same time, the hygienic conditions of people. With this purpose, a simple and low-tech HTC prototype reactor for research purposes was designed and constructed in Switzerland at *Eawag/Sandec*, one the most important aquatic research institutes to the world, in order to assess the suitability of this technology for treatment especially of biowaste and/or faecal sludge in developing countries.

The overall objective of this study is to test, for the first time, this constructed HTC prototype reactor with food waste from the canteen of Eawag, on varying of the solid loads and inner temperatures reached inside the reactor. Then, all the produced HTC-coals will be analyzed and compared, in terms of carbon content and higher heating value. In this way, based on these results, it will possible to evaluate the optimal operational parameters (inner temperature and residence time) to achieve a higher carbon content and higher calorific value inside the hydrochar, in a such way that it could be used as a valuable energy source in developing countries. In addition, through these experiments, it will also possible to understand the maximum amount of biowaste per batch allowable for this HTC prototype reactor, possibly with the lowest energy input and a positive energy balance.

This research consists of two parts: a literature study and an experimental part. In particular the methodology followed is:

a. *literature study:* this first phase (chapters 1, 2 and 3) has as goal that to know how the HTC-process works, what are its conditions, what are the characteristics of input and output before and after the HTC carbonization and what are the potential applications and benefits. This step consists of reading in-depth scientific literature review regarding the global science of HTC-process, the recently researches and the different existent HTC technologies. Firstly, a general overview of main issues in developing countries (e.g. solid waste management and faecal sludge management) and thermochemical processes are discussed.

b. *experimental part*: this second phase (chapters 4 and 5) consists of testing the constructed HTC-reactor with food waste from the canteen, after checking the correct functionality of the system with a model organic substrate (raw rice), called in this report “preliminary tests”. Then, 10 experiments are in total carried out with food waste, subdivided in two different series: 6 tests increasing the Total Solids (TS) and the last 4 tests varying the inner temperature recorded during the HTC-reaction. At the end of each experiment, the output products are analyzed for determining various parameters of hydrochar (Total Solids, Higher Heating Value, elementary analysis) and of process water (pH, electro-conductivity and Total Organic Carbon).

The structure of this work is thus summarized as follows:

- **chapter 1:** mention of hydrothermal carbonization and its potential benefits that could bring in developing countries and general description of two main problems (solid waste management and faecal sludge management) in these areas;
- **chapter 2:** outline of use of biomass in developing countries and rapid description of usual thermochemical conversion process;
- **chapter 3:** detailed overview of hydrothermal carbonization;
- **chapter 4:** description of HTC prototype reactor used in this work and description step by step of the execution procedures carried out with food waste;
- **chapter 5:** all the tests performed in this research are descripted through the tables of inner temperature and pressures recorded during the whole HTC-reactions. Then all the results obtained are summarized and finally discussed.

1 DEVELOPING COUNTRIES AND HYDROTHERMAL CARBONIZATION

The HTC prototype reactor, used in this research, has been designed, constructed and then tested, for experimental purposes, to assess the suitability of the hydrothermal carbonization (HTC), promising and innovative technology able to transform wet biomass into a solid and sterile coal-like product under heat, water and high pressure, for decentralized especially organic waste or sewage sludge (residue of wastewater treatment plants) treatment in developing countries (DCs).

In these regions, particularly in rural and urban areas of low- and middle-income countries, an inadequate service of the Municipal Solid Waste Management (MSWM) and an inappropriate or non-existent sanitation coverage cause serious local and global environmental problems (water and air pollution) as well as a critical life-conditions for people, which are exposed to a lot of illnesses (skin diseases, diarrhoea, eye infections, dengue fever, etc.).

In particular, most of the people, in rural areas of Africa and Asia, live in small houses with their family on subsistence farming, mainly rely on firewood to cover their daily energy needs. This predominant use of wood fuel causes a negative impact on the climate and the soil, determining: deforestation, loss of soil fertility, soil erosion (decrease in soil of organic matter), decrease of soil productivity and therefore food insecurity, triggering subsequently malnutrition *(Krause, 2010)*.

In this way, the hydrothermal carbonization, thanks to its interesting properties, could be a potential and novel technology, as well as for industrialized countries (predominantly in Germany where the first pilot HTC plants have recently been implemented for treatment of problematic biomasses like industrial waste), also for developing countries, where the municipal solid waste management (MSWM) and the fecal sludge management (FSM) lead to severe health and environmental risks.

Therefore, the HTC technology, as *Krause (2010)* reports, could bring about improvements mainly in the poorest areas of the developing countries, such as:

- efficient use of resources to protect the environment through the supply of HTC-coal as a substitute for firewood for cooking;

- improvement living conditions of the people, thanks to the increase of the soil fertility and thus productivity, insuring so long-term food security, as well as a better sanitation condition and sustainable resource-saving energy supply;
- improvement soil texture (nutrient and water retention capacity of the soil) through the increase of the humus conditions like in the "Terra Preta"[1] as an activity against soil erosion, soil degradation and desertification;
- reduction greenhouse-gas emissions and medium-term sequestration of carbon into the soil.

Given the various benefits, that the use of the hydrothermal carbonization could bring in developing countries, this research, through the experimental prototype HTC-reactor constructed at Eawag-Sandec[2] (Switzerland), has as an objective that to test, this particular thermochemical conversion, for the first time, with biowaste from the canteen and then to analyze and compare the end-products obtained. In this way, it will be possible to assess, through a series of experiments with different solid load, what are the optimal operational parameters, in terms of carbonization temperature and residence time, but especially the maximum amount of waste per batch to be treated to have thus a positive energy balance.

Therefore, in order to better understand which are the main problems in the developing countries that this HTC technology could improve, the solid waste management (SWM) and faecal sludge management (FSM) are, in general way, considered in the following paragraphs. This because hydrothermal carbonization (HTC) can efficiently transform problematic biomass, like organic fraction and faecal sludge, into a store, transportable solid fuel, called HTC-coal or Hydrochar, transforming, in this way, waste into value and resolving thus the problem regarding SWM and FSM respectively.

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[1] The "Terra Preta" is a very fertile and black soil with high carbon and nutrient content, as practiced by the Incas in South America a long time ago.

[2] Eawag/Sandec: Swiss Federal Institute of Aquatic Science and Technology – Department of Water and Sanitation in Developing Countries

1.1 Solid Waste Management in developing countries

The Solid Waste Management (SWM) includes all activities that seek to minimize the human health, environmental and aesthetic impacts of solid waste[3], through an effective service of **collection** (from point of production, such as residential, industrial commercial and institutional, to the point of treatment or disposal), **transfer**, **recycling** (separation and collection of secondary materials for remanufacturing), **treatment** and finally an adequate landfill **disposal** of the refuse *(Zurbrügg, 2003)*.

In particular, Municipal Solid Waste Management (MSWM) is defined to include refuse from households, non-hazardous solid waste from commercial and institutional establishments (including hospitals), market waste, yard waste and street sweeping, which are the responsibility of the municipal authorities. However, industrial and faecal sludge, although are not usually considered part of municipal waste, are often found in the municipal waste stream and thus handled by the same service *(Eawag-Sandec, 2008)*.

Therefore, the MSW contains degradable waste (e.g. paper, food waste, yard waste, etc.), partially degradable waste (e.g. wood, disposable napkins and sludge, etc.), and non-degradable waste (e.g. plastics, glass, electronic waste, automotive parts, etc.) *(Jha et al., 2011)*.

Unfortunately, in the developing countries, especially in low- and middle-income countries, the SWM is one of the most difficult and serious environmental problems (air pollution due to unpleasant odors, methane and other greenhouse gases emissions and water pollution caused by toxic leachate), because of a lack of an adequate service coverage and poor management practices. In addition to this, an inefficient SWM causes also a negative impact on public health because uncollected solid waste provides favorable habitat for insects, vermin and scavenging animals, which proliferate and spread air- and waterborne diseases such as plague, dengue fever, diarrhoea and other illness among local populations *(Zurbrügg, 2003; Lohri, 2009)*.

This problem occurs especially in the urban centers of Asia, Africa and Latin America, where the rapid economic development and population growth, due to high migration from villages to cities, accompanied, as a result, by the increasing density of population, traffic

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[3] The term "solid waste" refers to material, which is not in a liquid form and has no value to the person who is responsible for it.

congestion, air and water pollution, increasing per capita generation of solid waste and lack of sustainable lands for waste disposal make this situation worse and thus the SWM a major problem in developing countries *(Coffey et al., 2010)*.

The next ***Figure 1*** shows this rapid urbanization in urban areas in developing countries and also an estimate for the year 2025, compared with the industrialized countries.

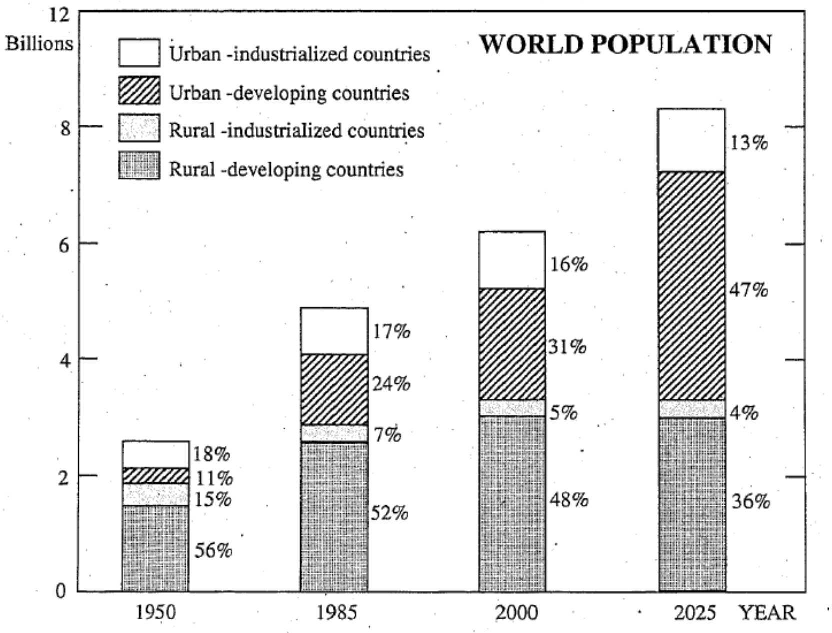

Figure 1: *World population projections for urban and rural areas (Schertenleib et al., 1992)*

These problems and issues of MSWM are present in many cities in the developing world, where services are often deficient and inadequate, aggravating this situation with increased urbanization *(Bobeck, 2010)*. In fact, typically one to two thirds of the solid waste generated in urban areas are not collected by the municipal authorities or not properly disposed of *(Eawag-Sandec, 2008)*. More specifically, the average waste collection rates are directly related to income levels; therefore, low-income countries (e.g. Africa, South Asia) have lower collection rates, around 41%, while high-income countries (e.g. some members of OECD[4] countries) have higher collection rates averaging 98%, thanks to the mechanized, efficient and frequent collection methods. However, it is important to remind that these

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[4] "OECD" countries is an acronym of "Organization for Economic Co-operation and Development" and it is an international economic organization of 34 countries founded in 1961 to stimulate economic progress and world trade. The mission of this co-operation is to promote policies that will improve the economic and social well-being of people around the world.

percentages of MSW collected can vary widely by region and income level *(World Bank, 2012; UN-HABITAT, 2010)*. Although, the collection, transportation and disposal of MSW represent a large expenditure for developing countries, around 30 – 50% of municipal operational budgets, only a little part of the refuse generated is collected *(Schertenleib et al., 1992)*. Therefore, as a result, in the absence of a regular solid waste collection service and a correct disposal of solid waste, the uncollected waste, often mixed with human and animal excreta, is dumped, in open spaces, on access roads, along watercourses or urban drainage systems and in seashore. In fact, in many developing countries, especially in Africa and Asia, the most common methods used for disposal and treatment of MSW, are open and uncontrolled dumpsites (for instance, in Nigeria about 70% is dumped at the riverside or stream while, in India, more than 90% of the solid waste is disposed in open dumps) and burning the refuse to reduce, thus, the volume or odors of it *(Eawag-Sandec, 2008)*. In this way, as already mentioned, this uncontrolled dumping sites of the refuse cause a serious environmental degradation (e.g. toxic gases emission, greenhouse gases emissions, toxic leachates pollute ground and surface water, etc.), health risks (e.g spread of gastrointestinal and parasitic diseases) and negative effect on the economic development in most cities of the developing countries.

The following two pictures, ***Figure 2a*** and ***Figure 2b***, show the typical situation of uncontrolled dumping sites in DCs. Specifically, the first one, *Figure 2a*, represent the Nile Delta (Egypt) village drain receiving an array of different waste *(Sandec News, 2012)* and the second one, *Figure 2b*, exhibits an open dump in Dar es Salaam, in Tanzania *(Lohri, 2009)*.

Figure 2a - Figure 2b: *Examples of uncontrolled dumping sites in developing countries (Sandec News, 2012 and Lohri, 2009)*

Moreover, the volume and the type of MSW generated in developing countries, as in high-income countries, depend on the standard of living, consumption patterns, income level, geographical location, cultural norms, as well as on the level of commercial and institutional activities. Depending on these factors, the waste characteristics and volume can vary from city to city and even within the same city, as well as from season to season.

Naturally, higher income level and rate of urbanization lead to increase the amount of solid waste produced; this it means that there is a strong correlation between gross national income[5] (GNI) and generated municipal solid waste. In fact, as soon as the income level and lifestyle increase, consumption of goods and services correspondingly increases, as does the volume of waste generated. Therefore, high-income countries produce the most waste per capita; while low-income countries produce the least solid waste per capita *(World Bank, 2012)*.

The next ***Table 1*** shows this difference in generation of MSW in different countries according to their GNI.

COUNTRY	MSW GENERATION [kg/capita/year]	INCOME LEVEL (GNI)	AVERAGE MSW GENERATION BY INCOME [kg/capita/day]
UNITED STATES ***FRANCE*** ***SWITZERLAND*** ***ITALY***	720 700 953 814	*High-income*	*1.0 – 4.5*
MEXICO ***EGYPT***	328 201	*Middle-income*	*0.5 – 0.9*
NEPAL ***INDIA***	175 128	*Low-income*	*0.4 – 0.7*

Table 1: *MSW generation and its average by income level in different countries*
(Adapted from Eawag-Sandec, 2008; World Bank, 2012)

Moreover, a study conducted by the *World Bank (2012)* reports also a projection for urban municipal solid waste generation in 2025, according to the rapid growth of the population and to their income level, compared with the data of 2010. More especially, according to this projection, the growth of urbanization, from 2010 to 2025, will be much

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[5] The *“gross national income”* per capita (GNI) permits an indication of the national consumption level of countries and thus a classification in income groups, which are: low income (with US$ 905 or less per year), middle income (with US$ 906 to US$ 11˙115 per year) and high income (with US$ 11˙116 or more per year) *(Data from World Bank, 2006).*

more obvious in lower income, with an increase of 333 million people, and in lower-middle income, with a growth of 787 million people, than the upper middle income and higher income with an increase of 46 and 138 million people, respectively.

The next ***Figure 3*** shows this great increase of solid waste generation in all the income groups, especially in lower income and in lower-middle income.

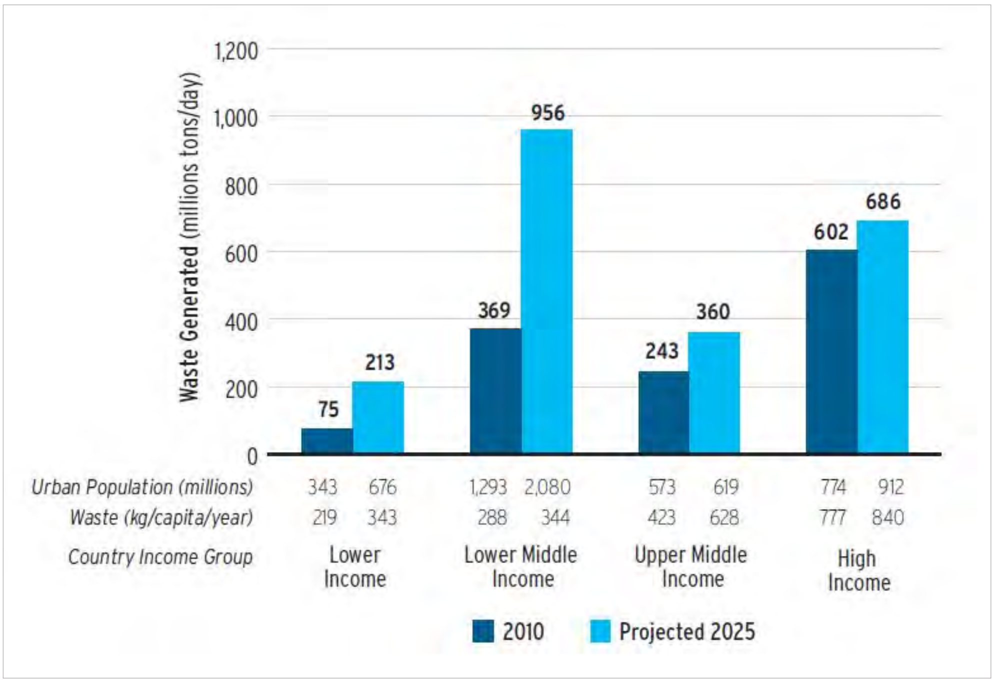

Figure 3*: Urban waste generation by income level and year (World Bank, 2012)*

Furthermore, in developing countries, most of the generated MSW contains high fractions of organics, also called biowaste or food waste (FW), which originate especially from households, compared to the lower amounts of plastics, glass and metals.

Waste composition is strongly influenced by many factors, such as level of economic development, lifestyle, cultural norms, geographical location, energy source and climate.

In fact, as a country urbanizes and populations become wealthier, consumption of inorganic materials (i.e. plastics, paper, aluminum, etc.) increases, while the relative organic waste decreases. Nevertheless, there are enormous differences in the typology of municipal solid waste from one region to another and even between different parts of the same city.

The next ***Table 2*** shows the waste composition and its characteristics (waste density and water content) by income level.

	Low-income countries	**Middle-income countries**	**High-income countries**
Waste density $[Kg/m^3]$	*250 - 500*	*170 - 330*	*100 - 170*
Water content [%]	*40 - 80*	*40 - 60*	*20 - 30*
Composition [%]			
organic	*40 - 85*	*20 - 65*	*20 - 50*
paper, cardboard...	*1 - 10*	*15 - 40*	*15 - 40*
glass and ceramics	*1 - 10*	*1 - 10*	*4 - 10*
metals	*1 - 5*	*1 - 5*	*3 - 13*
plastics	*1 - 5*	*2 - 6*	*2 - 13*
dust and ash	*1 - 40*	*1 - 30*	*1 - 20*

Table 2: *Waste composition by income level (Adapted from Vogeli – Sandec, 2007)*

Therefore, especially in low-income countries, households generate higher fraction of biodegradable waste (usually up to 75% on weight of all the MSW), including peeling from fruit and vegetables, food remnants and leaves *(Eawag-Sandec, 2008; Bobeck, 2010)*. This higher proportion of organic matter of MSW cause as a result a higher moisture content, so a dense and humid waste that affects not only the design and selection of waste collection equipment (i.e. collection and transport system) but also its recycling potential *(UN-HABITAT, 2010)*.

Moreover, as regards the issues and challenges of MSWM in developing countries, five typical and major problems in SWM have been identified by *Schertenleib and Meyer (1992)*, related all of them to institutional, financial and technical issues, which are summarized in the following points:

1) *inadequate coverage of the population to be served:* existing MSWM schemes generally serve only part of the urban population (the municipal service picks up about 50 to 70% of the refuse and serves less than 50% of the population);

2) *operational inefficiencies of MSW services and management*: even if municipalities expend substantial resources on WM (often 20 to 30% of municipal operating revenues), they tend to do a poor job operationally, due mainly to the inefficient institutional arrangements common to municipal governments;

3) *limited utilization of the formal and informal private sector in recycling activities*: the informal sector has been playing an important role in SWM schemes, especially

with regard to recycling activities. However, these recycling activities, although improve the environment and support large numbers of poor workers, can conflict with the efficient waste management practices.

4) *specific problems related to final disposal of solid waste*: the solid waste in DCs is generally disposed of in uncontrolled open dumps, causing evident environmental degradation (contamination of water resources, air pollution, bad odors, dusts and so on), triggering of a spread of diseases for the people.

5) *specific problems concerning the management of (non-industrial) hazardous waste:* this category of waste, generated especially by hospitals and clinics (for instance: health institutions, such as primary health care centers, dental and veterinary clinics), so pathogenic and infectious waste, is often enter the SWM stream, causing serious health risks to the public, to scavengers/collection crews and to workers at the landfill.

In order to handle growing volumes of waste and to solve this serious and critical problem of MSW in the developing countries, the proper policies need, first of all, to be enacted and implemented. Therefore, in these regions, a correct approach of solid waste management, called *"integrated solid waste management (ISWM)"*, is necessarily required, as in high-income countries. This approach consists of a hierarchical and coordinated set of actions that reduces pollution, seeks to maximize recovery of reusable and recyclable materials, and especially protects human health and the environment. ISWM aims to be socially desirable, economically viable and environmentally sound; this it means that this approach should be adapted to the local condition, depending on the specific country and income level *(World Bank, 2012).*

Moreover, according to *van de Klundert and Anschütz (2001)* this approach of *Integrated Solid Waste Management (ISWM)* should be based on the following four principle:

a. *equity* for all citiziens to have access to waste management systems for public health reason;

b. *effectiveness* of the waste management system to safely remove the waste;

c. *efficiency* to maximize benefits, minimize costs and optimize the use of resources;

d. *sustainability* of the system from a technical, environmental, social (cultural), economic, financial, institutional and political perspective.

Furthermore, ISWM is based on a hierarchical scheme that comprises: waste reduction (including prevention and minimization), re-use, recycling, recover (i.e. digestion and composting), sanitary landfilling and incineration *(Medina, 2010; World Bank 2012)*.

In particular, waste reduction initiatives and reuse seek to reduce the amount of waste at generation points by redesigning products or changing patterns of production and consumption, as well as to reduce the greenhouse gas emissions in the environment. Recycling and materials recovery permit to reduce the quantities of disposed waste and the return of materials to the economy; followed generally, according to the hierarchal scheme, by composting (aerobic biological process) or anaerobic digestion with consequent advantages for agricultural or lifestyle, thanks, for the last one, to generation of methane that can be used to generate heat or/electricity. However, the waste recycling rate is only 10-15% of consumption in low-income countries against 30-75% in OECD countries *(Jha et al., 2011)*. Incineration of waste (burning under controlled conditions), if possible with energy recovery, can reduce the volume of disposed waste by up to 90%. Finally, sanitary landfill is a final disposal site for waste, designed and operated to protect the environment and human health *(World Bank, 2012)*.

The next ***Figure 4*** represents this hierarchy that waste management sector follows.

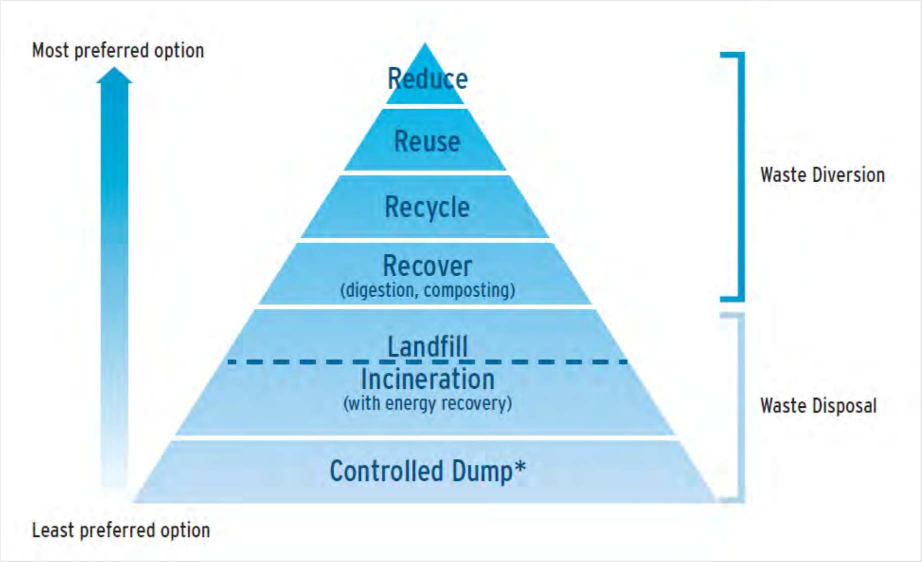

Figure 4: *Waste management hierarchy (World Bank, 2012)*

In this way, an adequate municipal solid waste management promotes the quality of the urban environment, generates employment and income, protects environmental health and supports the efficiency and productivity of the economy of all the developing countries.

1.2 Faecal Sludge Management (FSM) in developing countries

The term *"faecal sludge"* refers to undigested or partially digested slurry or solid resulting from storage or treatment of black-water (mixture of urine, faeces, flushing water, dry cleansing material) or excreta, removed so from all kind of on-site sanitation[6] (OSS) systems (e.g. septic tanks, bucket latrines, pit latrines, etc.). Therefore, faecal sludge comprises all liquid and semi-liquid contents of pits and vaults accumulating in OSS installations, namely non-sewered public and privates latrines or toilets, aqua privies and septic tanks *(Eawag-Sandec, 2008)*.

The following ***Figure 5*** shows the different faecal sludge management between sewered sanitation and on-site sanitation system.

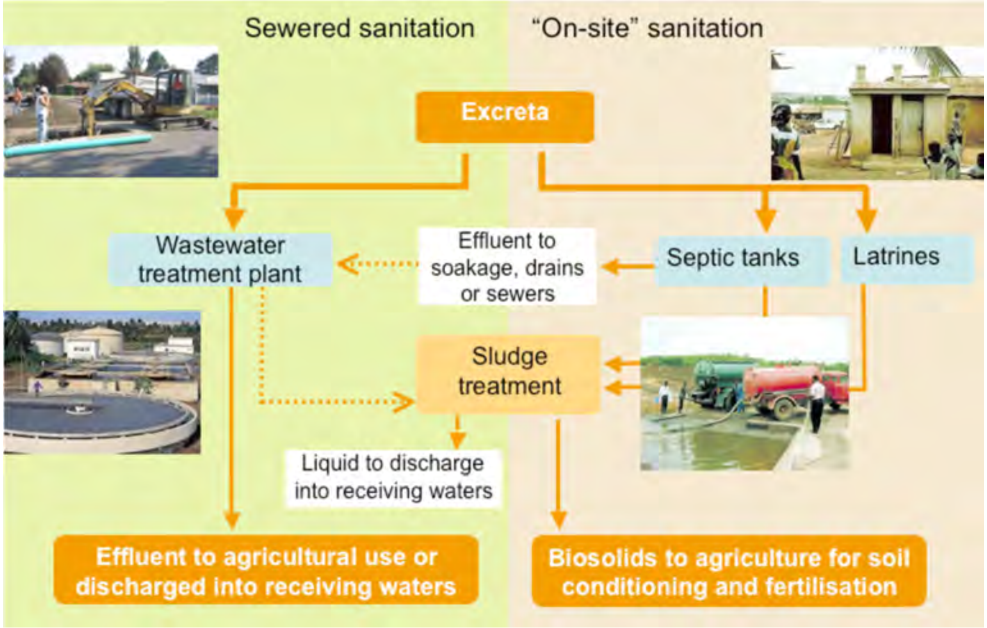

Figure 5: Faecal sludge and wastewater management side-by-side in urban environmental sanitation (Eawag-Sandec, 2008)

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[6] The term *"on-site sanitation"* refers to a system of sanitation whose storage facilities are contained within the plot occupied by dwelling and its immediate surroundings.

In particular, in urban areas of developing countries, this specific system of sanitation predominates over water-borne and sewered sanitation, as the following ***Table 3*** shows for different cities the relative percentages of inhabitants served by it *(Eawag-Sandec, 2003)*.

City or Country	% of inhabitants served by OSS system
Ghana	*85*
Bamako (Mali)	*98*
Tanzania	*> 85*
Manila	*78*
Philippines (towns)	*98*
Bangkok	*65*
Latin America	*> 50*

Table 3: Proportion of people served by on-site sanitation systems (Eawag-Sandec, 2003)

In fact, as the ***Table 3*** shows, more than 85% of houses in large cities in Africa (e.g. Ghana, Tanzania) are served by on-site sanitation facilities with the highest percentage in towns, close to 100%, like Bamako and Philippines *(Eawag-Sandec, 2003).*

Faecal sludge management (FSM) is strongly connected with all that concerns the on-site sanitation systems. However, a correct sanitation system consists of a series of possible process steps, as the next ***Figure 6*** shows, such as: pit/vault emptying (manual or mechanical emptying), haulage (transport), storage or treatment and use or disposal of faecal sludge.

Figure 6: Classification of process steps in sanitation (Eawag-Sandec, 2008)

Nonetheless, these phases (collection, haulage, treatment and reuse or disposal) are often a problem in developing countries, since even if the OSS are present in most urbanized areas, they need to be empty periodically and then the faecal sludge need to be properly manage to avoid negative impacts on the urban environment (water pollution) and on public health (diseases) *(WHO, 1992)*.

For this reason, in most cities of developing countries there are several problems, regarding the faecal sludge, such as: health hazard through manual emptying, indiscriminate disposal, lack or inadequate sludge treatment, lack of political will and awareness, as inadequate legal and regulatory basis and also unaffordability of mechanical emptying fees for a large number of households *(Eawag-Sandec, 2008)*. As a result, large amounts of faecal sludge removed from sanitation facilities are dumped indiscriminately into the environment or used in unhygienic way, i.e. without any treatment, in agriculture, because of lack of disposal facilities and available treatment.

It is important, furthermore, to underline that in these countries, according to various estimations, there are approximately 2.6 - 3 billion people living without proper sanitation services. Due to this inadequate water supply, sewerage systems and lack of sanitation, millions of people face death annually. In particular, over 2 million people die annually only to diarrhoea, wherefrom most are children, under the age of five. Every day approximately 6000 children die because of these infectious diseases *(TAMPERE, 2006)*.

This situation is particularly alarming in rural areas, characterized by inadequate treatment or disposal of human excreta, where half of the people do not have access to proper sanitation and water supply services and they are affected a spread of diseases.

Therefore, since sanitation and human health are closely connected to each other, it is very important to safeguard adequate sanitation and hygiene education to reduce the amounts of infections *(TAMPERE, 2006)*.

2 BIOMASS AND THERMOCHEMICAL PROCESSES

Energy is considered an essential factor for economical and social development, as well as for human well-being.

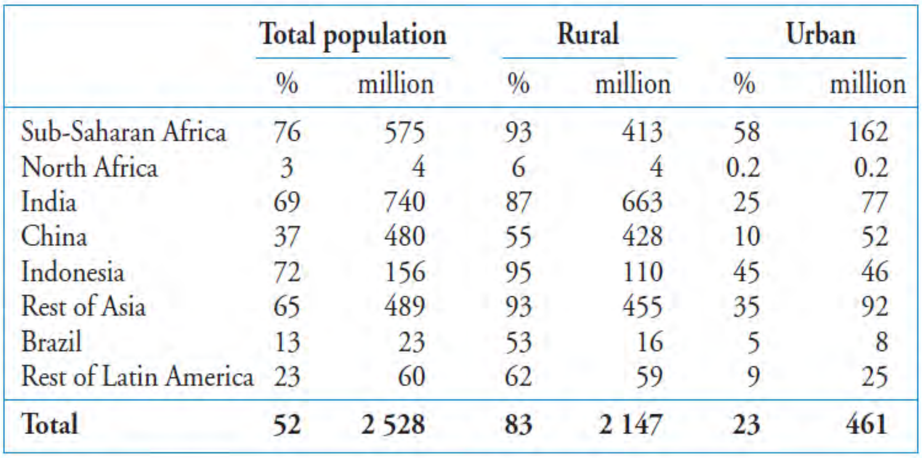
However, according to *International Energy Agency (IEA)* and *World Health Organization (WHO)*, **52%** of the population in developing countries, more precisely over 2.6 billion people, is still relying on the traditional use of biomass (i.e. firewood, charcoal, animal waste and crop residues) to meet their basic energy needs mainly for cooking then for heating and lighting. This means that energy from biomass plays an important role throughout the developing world.

In particular, 83% of these people live in rural areas, where biomass is usually abundant and represents the principal renewable energy source even though it is not used in an efficient manner. In fact, biomass is generally burned in open hearths or in simple and inefficient stoves, causing pollution (outdoor and indoor air pollution), deforestation due to the continual cut of live trees for household energy, with as a result a host of major environmental problems, such as: soil erosion, desertification, decreased of agricultural productivity and also significant impacts on human health. More especially, exposure to indoor smoke doubles the risk of pneumonia and acute lower respiratory infections and chronic obstructive pulmonary diseases (i.e. chronic bronchitis and emphysema) in women and children, resulting in an estimated 1.6 million annual deaths, most of them occurred in Sub-Saharan Africa and South Asia *(WHO, 2007)*.

The next ***Figure 7*** shows a typical situation of smoke exposure inside the households.

Figure 7: *Woman and child exposed to indoor air pollution while cooking (WHO, 2006)*

In addition to this, the following ***Table 4*** shows the percentages of population, in rural and urban areas, that uses biomass as their primary fuel for cooking.



	Total population		Rural		Urban	
	%	million	%	million	%	million
Sub-Saharan Africa	76	575	93	413	58	162
North Africa	3	4	6	4	0.2	0.2
India	69	740	87	663	25	77
China	37	480	55	428	10	52
Indonesia	72	156	95	110	45	46
Rest of Asia	65	489	93	455	35	92
Brazil	13	23	53	16	5	8
Rest of Latin America	23	60	62	59	9	25
Total	**52**	**2 528**	**83**	**2 147**	**23**	**461**

Table 4: *People relying on biomass as their primary fuel for cooking (IEA, 2006)*

As the ***Table 4*** shows, the proportion of the population depend on biomass is highest in Sub-Saharan Africa, where in many parts of this region, more than 90% of the rural population relies on traditional biomass, namely firewood and charcoal, for their energy needs.

In fact, in many African countries, large quantities of fuel-wood are consumed in the production of charcoal[7] (carbonaceous solid with a fixed carbon content of 70% or more and heating value near 31 MJ/kg), which is often used as household fuel and also has many commercial and industrial applications (e.g. restaurants, schools, hospitals, bread baking, etc.). It is produced in earthen kilns that typically yield only one kilogram of charcoal for every six kilograms of wood harvested. Therefore, in one year, a common household, cooking exclusively with charcoal, uses between 240-600 kg of this fuel, produced using between 1.5-3.5 tons of wood *(Kammen, 2006)*. As a result, the considerable use of charcoal as fuel is one of the major causes of environmental degradation, responsible of soil erosion, soil infertility, decrease of soil productivity, deforestation, extinction of wildlife and endangered crop species.

Naturally, the use of biomass to produce energy and therefore the energy demand can vary widely across countries and regions, depending on their resources and their levels of

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[7] Charcoal is usually produced by a process called *slow dry pyrolysis (carbonization)*, the heating of wood in the absence of oxygen at high temperature around 500°C, generally produced in traditional kilns.

economic development and industrialization/urbanization. In fact, for instance, in Thailand, where per capita income average is \$ 2490, biomass accounts for 33% of household energy consumption, while in Tanzania, with per capita income is only \$ 320, the share of biomass is nearly 95% *(IEA, 2006)*.

In general, in developing countries biomass energy uses are characterized by low efficiency so that the biomass fuels consumed could potentially provide a much more extensive energy service than at present if these were used efficiently. For instance, modern cook-stove designs can improve the efficiency of biomass use and reduce thus the biomass consumption for cooking by a factor of 2 to 3 compared with traditional biomass fired stoves, as well as other precious benefits (reduction emissions, improvements in human health, etc.) *(Bhattacharya, 2002)*.

The global energy demand is predicted to increase significantly over the next decades, so it is expected also that the consumption of fuel-wood will remain at very high levels or even increase, because of the expected growth in world population and the expected economic growth and urbanization of the developing countries *(AFREA, 2011)*. In fact, according to *IEA – World Energy Outlook 2013*, the global primary energy demand will increase by 56% between 2010 and 2040 but especially over 70% of this increase will come from developing countries. In order to reduce global GHG emissions, due especially to heavy dependence/combustion on fossil fuels or use of inefficient technologies (i.e. simple cook-stoves or traditional kilns with low efficiency) and in order also to solve the global environmental problems such as global warming, it is necessary to find new ways to satisfy this energy demands and to improve the energy efficiency, especially in developing countries. In addition, deforestation needs to be halted, agricultural practices need to be changed and if it were possible, a large-scale sequestration of carbon dioxide (CO_2) from the atmosphere would be desirable.

Therefore, hydrothermal carbonization, which is a highly efficient thermochemical process, could be an innovative solution in developing countries because it permits to use and transform abundant low-value biomass into environmentally friendly bio-coal, called precisely HTC-coal, in just few hours. By processing biowaste via HTC, a valuable renewable energy carrier would be produced and the hygienic conditions could be improved at the same time, leading thus improvements in ecological sustainability, local economic development and human health *(Fink, 2011)*. In this way, HTC-process could make an important contribution to climate protection and the efficient use of biomass/waste.

For this reason, before to introduce the theoretical part about HTC-process, a general overview of biomass and then of principal thermochemical process (i.e. combustion, carbonization, pyrolysis and gasification) used, especially in developing countries, to transform biomass in energy, are discussed in the next paragraphs.

2.1 Biomass: definition, properties and typologies

The definition of "biomass" in the Directive 2009/28/EC is: "biodegradable fraction of products, waste and residues from biological origin from agriculture, forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste".

Biomass is all non-fossil organic materials that have intrinsic chemical energy content; therefore plant and animal matter such as wood from forests, material left over (by-products) from agricultural and forestry processes (i.e. rice straw, rice husk, sawdust, saw mill dust, etc.), aquatic plants and organic industrial, human or animal waste (i.e. MSW, kitchen garbage, animal dung, excrement, sewage sludge, etc.).

The next ***Figure 8*** summarizes these different sources of biomass.

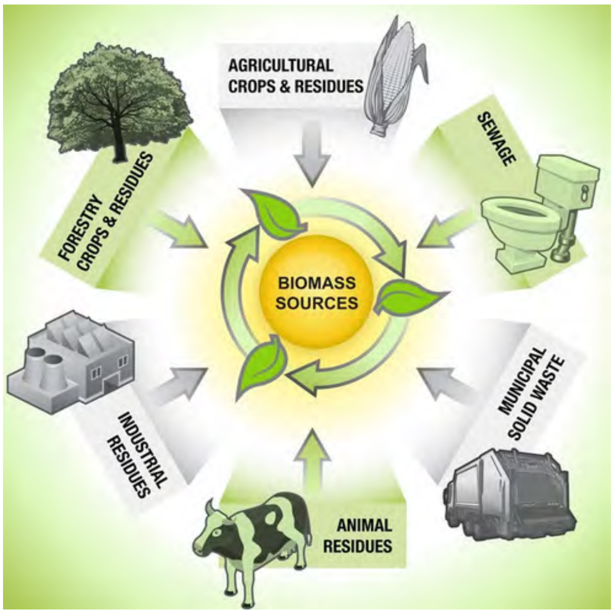

Figure 8: *Different typologies of biomass*
(Source: www.bioenergyconsult.com/biomass-energy-introduction/)

Naturally, in this report, concerning the use of biomass and promising conversion technologies in developing countries, the dedicated energy crops (i.e. herbaceous energy crops or short-rotation energy crops for other purposes than food and feed, such as sugar crops, oil crops and starch crops), namely plants grown specifically for production of bio-based products, are not considered. For this reason, all the different typologies of biomass, listed before, can generally be called as ***biowaste***; that is a material, which has been traditionally thrown away because it has no apparent value or represents a nuisance or even a pollutant to the local environment *(Lilliestrale, 2007)*.

In particular, in the context of energy production, biomass is classified, unlike fossil fuels, as a ***renewable resource***, whose utilization has received great attention due to environmental benefits and the increasing demands of energy worldwide *(Balat, 2008)*. In fact, biomass is an environmentally friendly energy source, defined as CO_2-neutral or carbon neutral, because when biomass is combusted, the carbon dioxide (CO_2), which was absorbed, during the growth of plant through the process of photosynthesis, is released back into the atmosphere, completing a natural closed carbon cycle *(Balat et al., 2005)*.

In addition, biomass provides, as already said previously, basic energy requirements for cooking and heating of rural households and for process in a variety of traditional industries in developing countries *(Bhattacharya, 2002)*. In fact, nowadays, biomass resources provide about 14% of the worldwide primary energy supply and represents the fourth largest source of energy in the world behind oil, coal and natural gas *(Bocci et al, 2011)*. Most of this biomass use occurs in rural areas in DCs, where three quarters of the world’s population live without access to modern energy services and therefore without clean cooking facilities *(Habitat, 1993)*.

Moreover, the use of biomass produce several environmental benefits. First, it does not increase the global amount of carbon dioxide in the atmosphere, so does not contribute to global warming. Second, it can lead a minor dependence on fossil fuels, especially in rural areas. Other advantages are its abundance, the easy way to extract energy and the low cost.

The several biomass sources, due to the natural variation in trees, plants and waste, have a different chemical composition and distribution, therefore, as a result, each typology of biomass require a specific process (i.e. dry or wet techniques depend on the moisture content of biomass). In general, biomass is composed of a mixture of organic molecules, mainly of cellulose (i.e. glucose polymer), hemicellulose (i.e. mixture of polysaccharides) and lignin (i.e. group of amorphous, high molecular weight, chemically related compounds).

These relative concentrations can vary widely between plant species, in particular between hardwoods (higher proportion of cellulose 43-48% and hemicellulose 27-35%) and softwoods (higher proportion of lignin 26-33%) *(Balat, 2008)*. Therefore, the elemental composition of biomass is commonly consisting, depending always on sources, of: carbon (C), oxygen (O), hydrogen (H), nitrogen (N) and sulphur (S) *(Johnson, 2007; McKendry, 2001)*.

The following ***Table 5*** shows these characteristics for some sources of biomass.

Materials	**Elemental analysis [% dry weight]**						**Heating Values [MJ/kg]**
	C	**H**	**N**	**S**	**O**	**Ash**	
Pine bark	53.2	5.8	0.2	0.0	38.8	2.9	20.4
Rice straw	39.2	5.1	0.6	0.1	35.8	19.2	15.2
Municipal solid waste (MSW)	47.6	6.0	1.2	0.3	32.9	12.0	19.9
Feedlot manure (fresh)	45.4	5.4	1.0	0.3	32.0	15.9	17.4

Table 5: *Chemical analysis and properties of selected types of biomass (Adapted from Capareda, 2011)*

Hence, it is important to careful know the properties of each typology of biomass, that is elementary analysis, moisture content, higher heating value, volatile matter, ash/residue content, fixed carbon and so on, in order to understand the amount of energy available from biowaste and also to choose the appropriate energy conversion technology.

2.2 Biomass conversion techniques

Biomass energy, also called ***bioenergy*** or ***biopower***, is the conversion of biomass into useful form of energy such as heat, electricity (marked as “green power”), liquid biofuels (e.g. ethanol, biodiesel, etc.) or gas biofuel (i.e. biogas, which is produced when organic matter rots without oxygen, so in an anaerobic process).

In each case, the biomass feedstock has to be harvested/collected, transported, stored and usually pre-dried before being processed into a suitable form for the choice of energy conversion technology *(McKendry, 2001)*. However, transportation and storage of biomass are not easy steps because of its bulkiness and degradation, for this reason, the use of waste biomass is more reasonable and cheap in the areas where it is produced in abundance.

There are therefore various technologies to convert biomass resources into biopower, depending on conversion parameters used (conditions such as residence time and temperature) or the end-product produced (i.e. solid, liquid and gas) that it is more desired.

In general, there are two routes for converting biomass into biofuels, namely:

a) ***Biochemical processes:*** work thanks to the action of enzymes, fungi and bacteria that grow in the biomass in specific conditions of temperature and moisture content. In general, these complex conversion processes are used for biomass characterized by C/N ratio lower than 30 and moisture content higher than 30%. The main biochemical processes allow to obtain energy throughout a chemical reaction are *anaerobic digestion* (AD) and *fermentation* which respectively permit to produce biogas (mixture of gases predominantly methane 50-70% and carbon dioxide, which can be used for heating purposes) and bioethanol (alcohol that can be used as a car fuel, obtained from the fermentation of the sugars of beets and sugar cane). This type of conversion is characterized by: long residence times (several days to months), consistent feedstock and mild temperatures;

b) ***Thermochemical processes:*** are based on the action of heat (i.e. high temperatures above 100°C) that activates the chemical reactions needed to transform the organic matter into energy. In general, these conversions processes are used when C/N ratio is over 30 and the moisture content is lower than 30%. The main thermochemical processes used to convert biomass into energy are: *combustion*, *pyrolysis*, *gasification*, *carbonization* and finally *hydrothermal carbonization (HTC)*, the innovative technology discussed in this report (the last one is carefully descripted in the next chapter 3). All these thermochemical processes have been widely applied to biomass and they are characterized, compared to the biochemical processes, by short residence times (seconds up to hours) and high temperatures (200-1000°C). The choice of which conversion process is used depends upon the type and amount of the biomass feedstock, the desired type of fuels, the economic conditions and the various project specific factors.

Seeing that the HTC-process is a highly efficient thermochemical process for generating renewable energy, only this category of conversion techniques will be briefly subsequently described; in this way, it will be easier to draw a comparison between HTC and other thermochemical processes.

2.3 Thermochemical processes

The following ***Table 6*** shows a schematic diagram of all the thermochemical conversion technologies used for converting biomass into energy.

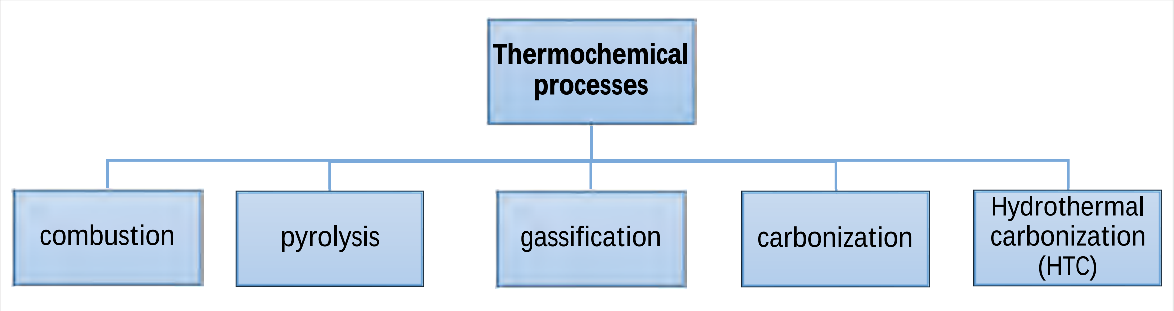

Table 6: *Flow diagram of thermochemical processes*

Each method gives a different range of products and employs various system configurations.

Following, an overview on these thermochemical processes is reported.

2.3.1 Combustion

Direct combustion (also called simply burning of organic fraction) is the most common technique and the most frequently applied for generating energy from biomass, in form of heat, using various items of process equipment, for example stoves, furnaces, boilers and so on. Combustion is a process whereby the carbon and hydrogen in the fuel react with oxygen ultimately to form carbon dioxide (CO_2) and water (H_2O) in form of vapor, through a series of free radical reactions resulting in the liberation of heat and steam.

In particular, combustion is an exothermic chemical reaction and it defined as a complete oxidation of organic matter at high temperatures, usually between 850-950°C, in presence of excess of oxygen, i.e. it is necessary to have an excess air ratio well above one, usually above 1.5, to ensure a sufficient mixing of air and feedstock *(Bocci et al., 2011)*.

The most common combustion feedstock is wood but almost any plant material can be used for this thermal conversion process; however, the combustion process is feasible only for biomass with a moisture content smaller than 50%, unless the feedstock is pre-dried in order to sustain combustion. More precisely, biomass constituents beside C, H and O are undesired since they are related to pollutant and deposit formation, corrosion and ash. The main difficulty in combustion is in starting the process, as high temperatures (at least 550°C) are required for the ignition of biomass.

However, once ignition starts, the conversion process carries on only if sufficient air supply is available and if the moisture of biomass is not too high, until the biomass is completely converted into residual ash. The residence time needed for complete combustion is directly influenced by the combustion temperature (above 850°C) and by the optimal mixing of biomass fuel and air. These factors, i.e. combustion temperatures, residence times and contact biomass and oxygen, are also determined by the technology and design of the furnace.

The scale of combustion plant ranges from very small scale for domestic heating (few kW) up to large scale (more than 1000MW) for industrial plants *(McKendry, 2001)*. Unfortunately, in developing countries, small-scale combustion appliances are mainly used for heating or cooking through simple stoves than work in an inefficient manner (incomplete combustion), causing air indoor pollution and as a result long-term respiratory health problems and deaths *(AFREA, 2011)*.

The combustion efficiency is mainly determined by the completeness of the combustion process, depending primarily on good contact between the oxygen in the air and the biomass fuel and the heat losses from the furnace *(Susta et al., 2003)*. The flame temperature plays an important role in deciding the overall efficiency of the combustion device. Usually efficiencies are in the range 60% – 80%, depending on the ultimate analysis of fuel, moisture content, excess air factor and design of combustion technology.

However, biomass combustion produce significant pollutant formation and hence need to be improved in order to reduce these emissions. In fact, especially when the combustion is incomplete, different unburnt pollutants are emitted in huge amounts in the atmosphere in form of carbon monoxide (CO), methane (CH_4), polycyclic aromatic hydrocarbons (PHA), volatile organic compounds (VOC) and fine particles (PM10 and PM2.5), caused by inadequate mixing of combustion air and fuel in the combustion chamber, lack of available oxygen, too low combustion temperatures and too short residence times. For these reasons, it need to add the flue gas cleaning system in the design of modern combustion technologies, especially for large-scale applications, in order to reduce the problem concerning emissions whereas for small-scale, especially in households, it is necessary to improve cook-stoves for reducing air pollutants from biomass use and increasing the efficiency of combustion *(AFREA, 2011).*

The next ***Table 7*** contains the main characteristics of combustion.

PARAMETER	***FEATURES OF COMBUSTION***
Range of temperature	850-950°C
Residence time	for a complete combustion t >2.5 s with T above 850°C
Oxidizing agent	excess of oxygen
Biomass Feedstock	dried feedstock (wood, agricultural waste, MSW, etc.)
Advantages	robust process and easy to maintain
Disadvantages	great deal of pollutants, huge amount of biomass and air pollution
Energy or fuel produced	heat

Table 7: *Characteristics of biomass combustion*

2.3.2 Gasification

Gasification is a partial oxidation of biomass at high temperature, between 800-1000°C in the presence of an oxidizing agent in sub-stoichiometric[8] amount (with the main purpose to convert feedstock into combustible gases, called *synthesis gas* or *syngas,* consisting of carbon monoxide (CO), hydrogen (H_2) and traces of methane (CH_4).

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[8] The stoichiometric amount is defined as the theoretical amount of air or any other oxidizing agent required to burn the fuel completely.

However, this conversion process produces also small amounts of liquid and solid (char), as well as the gas phase; their proportions are summarized in the next ***Table 11*** shows.

End-Products of gasification		
Gas	**Liquid**	**Char**
85%	5%	10%

Table 8: *Distribution end-products for gasification (Adapted from Bocci et al., 2011)*

This specific thermal conversion with these characteristics can be defined as an intermediate step between combustion and pyrolysis.

The quality and composition of syngas significantly changes depending on the choice of gasification agent used during the reaction (air, steam, oxygen, enriched air, etc.), operating conditions (e.g. temperature, pressure) and type of feedstock.

More precisely, in case of air used as oxiding agent the mixture of gas is characterized by low values of lower heating value (LHV of around 5.5-7.5 MJ/Nm^3) that it could be used in engines and boiler while the use of oxygen generates a gas composed mainly of CO e H_2 that it could be used as a combustible (LHV of around 11 MJ/Nm^3).

The characteristic of the biomass feedstock have a significant effect on the performance of the gasification, especially for moisture content, particle size and ash content.

The syngas can be used for heat production and for generation of mechanical and electrical power (e.g. internal combustion engines, direct heat applications and produce methanol).

Until now, various types of gasifiers have been developed and commercialized for the production of heat and power from syngas (fixed bed gasification classified in updraft gasifier, downdraft gasifier and crossdraft gasifier; fluidized-bed gasification). However, the main differences between these typologies of gasifiers are: type of injection, gasification agent used, type of heating, temperature range and pressure range.

The next ***Table 12*** contains the main characteristics of gasification.

PARAMETER	***FEATURES OF GASIFICATION***
Range of temperature	800-1000°C
Residence time	10-20 seconds
Oxidizing agent	air or oxygen but in sub-stoichiometric amount
Biomass Feedstock	dried and uniform size of feedstock before starting the process
Advantages	high thermal efficiency
Disadvantages	high cost of investment, complex and sensitive process, biomass feedstock need to be reduced in size
Energy or fuel produced	syngas/electricity/heating

Table 9: *Characteristics of biomass gasification*

2.3.3 Carbonization

Carbonization is a pyrolytic process of thermo-chemical conversion process, which allows transforming wood at temperatures between 450-600°C into *charcoal* under slow heating rate conditions, in the absence of air through simple closed kilns (e.g. earth pit kilns, earth mound kilns, steel kilns, etc.).

It is especially used in developing countries, for instance in many African countries where the charcoal production, transport and sale are of great economic importance. The goal of this thermal conversion is to increase the higher heating value of wood through the increase of carbon content of the product and to achieve furthermore high charcoal yields at the end of the carbonization process *(Seidel, 2008)*.

The carbonization temperature is one of the main factors affecting quality (physic-chemical characteristics) and yield (mass ratio of charcoal made and wood fed) of charcoal, as well as moisture content, wood size, heating rate and species *(Nag, 2007)*. In fact, at relatively low temperatures, around 300 °C, a higher yields of charcoal is obtained but with low quality (characterized by high content of volatile material, which is undesirable because it produces noxious fumes during use) while higher temperatures, around 600°C, give lower yields but a better charcoal, since it has a fixed carbon content of about 75% and low content of volatiles, making it a preferred fuel.

The following ***Table 10*** shows typical values of yield and characteristics of charcoal at different temperatures.

Carbonization temperature	**Chemical analysis of charcoal**		**Charcoal yield based on oven dry wood**
[°C]	***% fixed charcoal***	***% volatile material***	***[%]***
300	68	31	42
500	86	13	33
700	92	7	30

Table 10: *Effect of carbonization temperature on yield and composition of charcoal*
(Adapted from Nag, 2007)

Charcoal, at the end of carbonization process, has a relatively low moisture content of around 3 to 10% and its gross calorific value is linked to the amount of fixed carbon and depends strongly on the carbonization temperature, ranging from 27 to 33 MJ/kg (double energy content of fuelwood).

Charcoal can be made from both hardwood and softwood. However, hardwood is usually preferred because the charcoal has higher energy content and is easier to handle.

The main use of charcoal is for cooking and heating purposes in urban areas of many developing countries, especially in African countries. In addition, charcoal is used partly for commercial purpose and also in traditional industrial and commercial activities (e.g. steel making industry) finally as a precursor for activated carbon.

Unfortunately, the traditional earth charcoal kilns have low conversion efficiencies, ranging from 10 to 20%, this causes high annual rate of deforestation due to wood harvesting *(Luwaya, 2011)*. In fact, in general, the average conversion ratio is only 6:1; this means that 6 kg of dried fuelwood is burnt to produce 1 kg of charcoal. On this subject, in order to improve the conversion efficiency, it is necessary to pre-dry the wood as much as possible before carbonization, simply using the sunlight to evaporate, in this way, the water content of wood that otherwise requires a lot of energy. Another way to enhance the efficiency of charcoal consumption is to use improved charcoal stoves, which have a better efficiency and also emit much less or even no noxious fumes compared to traditional stoves *(Seidel, 2008)*.

The next ***Table 11*** contains the main characteristics of carbonization.

PARAMETER	***FEATURES OF CARBONIZATION***
Range of temperature	400-650°C
Residence time	several days
Oxidizing agent	no
Biomass Feedstock	dry wood
Advantages	simple, quick and economic method, easy to store the charcoal
Disadvantages	low efficiency, cutting of wood
Energy or fuel produced	charcoal

Table 11: *Characteristics of wood carbonization*

2.3.4 Pyrolysis

Pyrolysis (*pyro* "fire" and *lysis* "separating") is the thermo-chemical decomposition of organic materials that is obtained through heat application, at temperatures between 450-850°C, in complete absence of any oxidizing agents.

The products of this thermal degradation, as the following ***Table 8*** shows, can be: gaseous (mainly composed of CO_2, CO, H_2 and CH_4) liquid (called *pyrolysis oil* or *bio-oil* that is a dark brown liquid) and solid (called *char* or *biochar* that is a solid residue richer in carbon content). Their relative proportions depend especially on the pyrolysis method (slow, fast and flash), the characteristics of the biomass, the rate of heating and the reaction parameters (mainly temperature and residence time).

Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported liquid and solid end-products, which can be successfully used for the production of heat and power *(Bocci et al., 2011).*

A wide range of biomass feedstock can be used in pyrolysis process however it is very dependent on the moisture content of the feedstock, which should be around 10%. At higher moisture contents, higher levels of water and lower quality of products are produced with the risk that the process produces dust instead of oil. On this subject, for feedstock with high water content, it is required drying process before subjecting to pyrolysis, for this reason it also known as *dry pyrolysis*. In addition, the efficiency and nature of the pyrolysis process is also dependent on the particle size of feedstock, therefore small particles of biomass (maximum 2 mm) are needed before being used for pyrolysis with the purpose of accelerating the heat transfer during the reaction *(Bocci et al., 2011).*

This conversion technology is more similar than the innovative hydrothermal carbonization, since both convert biomass in three different phases and both produce a solid residue with high carbon content even though with different proportions. In fact, also the solid pyrolysis byproduct, i.e. biochar, can be used for various potential applications such as soil amendment, activated carbon, remediation of water and soil, energy and carbon sequestration *(Verma et al., 2011).*

Moreover, as already said, there are three types of different pyrolytic reactions, depending on temperatures and residence time used, in particular: *slow pyrolysis*, *fast pyrolysis* and *flash pyrolysis*. The first one, slow pyrolysis, works at low temperatures of around 400°C and long reaction times (hours) while fast and flash pyrolysis function with higher temperatures (above 500°C for fast and above 700°C for flash) at very high heating rates and short residence times (typically less than 2 seconds).

More precisely, flash pyrolysis is very similar to fast pyrolysis but involves an even rate of heating and a brief residence time (less than 1 second). In general, fast and flash pyrolysis are used to maximize either the gas or the liquid products whereas the main product produced by slow pyrolysis is the char *(Bocci et al., 2011).*

The distribution of the end-products obtained from these different typologies of pyrolysis are reported in the following ***Table 9***.

Typology of pyrolysis	**Characteristics**	**End-Products**		
		Gas	**Liquid**	**Char**
Fast and flash pyrolysis	short residence times and high temperatures	13%	75%	12%
slow pyrolysis	high residence time and low temperatures	35%	30%	35%

Table 12: *Distribution end-products for slow, fast and flash pyrolysis (Adapted from Bocci et al., 2011)*

One of the main problems linked to the production of energy through pyrolysis is the quality of the products, which has not reached an adequate level in its applications, neither with gas turbines nor with diesel engines.

The next ***Table 10*** contains the main characteristics of pyrolysis.

PARAMETER	***FEATURES OF PYROLYSIS***
Range of temperature	450-850°C
Residence time	from seconds to hours depending on typology of pyrolysis (slow, fast or flash)
Oxidizing agent	no air
Biomass Feedstock	dried feedstock with small particles of 2 mm
Advantages	bio-oil can be used in engines, turbines and for refineries; biochar can be used for energy carrier or soil amendment
Disadvantages	high cost of bio-oil compared to traditional fossil fuel
Energy or fuel produced	bio-oil and biochar

Table 13: *Characteristics of biomass pyrolysis*

2.3.5 Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC) is the novel thermo-chemical conversion process that allows the conversion of organic material into a carbonaceous residue with higher carbon content, referred to as *hydrochar*. This process occurs in aqueous phase (wet pyrolysis) under applied relatively high temperatures (180-220°C) and pressures for several hours.

The final products are present in gas, solid and liquid phases and their proportions depend on the characteristics of input feedstock and on the process conditions.

Seeing that the hydrothermal carbonization is the object of this work and it will in-depth descripted in the following *chapter 3*, it is straight away reported the next ***Table 15*** that contains the main characteristics of this conversion process.

PARAMETER	***FEATURES OF HTC-PROCESS***
Range of temperature	180-220°C
Residence time	several hours
Oxidizing agent	no
Biomass Feedstock	any type of organic material
Advantages	simple method, high conversion efficiency, use of wet material without pre-dry process
Disadvantages	high cost of investment, post-treatment of water process, requirement of energy supply
Energy or fuel produced	hydrochar

Table 14: *Characteristics of hydrothermal carbonization*

3 OVERVIEW OF HTC PROCESS

Hydrothermal carbonization (HTC) is a thermo-chemical process able to convert completely biomass[9] into a coal-like material with a high carbon content and accordingly with a high calorific value[10].

This type of conversion process, also known as *wet pyrolysis,* opens up a wide field of potential feedstock for HTC-coal production to a variety of non-traditional sources, such as: municipal solid waste (MSW), wet agricultural residues, human waste (faecal sludge), sewage sludge, algae and finally aquaculture residues. This is due to the fact that HTC-process allows to treat, unlike the traditional "dry pyrolysis", substrates characterized by an elevated moisture content, with values of 75-90%; it permits, therefore, to use any kind of biomass as a feedstock *(Libra et al., 2011)*.

This thermal conversion is realized in a pressure vessel (reactor) by applying high temperatures (generally between **180-220°C**) and high pressures (approximately **20-35 bar**) to biomass in aqueous phase, that is in presence of water under saturated pressure, for several hours (about **4-12 h**) in the absence of air. More specifically, the biomass is surrounded by water during all the reaction (this is the *"hydro"* part), which it is kept in a liquid state thanks to the elevated pressure reached into the reactor. Under these specific conditions, heat (this is the *"thermal"* part) and pressure, the HTC-process removes water molecules from biomass and converts the residual carbon to high-value bio-coal (this is the *"carbonization"* part of the process) within a few hours. In this way, the initial biomass is transformed in bio-coal through a chemical process.

Once activated, HTC is an exothermic process; this means that it is spontaneous, self-sustaining, i.e., it gives off more energy than is required for the process, as the bio-renewable resources are constituted of sugar building blocks that contain a lot of energy. In this way, it is possible to have a positive energy balance.

Nevertheless, the release of energy depends on the feedstock and on the process conditions (i.e. temperature, pressure and residence time). In literature, it is reported that this

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[9] The term "biomass", also called as bio-renewable resources, is defined as all materials of biological origin, excluded materials that have been imbedded in geological formations and have become fossilized (such as oil and coal).

[10] The term "calorific value" refers to the higher heating value (HHV) also called gross calorific value (GCV).

release is around one third of the combustion energy of the biomass. However, it is necessary to heat the reactor, and consequently the biomass inside, at least 180°C, before this energy can be used *(Ramke et al., 2009)*. So at the beginning, an external energy is required to sustain this process but above all to reach and to overcome a mound of activation energy.

During the conversion, different and simultaneous reactions, similar to those in dry pyrolysis, happen for transforming biomass residues into HTC-coal, in particular: hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization *(Funke et al., 2010)*. At the end of the process, after the mixture is cooled down and the pressure vessel is opened, the final products are present in the three different states: solid, liquid and gaseous phases.

More precisely, the reactor contains inside a black watery fluid (black broth: water-carbon) comprised of finely dispersed spherical carbon particles (colloids). Carbon, which was previously bound in the organic material, now is present in particle form as small, porous brown-coal spherules *(Ramke et al., 2009)*.

The main fraction of this thermo-chemical process is the solid part, called ***HTC-coal*** or ***Hydrochar***[11]. It is an agglomeration of different chemical substances similar to natural coal products, such as lignite or sub-bituminous coal and it can easily be separated from the process-water by filtration *(Fink, 2011)*. Moreover, it is an easy to handle product with good dewatering properties and an elevated higher heating value after to be dried.

The HTC process essentially reproduces the natural coalification with the only difference that it asks a few hours, approximately 12 hours, to transform biomass into a material comparable to brown coal. In fact, nature does exactly the same thing but very slowly, it requires in fact some hundred to some million years. More precisely, the natural process needs 500 to 5000 years to form peat, 50000 to 50 million years to obtain lignite and 150 million years to have anthracite *(Röthlein, 2006)*.

Therefore, the hydrothermal carbonization, reflecting the natural process of coal generation, can be described as "coal formation in one day" that permits to transform sugar

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[11] The term "hydrochar" means char produced from hydrothermal carbonization (HTC) and it is used for distinguishing from the other nomenclatures, such as: char, biochar and charcoal. In particular: char is a solid decomposition product of a natural or synthetic organic material; biochar (refers to black carbon formed by the dry pyrolysis of biomass, i.e. by heating biomass in an oxygen-free or low oxygen environment such that it does not combust or only partially combust) is applied to soil in a deliberate manner, which the intent to improve soil properties and finally charcoal (formed by slow dry pyrolysis/carbonization without oxygen) is usually used for cooking purposes.

and carbohydrates, important constituents of biomass, into different carbonaceous materials, with characteristics similar to those of fossil coal *(Lilliestrale, 2007)*.

In nature, this gradual alteration leads to an increase of carbon (C) content and, at the same time, a decrease of hydrogen (H) and oxygen (O) contents. For this reason, depending on the degree of the transformation, we can classify different kind of coals, from lowest to highest carbon content: peat, lignite, sub-bituminous coal, bituminous coal and anthracite *(Taylor et al., 2009)*.

HTC-coal possesses interesting characteristics (permeability, water holding capacity, nutrient availability, etc.) and also various applications (energy source, soil carbon sequestration[12], soil amelioration[13]) that makes HTC process an important methodology to also apply in developing countries in order to treat problematic biomass (e.g. food waste, faecal sludge, etc.).

In particular, this research is addressed to use the HTC-prototype with biowaste or faecal sludge to contribute, in this way, to the development and especially the well-being of rural areas in developing countries, where the inadequate solid waste management (SWM) and inappropriate sanitation coverage (FSM) lead to severe health (diseases, infections, and so on) and environmental problems (air and water pollution).

In these last years, in order to promote and to extend the field of application of the HTC-process, especially in German and Switzerland, clean-technology companies (like *AVA-CO2*, *TerraNova Energy*, etc.), industrial users and research institutions have together founded a German *Federal Association Hydrothermal Carbonization*[14]. The aim of this union is to extend the use of hydrothermal carbonization, promising and highly efficient technology for generating renewable energy, not only in Switzerland and Germany but also to European level. Another important objective of this foundation is to promote the standardization and approval/certification of the final product, hydrochar, like other biofuels; in such way, it could be used in a safe way for producing renewable energy (electricity and heat).

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[12] The term “soil carbon sequestration” means addition of degradation-resistant carbonaceous substrates to soil.

[13] The term “soil amelioration” means soil quality build up or improvement of soil fertility.

[14] The exact name of this foundation in German is: “*Bundesverband Hydrothermale Carbonisierung e.V.*”.

3.1 Historical overview of HTC

Despite the hydrothermal carbonization (HTC) has had, in the last decade, a detail and ample attention, follow subsequently from an industrial development, especially in Germany and in Switzerland, thanks to the strong interest of many researchers and Cleantech companies, such as *TerraNova Energy* and *AVA-CO2*, the basic mechanism of the thermo-chemical conversion of biomass into coal-like materials is known from almost one century.

In fact, the German chemist **Friedrich Bergius** (Goldschmieden 1884 – Buenos Aires 1949) first described the HTC-process in the year **1913** as a method for simulating natural coalification of organic matter in the laboratory *(Funke et al., 2010)*.

He won in 1931, jointly to *Carl Bosch*, the Nobel Prize in Chemistry in recognition of their contributions to the invention and development of chemical high-pressure methods.

In particular, Bergius explained the hydrogenating effect of hydrogen on coal and heavy oils under high pressure and high temperature *(Bergius process)*. He described, therefore, always in 1913, the hydrothermal transformation of cellulose into coal-like materials.

In the next ***Figure 9***, a portrait of Friedrich Bergius is depicted.

Figure 9: *Picture of Friedrich Bergius*

(Source: http://en.wikipedia.org/wiki/Friedrich_Bergius)

The next year to the Nobel Prize, other researchers, *Berl* and *Schmidt*, carried on the experiments varying the type of biomass, at temperature between 150 and 350°C.

Later, also *Schuhmacher*, interested in this conversion process, analyzed the influence of pH on the outcome of the HTC reactions and found some differences, through the elementary composition (C, H, and O) *(Titirici et al., 2007)*.

During the following years, the investigations for this thermo-chemical process had fallen into a relative obscurity until the last decade, when HTC has regained a lot of interest as an alternative source of energy and thus a possibly promising way to transform biomass into a stable, solid and sterile product *(Fink, 2011)*.

In fact, in the year **2006**, the German scientist **Markus Antonietti**, director at the *Max Planck Institute of Colloids and Interfaces in Golm/Postdam* (*MPI* - Germany), examined this process in more details and he developed, with his research team, a simple method, with which biomass can easily be converted into coal-likes materials under increased temperature and pressure *(Röthlein, 2006)*. Scientists have described this conversion of biomass into coal as the "black revolution" for climate protection and since then, from 2006, the hydrothermal carbonization has attracted the interest of many researchers.

However, literature on the wet pyrolysis and its product (hydrochar) is still limited in comparison to that on char from dry pyrolysis *(Libra et al., 2011)*.

In the next ***Figure 10***, a portrait of Markus Antonietti is depicted.

Figure 10: *Picture of Markus Antonietti*

(Source: http://www.mpikg.mpg.de/28563/2Leitung)

It is possible to describe the HTC-process, according Markus Antonietti, in these easy general following steps:

- put, firstly, biomass and water into a pressure vessel;

- add a couple of bits of catalyst (the aim is to accelerate the reaction mechanism even if they can change the composition of HTC-coal, but this is still subject to further researches *(Hu et al., 2008)*; however, they are not necessary for the conversion);
- heat it all up to 180°C in the absence of air;
- after about 12 hours, the mixture is so transformed in a black broth, where finely spherical coal particles are distributed;
- then, HTC-coal can be easily separated from the liquid phase by filtration and finally, it is put under a constant pressure of 15 bar, using a press and subsequently it can be dried (dewatering and drying properties of HTC-coal) *(Ramke et al., 2009).*

In this way, many types of biomass (oak foliage, grass, pine needles, pinecone, etc.), including also different organic waste, were successfully carbonized. In fact, the plan of Antonietti is to use vegetable waste and not precious and useful resources for the humanity, as it usually happens in the traditional biomass plants.

The following images, ***Figure 11a*** and ***Figure 11b***, show some moments of HTC-process. The first one, *Figure 12a*, the experimental set-up used at *Max Planck Institute*, with Prof. Markus Antonietti and his colleague Anna Fischer, and the second one, *Figure 12b*, the final product (hydrochar), which is the black powder consisting of coal nanospheres.

Figure 11a – Figure 11b: *HTC-process at Max Planck Institute (Röthlein, 2006)*

Prof. Antonietti, considered the inventor of “coal from the steam cooker”, affirms that the point of strength of this process is its extreme simplicity and he hopes that this technology will be taken, in future, in greater consideration and mostly implemented to industrial level. This because the HTC-process, being very stable and highly efficient, allows to get a final product, a biological coal of high quality, with a high calorific value and a CO_2-neutral energy source.

3.2 HTC transformation process

In hydrothermal carbonization, the biomass needs to be totally submerged in liquid water during the whole process under high temperatures and autogenous pressures for several hours. The high pressures used ensure that the water remains in a liquid state throughout the reaction, leaving the water in subcritical condition[15] *(Funke et al., 2010)*.

As in dry pyrolysis, the temperature and pressure determine the state of the products of the reaction, i.e. the products distribution. In fact, with temperature up to 200°C and corresponding pressures up to 20 bar, little gas is generated and most of the products are solids (*hydrothermal carbonization*). If temperatures instead increase up to 400°C, more liquid hydrocarbons are created and more gases are produced (*hydrothermal liquefaction*). Finally, if temperature and pressure are more increased, the supercritical state of water is reached and the product is mainly gaseous (*hydrothermal gasification*) *(Libra et al., 2011)*.

For this reason, in order to produce mostly a solid product, HTC-coal, where most carbon of the original feedstock could be stored, the reaction temperature must be limited (around 200°C) to avoid liquefaction and gasification *(Krause et al., 2013)*. This means that both temperature and pressure have a great influence on the final HTC-coal.

During hydrothermal carbonization both the oxygen content (characterized by O/C ratio) and the hydrogen content (characterized by H/C ratio) of the feedstock are reduced which results in an increase of the carbon content. This happens maintaining a high carbon efficiency (CE), defined as the relative amount of carbon from the starting biomass bound in the final product.

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[15] The term “subcritical condition of water” refers to liquid water at temperatures between the atmospheric boiling point (100°C) and the critical temperature (374°C), under high pressure to maintain water in the liquid state. Therefore the necessary pressure to keep water in liquid phase range from at least 16 bar at 200°C to 221 bar at 374.1°C. Alternative terms are often used such as pressurized hot water (PHW), hot compressed water (HCW), near-critical water (NCW) or superheated water.

In particular, the temperature must be above 100°C because first reactions have been observed around this range. However, according to *Funke* and *Ziegler (2010)*, it is unlikely that practical implementations of hydrothermal carbonization work outside the temperature range of **180-250°C**, since the first reaction of HTC-process, hydrolysis, begins at temperature of about 180°C *(Funke et al., 2010)*.

Therefore, the main process conditions to develop a correct hydrothermal carbonization, with the major formation of solid residue, are:

- biomass surrounded by water during all the reaction;
- water in a liquid phase (subcritical condition) throughout the reaction thanks to the high pressure (at least saturated pressure);
- range of temperature between 180-250°C with pressure around 20 bar;
- residence time between 1-72 hours.

3.2.1 Reaction mechanisms

Hydrothermal carbonization is a thermo-chemical process, which converts biological material into HTC-coal through a series of reactions similar to those in dry pyrolysis. These reaction mechanisms include hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization, leading to the generation of a carbon-rich and high energy density *(Libra et al., 2011)*.

Funke and *Ziegler (2010)* specify that these reactions are not consecutive steps but rather a parallel network of different reaction paths and that their detailed nature depends on the type of feed.

Although these chemical reactions are mentioned in the literature, only just few of them have been studied in detail, such as the hydrolysis of cellulose. Therefore, the complex nature of these reaction pathways is not well-known yet.

In general, the HTC-process is mainly governed by dehydration and decarboxylation *(Funke et al., 2010)*; both of which exhibits a negative enthalpy, i.e. the exothermic nature of this process. For these reason, the amount of energy released progressively increase with stronger carbonization, i.e. higher temperature and longer residence time. At these conditions, the HTC-coal carbonizes more strongly with the result of a further decrease of its atomic ratios H/C and O/C *(Funke et al., 2011).*

Therefore, the degree of carbonization depends on the reaction temperature and residence time, where higher temperatures and longer residence times lead to a higher carbon content and thus a higher heating value, but also to a lower mass and energy yield *(Erlach et al., 2012).*

In general, during HTC-process, oxygen is separated from the organic compounds in the form of carbon dioxide (CO_2) and water (H_2O). This de-oxygenation is an important characteristic of this chemical conversion and is desired because it reduces the polarity of molecules, simplifying their separation from the water, and also increases the heating value in the final HTC-coal.

Bergius (1913) described, for first, the hydrothermal carbonization of cellulose with the following stoichiometric formula (1):

$$\boxed{\begin{array}{l}(C_6H_{12}O_5)_4 \rightarrow C_{21}H_{16}O_2 + 3CO_2 + 12H_2O \\ \Delta H_R = -297.9\,\mathrm{kJ/mol}\end{array}} \qquad (1)$$

The presence of water, necessary and key ingredient of HTC, in subcritical conditions at elevated temperatures increases the solvent properties of water and facilitates **hydrolysis** of organic compounds. During this first hydrolytic reaction, the presence of water leads to the cleavage of chemical bonds of the bio-macromolecules.

In fact, these bio-macromolecules are being hydrolyzed resulting in highly reactive decomposition fragments. In particular, hemicellulose decomposes between 180-200°C, most of the lignin between 180-220°C and cellulose, the main component of plants and the most abundant biopolymer on earth, hydrolyzes above 220°C *(Libra et al., 2011).*

Hydrolysis has lower activation energy than most of the other decomposition reactions, so it requires lower decomposition temperatures and it is therefore the initiating reaction *(Libra et al., 2011).*

During chemical **dehydration** (splitting of water from carbohydrates), the biomass is carbonized significantly by lowering the H/C and O/C ratios. *Titirici et al. (2007)* worked out a formula (2) for the dehydration of glucose as follows (this equation is also used to describe the whole transformation process of carbohydrates):

$$\boxed{\begin{array}{l} \mathrm{C_6H_{12}O_6 \rightarrow C_6H_4O_2 + 4\,H_2O} \\ \Delta H_R = -1040\,\mathrm{kJ/mol} \end{array}} \qquad (2)$$

or also commonly found (mentioned for example by *Ramke et al. 2009*):

$$\boxed{\begin{array}{l} \mathrm{C_6H_{12}O_6 \rightarrow C_6H_2O + 5\,H_2O} \\ \Delta H_R = -950\,\mathrm{kJ/mol} \end{array}} \qquad (3)$$

During **decarboxylation**, at temperature above 150°C, carboxyl (-COOH) and carbonyl (-C=O) groups are rapidly degraded, yielding respectively CO_2 and CO. The elimination of hydroxyl (-OH) and carboxyl groups lead to the creation of unsaturated fragments of bio-macromolecules. Some of these fragments are highly reactive and join together mainly by **condensation polymerization**, process in which two molecules join leading to the loss of a small molecule (often H_2O)**.** Aromatic structures, which result from the **aromatization** of polymers, are very stable under hydrothermal conditions and are therefore considered as the building blocks of the HTC-coal *(Funke et al., 2010)*.

All these conversions happen with only very slight loss of carbon in the solid phase, this means that most of the original carbon stays bound to the final structure; therefore the process works with high carbon efficiency (CE) *(Titirici et al., 2007)*. In fact, different studies, with vary type of biomass, have demonstrated that a large fraction of carbon initially present in the feedstock remains integrated within the hydro-char during the carbonization; this final solid product resemble if brown-coal for its energy-related properties and structure *(Funke et al., 2010; Libra et al., 2011)*.

3.2.2 Role of water in HTC

Water is a fundamental ingredient for the correct execution of the HTC-process and it plays several different roles during the thermal conversion. In fact, although it is possible to use another reaction medium to carbonize biomass, like for example oil, it has been observed that the hydrothermal carbonization is accelerate by water, as well as the water conducts heat more easily than any liquid, except mercury *(Funke et al., 2010)*.

In particular, as temperature increase, the physical and chemical properties of water change significantly. In fact, its viscosity, surface tension, density and dielectric constant drop at elevated temperatures, while its diffusivity and its self-ionization increase with increasing temperature; this means that water is a high ion product at elevated temperatures, so it can act an acid or base catalyst (catalytic role). In particular, the density of liquid water varies with temperature and changes dramatically as the temperature approaches the critical temperature. An effect of this change is shown by the fact that, at high temperatures, liquid water expands significantly decreasing its density.

The next ***Figure 12*** shows this drop of physical properties of water at high temperature and at different pressures, at 24 MPa and at 38 MPa.

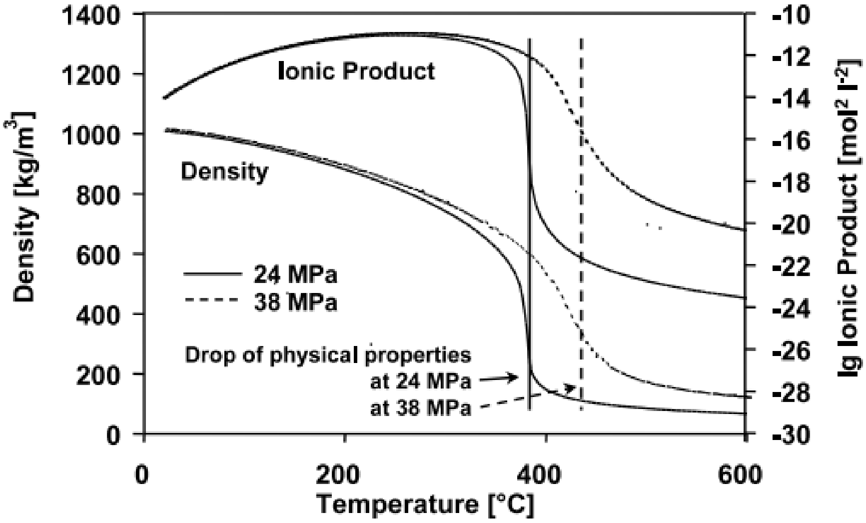

Figure 12: *Changes of physical properties of water at high temperature (Kritzer, 2003)*

As water is a very stable molecule, the removal of each water-molecules from the biomass, frees a certain amount of energy, making the HTC-reaction an exothermic process. Therefore, water represents the ideal reaction medium for HTC, with good properties of heat transfer and storage; it can also serve as a distribution medium for homogeneous and heterogeneous catalysts/additives.

In particular, under the HTC-conditions, water is also a strong polar solvent for organic compounds; for this reason, it is often referred to as the *universal solvent*, due to the decrease of its dielectric constant with temperature. The presence of water in some organic reactions (also some hydrolysis and decarboxylation reactions) can cause a decrease of the activation energy, altering thus their kinetics.

The following ***Figure 13*** represents the phase diagram of water, which shows, in temperature-pressure space, the lines of equilibrium between the three phases of solid, liquid and gaseous.

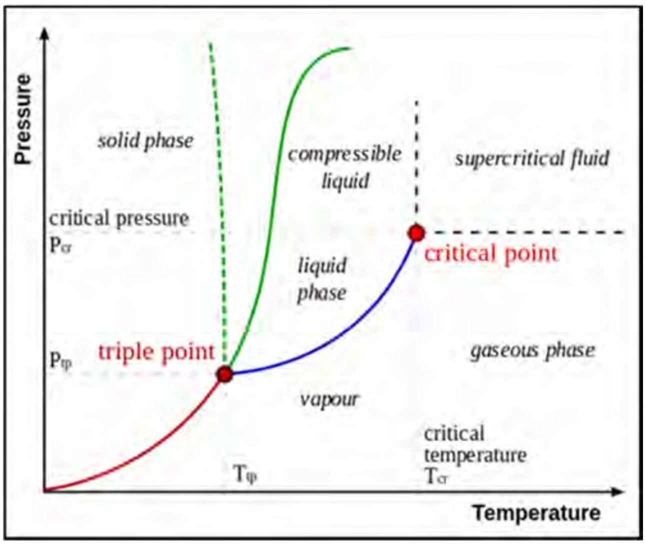

Figure 13: *T-P phase diagram of water*

(Source: http://en.wikipedia.org/wiki/Phase_diagram)

Under subcritical condition of water, increasing temperature always means an increasing pressure due to the conditions set by the vapor-pressure curve; this means that the vapor pressure of water is a direct function of the temperature *(Kruse et al., 2013)*.

For all these reasons, subcritical water treatment is an environmentally compatible technique with a wide range of applications, such as extraction, hydrolysis and wet oxidation of organic compounds.

3.3 Energetic aspect of the process

In literature, hydrothermal carbonization is described as a spontaneous, exothermic process, during which part of the chemical energy presented in the initial biomass is released in form of heat; this is confirmed by the negatives signs of the enthalpy of reaction ΔH_R of equations (1), (2) and (3) *(Robbiani, 2013)*.

Nevertheless, before to releasing and utilizing this energy, a mound of activation energy has to be overcome; for this reason, it is so necessary to heat, with external energy, the reactor, at least 180°C, temperature with which the hydrolysis begins its chemical reaction *(Funke et al., 2010)*. Moreover, this external energy supply is also required, as in dry pyrolysis, because the initial phase, represented by the hydrolysis, is an endothermic reaction. *Libra et al. (2011)*, on this subject, declare that a mild HTC can be endothermic, as the amount of energy used by hydrolysis is not sufficiently compensated by the following exothermic reactions.

According to *Titirici (2007)*, once activated, HTC-process liberates up to a third of the combustion energy stored in the carbohydrates through dehydration (equations (2) and (3)). The amount and proportion of heat released is an indication of the intensity of the process and it depends especially on the input material used and on the process conditions, mainly temperature and residence time.

However, it is important to keep in mind that although the temperature has a strong influence on the kinetics of the reaction mechanisms, it does not influence the quantity of the heat released *(Funke et al., 2011)*. This means that it is possible to have the same amount of heat released with a lower temperature but longer residence time.

In particular, *Ramke et al. (2009)*, to well understand the energy balances of the HTC-process, compared the energy content of the input and output material using the higher calorific values. It was discovered that 60% – 90% of the higher calorific value of the input material is available in the solid HTC-coal. The remaining energy (10-40%) is released as heat during the exothermic process or chemically bonded in carbon compounds dissolved in the liquid phase.

However, the heat released by the exothermal reaction does not compensate the heat losses during the process; therefore, an external power has to be provided in order to sustain the reaction. In fact, on this subject, *Glasner (2011)* reports that up to date the HTC process has not been maintained without external energy supply.

Finally, in order to improve and optimize the energy balance of a HTC system and so to decrease the need of external energy supply, required for heat biomass and for mechanical dewatering-drying of the hydrochar slurry, an efficient design of the heat recovery system is essential. Reduction of heat losses can be achieved by recirculating the hot process water (liquid phase), in this way, the energy content of the process water is recovered and the consumption of fresh water is also decreased *(Funke, 2010)*.

3.4 Influence of process parameters

The principal physical parameters that regulate the hydrothermal carbonization (HTC) and determine the product distribution are, as in dry pyrolysis, mainly *temperature* (T measured in °C) and *pressure* (p measured in bar) *(Libra et al., 2011)*.

Others parameters must be took in consideration during the wet thermal conversion process, such as *residence time* (t), *solid load* and *pH value*.

Varying therefore one of these listed parameters are obtained, as in the dry pyrolysis, a diverse results, i.e. a different distribution of the final products (solid, liquid and gas phases). However, this variation also depends on the type of feedstock (carbon content, moisture content, etc.) used during the HTC-process.

3.4.1 Temperature

Temperature is the decisive process parameter, which influence mostly on product characteristics. It governs at large extent the reaction rate of the HTC-process; this means that high temperatures lead to higher reaction rates, as temperature intervenes directly in the kinetics of the reaction mechanisms during the wet thermal conversion and accordingly on the number of biomass compounds that can be hydrolyzed *(Funke et al., 2010)*.

In particular, with increasing reaction temperature, the carbon content increase but the solid yields (i.e. mass ratio of product formed to initial feedstock based on dry weight) and accordingly the energetic yield and also the H/C and O/C ratios decrease.

However, it is important to keep in mind, especially for the developing countries, where the energy supply is poorly present, that higher temperature not only accelerate the process but also increase the energy consumption.

In the HTC-process, biomass is usually heated in a water medium to temperatures around 180-220°C in order to maximize the solid phase (HTC-coal). In fact, temperature influence also the carbon distribution, in particular, at higher temperatures, above 250°C, gas evolution is increased, due to decarboxylation and/or volatilization of organic compounds, thus greater retention of carbon in the solid and liquid phases results at lower temperatures *(Falco et al., 2011; Lu et al., 2013).*

The *reaction severity "f"* has been defined to model the influence of temperature and residence time on the products. Both higher temperatures and longer residence times increase reaction severity. The higher the reaction severity is, the higher the carbon content of the HTC-coal produced *(Funke et al., 2010; Escala et al., 2012).*

The reaction severity "*f*" is expressed with the following formula (4):

$$\boxed{f = 50 \cdot t^{0.2} \cdot e^{-\frac{3500}{T}} = (O_{feed} - O_t) / (O_{feed} - 6)} \tag{4}$$

Where:

f = severity of the reaction factor;

t = carbonization time, i.e. total time above 180°C (s);

T = maximum temperature (K[16]);

O_{feed} = percentage of oxygen in biomass;

O_t = percentage of oxygen in coal;

6 = assumption that 6% of O in coal shows complete conversion of biomass.

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[16] The maximum temperature need to be converted from degree Celsius to Kelvin according this following formula: T_{max} [K] = T_{max} [°C] + 273.15.

This semi-empirical model suggests that if a HTC reaction is carried out with a lower temperature, a similar HTC-coal can be produced by adjusting the residence time that is with longer residence time.

3.4.2 Residence time

Residence time is the second important carbonization parameter process, after temperature, which influences product characteristics. This parameter defines the total length of the conversion of the biomass inside the reactor.

To date, it is not possible to limit its range, since reaction rates remain largely unknown. However, typical residence times vary between 1 and 72 hours, i.e. from some hours to several days.

Many experiments have been systematically varied the residence times but its influence was not elaborately evaluated; therefore, residence time requires more in-depth explorations and investigations to better understand its influence on the product formation.

Experiments with short residence time, less than an hour, have been carried out and also resulted in a significant increase of heating value of the HTC-coal produced *(Funke et al., 2010)*.

In particular, a longer exposure time allows to achieve a “complete” reaction and thus a higher reaction severity and also to reduce the amount of organic losses in the wastewater, since a larger fraction of organic compounds condensate to HTC-coal *(Fink, 2011)*. Finally, an economical way of increasing the residence time as long as possible would be by recirculation of the process water *(Funke et al., 2010)*.

3.4.3 Pressure

Hydrothermal carbonization takes place with elevated pressures, approximately 20 bar, to keep water in liquid phase (subcritical condition of water) for the whole thermo-chemical conversion process. In order to maintain water in the liquid state during the HTC-process, the pressure must be maintained equal or above the vapor pressure.

In a close pressure vessel, the increase of the pressure is a result of rise in temperature; this means that pressure inside the reactor rises isotropically with the increase of the temperature *(Funke et al., 2010).*

In particular, if the temperature rises above 100°C then the resulting vapor pressure is the saturated pressure of water, which means that further evaporation of water will lead to condensation of the same amount of water vapor (reaction equilibrium) *(Robbiani, 2013).* For example, with temperature from 180-220°C, the resulting water vapor pressure (saturated vapor pressure) ranges between 9-22 bar *(Ramke et al., 2009).*

However, if the reactor, heated above 100°C, contains biomass as well, so the resulting pressure will be higher than the saturated vapor pressure due to the formation of gases. In fact, on this subject, *Glasner et al. (2011)* report that the pressure in a reactor, heated at 185°C, can reach 22-24 bars during the wet thermal conversion process of biomass.

Finally, it is important remind that higher pressure, obtained with elevate temperature, leads to higher investment cost for pressure equipment *(Fink, 2011).*

The next ***Table 15*** shows the different ranges of pressure at determined values of temperature and the relative density of the water.

Saturation Temperature **[°C]**	***Pressure*** **[bar] gauge**	***Density of Water*** **[kg/m³]**
160	5.16	907.5
170	6.90	897.5
180	9.01	887.1
190	11.53	876.1
200	14.52	864.7
210	18.05	852.8
220	22.17	840.3
230	26.94	827.3
240	32.43	813.5
250	38.72	799.1

Table 15: *Saturated steam table (Adapted from Robbiani, 2013)*

3.4.4 Solid load

The solid load is another important parameter for the HTC-process and it is the ratio of biomass to water.

In particular, the biomass, with solid load close to zero, can be almost completely dissolved, leaving so only a little residue. Raising, on the other hand, the solid load, increase also the solid product, i.e. large parts of the dissolved organic fraction as solid material *(Funke et al., 2010).*

Depending on the nature of the substrate, the resulting pressure during HTC can increase very fast. Therefore, when using a new substrate for HTC, the reactor shouldn't be filled with a too high amount of feedstock **(TS not above 5%)**. This allows for a better control of the pressure increase.

Then, it possible to gradually increase the solid loads, depending on the design of the HTC-reactor, namely volume and maximum allowable pressure. In fact, in order to maximize the coal production during the conversion process, the solid load should be kept as high as possible *(Funke et al., 2010)* but in a way that the input biomass is completely covered with water and that the mixture can be easily pumped or stirred if devices such as pumps or stirrer are used *(Robbiani, 2013).*

3.4.5 pH

In different studies and experiments, the pH value undergoes automatically a drastic drop during the hydrothermal carbonization. For this reason, the pH value should be below seven, since alkaline conditions lead to a different product.

However, a too low pH value can have an inhibiting effect on the HTC-reactions *(Funke et al., 2010).*

The addition of acids in the initial mixture implies an influence on the kinetics of the reaction (reaction rate) and on product characteristics or distribution too. This means that catalysts can accelerate the chemical reactions but, at the same time, they can alter the composition of the solid product *(Fink, 2011).*

In particular, weakly acid conditions increase the overall rate of the HTC and increase the carbon yield as well as carbon content of the HTC-coal.

Moreover, a neutral to weakly acidic conditions seems to be necessary for simulating natural coalification *(Funke et al., 2010)*. In spite of this, more investigations are need to better understand the role and the real influence of catalyst/acids during HTC-process and especially on the composition of the HTC-coal.

3.4.6 Summary of process parameters for HTC-process

The following ***Table 16*** summarizes all the process parameters, described until now, with their usually range.

PARAMETERS	**RANGE**
Temperature	180-220°C
Residence time	1-72 h
Pressure	around 20-35 bar
Solid load	TS < 5% for the first time with a new substrate
pH	< 7 (acid conditions)

Table 16: *Summary of process parameters for HTC-process*

3.5 Typologies of feedstock for HTC

The HTC-process is well appropriated for a large variety of different types of biomass. In fact, one of its main advantages is that the biomass does not need to be pre-dried; in this way, complicated drying schemes and costly procedures can be avoided *(Titirici et al., 2007)*.

Therefore, it allows, unlike the traditional dry pyrolysis, to widen the field of potential biomass to substrates with **higher moisture content**, typically around **75-90%** or even higher *(Libra et al., 2011)*. Thus, in principle, any kind of feedstock, wet and dry, can be hydrothermally carbonized in just a few hours *(Funke et al., 2010)*.

In general, the HTC reaction works best with biomass rich in hydroxide anions such as sugars, cellulose or hemicelluloses (any type of biomass made of carbohydrates) and less with feedstock poorer in the same hydroxide anions, such as protein (present in the meat) or lignin, because their structure remain stable in the rather mild conditions of HTC. Thus, the protein and lignin are carbonized less under hydrothermal conditions than cellulose; nevertheless, literature reports that it is acceptable to include up to 20% meat waste in an otherwise vegetal feedstock.

The potential biomasses for HTC do not only include the traditionally sources, like wood and crop residues (agricultural residues) but also a variety of non-traditional resources, such as: animal manure, human waste (faecal sludge), sewage sludge (primary and secondary sludges from wastewater treatment processes), municipal solid waste[17] (MSW), algae and aquaculture residues *(Fink, 2011)*.

In particular:

- ***Animal manure*****:** their characteristics can vary widely, depending to the animal and the feeding. However, manure is mainly used for fertilization of local field and should be used for other purposes only if plentiful, to avoid, in this way, enrichment of surface and ground waters with nitrogen and phosphorus compounds or also ammonium content, leading to eutrophication *(Fink, 2011)*. In particular, in a recent research, horse manure gave a positive results, a higher

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[17] The term *"municipal solid waste"* refers to solid wastes from: houses, streets and public places, shops, offices and hospitals. The industrial waste and faecal matter, though not considered part of municipal waste, they are often found in the municipal waste stream and thus collected with the same services.

heating value and nutrient contents, mainly thank to the high undigested cellulose content present in it; therefore, it can be used for energy carrier and soil improvement *(Lilliestrale, 2007)*.

- ***Human waste (faecal sludge) and Sewage sludge:*** their amount is continuously increasing, both through intensified wastewater treatment in developed countries and through the utilization of new sanitation services in developing countries *(Libra et al., 2011)*. However, to date, the sanitation coverage of these areas is unfortunately very low; human excreta is often disposed in the landscapes or in shallow holes in the ground, called *"pit latrines"*, causing so various problems of pollution to the environment (air, surface-ground waters and soil pollution) and many illnesses (typhoid fever, malaria, diarrhea, etc.) to the people. For this reason, there is a need, as soon as possible, of an appropriate sanitation system that permits to improve living conditions of the people and other important benefits, such as: improvement soil fertility (soil texture, nutrient and water retention capacity) and as a result its productivity and also reduction of greenhouse gas emissions *(Krause, 2010)*. Moreover, these new sanitation systems, characterized from separated waste streams and reduced water use, permit to have concentrated and quite homogeneous waste streams, requiring, thus, only minor pre-treatment before HTC-process *(Libra et al., 2011)*.

- ***Municipal solid waste (MSW):*** represent a serious problem and issue in the developing countries, especially in low-income countries, where the rapid population growth increases also the waste generation without an adequate service coverage, management and disposal. In fact, most of the MSW in developing countries is dumped on land, streets or drains, in a more or less uncontrolled manner, or even simply burn it in backyards, so contributing air-water pollution (emission of greenhouse gases, like methane or toxic gas emission such as dioxins and furans in case of burning), breeding of insects (flies, mosquitoes, etc.) and rodents and finally spread of diseases *(Zurbrügg et al., 1998)*.

  The MSW, in terms of generation and composition, can vary with location, villages or cities, and especially with average income, that is lifestyle, level of institutional and commercial activities. The MSW volume range thus from 0.1 tons/person-year for low-income countries to over 0.8 tons/persons-year for high-income countries *(Libra et al., 2011).*

In general, most of the generated MSW contains high fractions of organic and paper, compared to the lower amounts of plastics, glass and metals. In fact, in general, in developing countries, up to 70% of MSW is biodegradable *(Zurbrügg, 2002)*; for this reason, HTC-process can be an appropriate technology, in a small villages, even if the heterogeneous nature of MSW (composition and chemical properties) complicates its use with this type of feedstock. Hence, it would be opportune to apply a correct waste management in such way to pick up separately only the organic fraction, i.e. the biowaste.

- ***Algae and aquaculture residues:*** are an aquatic biomass generally comprising of proteins, carbohydrates, fats and nucleic acids in varying proportions depending on the species. Their potential use for HTC-process remain uncertain, as there is no still work published. However, they would be an interested idea in regions with an intensive aquaculture *(Fink, 2011)*.

Therefore, the main appropriate typologies of biomass for HTC-process in developing countries are: human waste, sewage sludge and municipal solid waste (for the last one only the organic fraction/biowaste). This because the high temperatures of hydrothermal carbonization assure to obtain a sterile solid product, improving thus the hygienic conditions through the HTC treatment of these problematic biomass.

Another important thing for the hydrothermal carbonization is the moisture content of the feedstock at the beginning, because a water content under 40% is unlikely to have any energetic advantages (in terms of input of external heat) over dry pyrolysis *(Libra et al., 2011)*. It is necessary, thus, to know the physical and chemical characteristics (elemental analysis (in %) in terms of C, H, O, N – moisture content – total solids – energy content) of the initial biomass, since they determine the efficiency of the conversion and accordingly the specific qualities of the final HTC-coal.

In addition to this, the feedstock, before to introduce it into the reactor, is usually blended and shredded (*pre-treatment*), such that the uniform mixture with water can be pumped or stirred easily. During this pre-treatment, physical changes of biomass such as wetting, swelling and pre-hydrolysis take place.

Grinding of the feed may be an advantage because hydrolysis, the first reaction of the HTC process, is diffusion controlled and seems to be a rate-determining step.

Therefore the smaller the feed is the faster the reaction. Nevertheless, since this requires a higher energy demand and investment costs, it is still uncertain if this lead to a significant advantage *(Funke et al., 2010)*.

Finally, it is important to remind that HTC-process has been mostly applied and studied in a small-scale on a limited number of feedstock, ranging from pure substances such as glucose and cellulose to slightly more complex biomass *(Berge et al., 2011)*. For this reason, it is necessary that other researches are conducted to understand the real differences among the feedstock and as a result to identify the best typology of biomass.

Table 16 shows the main properties of these potential substrates previously described.

Feedstock		**Woods**	**Grasses**	**Manures**	**Sewage sludges**		**Municipal Solid Waste**	
					Primary	*Digested*	*Total*	*Organic*
Elemental analysis (%, daf)	***C***	50-55	46-51	52-60	53.3	54.4	27-55	47-52
	H	5-6	6-7	6-8	7.2	7.7	3-9	0.63
	O	39-44	41-46	26-36	32	29	22-44	40-42
	N	0.1-0.2	0.4-1.0	3-6	5.3	5.6	0.4-1.8	0.16-0.25
	S	0-0.1	<0.02-0.08	0.7-1.2	2.1	3.2	0.04-0.18	0.002-0.003
Moisture content (%, fresh weight)		5-20 (dried wood) 35-60 (green wood)	NR	21-99.7	90-95	88	15-40	45-70
Energy content (MJ/kg $_{db}$)		19-22	18.3-20.6	13-20	23-29	9-14	2-14	8.9-11.5
daf: Dry ash-free weight; db: Dry weight; NR: Not reported								

Table 17: *Feedstock properties (Adapted from Libra et al. 2011)*

3.6 Products of HTC

At the end of the hydrothermal carbonization, the final products are present in three different phases: *solid*, *liquid* and *gaseous* state.

In particular, their relative proportions and their characteristics depend on the input material (carbon content and moisture content) and on the process conditions (mainly temperature and residence time).

In general, with temperature from 180°C to 250°C and pressure approximately around 20 bar, the main output of the HTC reaction, as already said, is the solid phase (50-80% weight), called **HTC-coal** or also **hydrochar** in literature, followed by the liquid phase (5-20% weight), usually called process water. In addition, also a small amount of gas, moistly CO_2, is generated (2-5% weight).

The next ***Figure 14*** shows these typical values of the different phases after HTC.

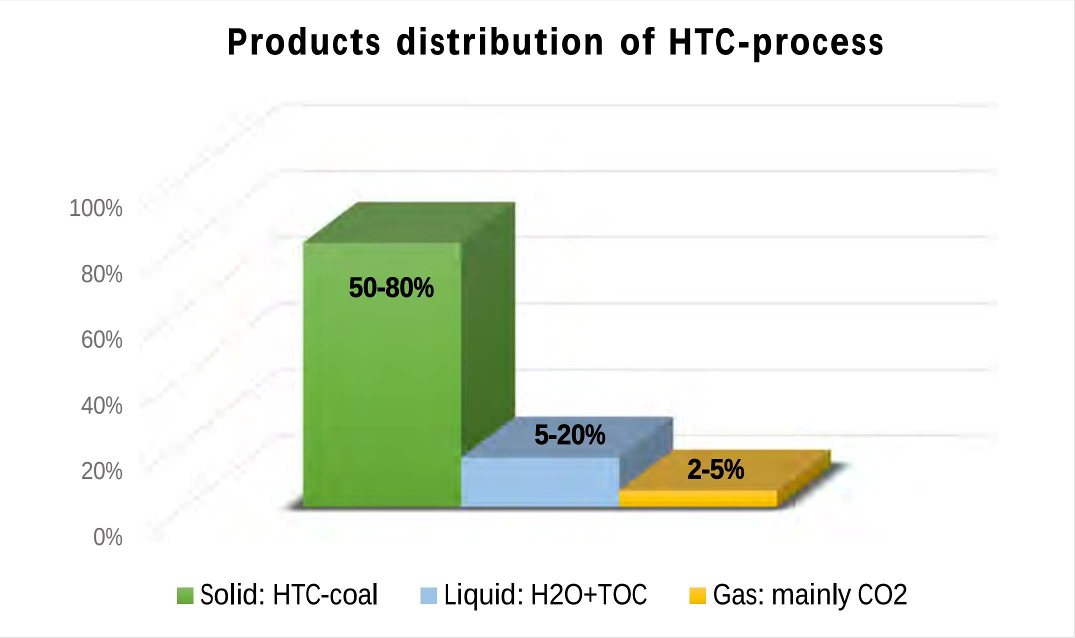

Figure 14: *Products distribution of HTC-process (Adapted from Libra et al. 2011)*

The products distribution and the typical reaction conditions of HTC-process are also compared, in the following ***Table 18***, with those of dry pyrolysis, fast and slow, and gasification.

	HTC	**Dry pyrolysis: slow**	**Dry pyrolysis: fast**	**Gasification**
Reactions conditions	180-250°C; 1-12h	~400°C; h	~500°C; ~1s	~800°C; ~10-20s
Solid [% weight]	**50-80**	**35**	**12**	**10**
Liquid [% weight]	5-20	30	75	5
Gas [% weight]	2-5	35	13	85

Table 18: *Comparison of reaction conditions and product distributions (Adapted from Libra et al. 2011)*

Therefore, the principal differences that distinguish these thermochemical conversion processes reside in: maximum temperature reached during the reaction, residence time of the input materials under relative conditions, how fast heat is transferred to initial feedstock (in particular for slow and fast dry pyrolysis) and finally in product distribution between the three different phases.

The distribution of the carbon fractions, after HTC-process, in all three phases is dependent on the typologies of feedstock used. An example of this distribution for different substrates is shown in the following ***Table 19***.

Substrate	**C in solid [%]**	**C in liquid [%]**	**C in gas [%]**
Organic waste	74.9	19.0	6.1
Green cutting	75.3	19.7	5.0
Digestate (Biogas slurry)	72.2	22.1	5.7
Straw	75.4	19.7	4.9
Chipped wood	82.9	14.1	3.0

Table 19: *Distribution of the carbon fraction in the HTC product phases (Adapted from Ramke et al. 2009)*

From these values, it so results that the typical ranges of the distribution of the carbon fractions are: **72 - 83%** of the C from the original biomass is bound in the solid phase, around **14-19%** of the organic carbon originally present in the substrate remains in the liquid part in form of TOC and finally only **3** to **6%** of the initial C is transformed in form of gas (mainly carbon dioxide).

3.6.1 Solids

After HTC-process, the solid fraction, referred to as *HTC-coal* or *hydrochar,* represents an agglomeration of different chemical substances. It can easily be separated from the liquid phase, usually by a simple filtration. The solid mass inside the reactor is bound to decrease during the HTC-process; this is mainly due to the chemical dehydration of the mass during carbonization.

The chemical structure of hydrochar resembles to natural coal, approaching in particular to lignite or even sub-bituminous coal depending of the reaction severity, in many properties: the type of chemical bonds and their relative quantities, as well as their elemental composition (e.g. H/C and O/C ratios) *(Libra et al., 2011; Funke et al., 2010)*.

3.6.1.1 Characteristics of HTC-coal

The main characteristic of HTC-coal is that it has higher carbon (C) content and lower H/C and O/C ratios than the initial substrate, owing to the evolution of H_2O and CO_2 in the dehydration and decarboxylation reactions during the thermal conversion.

The following ***Table 20*** shows examples of the solid yield (mass ratio of product formed to initial feedstock based on dry weight) and composition of HTC-coal, in terms of C, H and O, from different substrates.

		Solid yield [% dry substance]	**C** [% dry ash-free]	**H** [% dry ash-free]	**O** [% dry ash-free]	**Reference**
Cellulose	**BEFORE HTC:**	-	44.4	6.2	49.4	*Schumacher et al. 1960*
	AFTER HTC: 225°C, 3h	63	51.9	5.6	42.5	
Biowaste	**BEFORE HTC:**	-	54.6	7.5	37.9	*Ramke et al. 2010*
	AFTER HTC: 230°C, 4.5h	57	70.5	6.9	22.6	
Food waste	**BEFORE HTC:**	-	45.7	6.2	43.9	*Berge et al. 2010*
	AFTER HTC: 250°C, 20h	46	75.2	6.4	11.1	
Digestate (biogas slurry)	**BEFORE HTC:**	-	51.8	6.8	37.9	*Mumme et al. 2010*
	AFTER HTC: 230°C, 6h	51	72.6	7.2	15.6	
Wood	**BEFORE HTC:**	-	50.3	6.0	43.3	*Yan et al. 2010*
	AFTER HTC: 230°C, 5 min.	75	56.1	5.9	37.9	

Table 20: *Examples of solid yields and elementary compositions of HTC-coal from different substrates (Adapted from Robbiani, 2013; values from Funke, 2012)*

From these results, it is possible to notice, in all the types of feedstock, the increase of the carbon content and, at the same time, the diminution of the hydrogen and oxygen content after the hydrothermal carbonization.

The HTC-process can be well visualized through a graphic representation as in the coalification diagram, also known as *Van Krevelen diagram*. In this diagram, the hydrogen/carbon (H/C) molar ratio is plotted against the oxygen/carbon (O/C) molar ratio. The coalification diagram shows also the different steps from cellulose, wood, peat, lignite to the various forms of brown coal and finally through to black coal and anthracite.

During the course of HTC, both H/C and O/C ratios are decreased and a dot representing the substrate at its initial state moves towards the downwards-left direction during the carbonization process. Therefore, the length of the vector, that binds the two dots representing the input and the output feedstock, can visualize the degree and the intensity of carbonization.

The following ***Figure 15*** shows the coalification diagram with the representation of input and output values for different substrates.

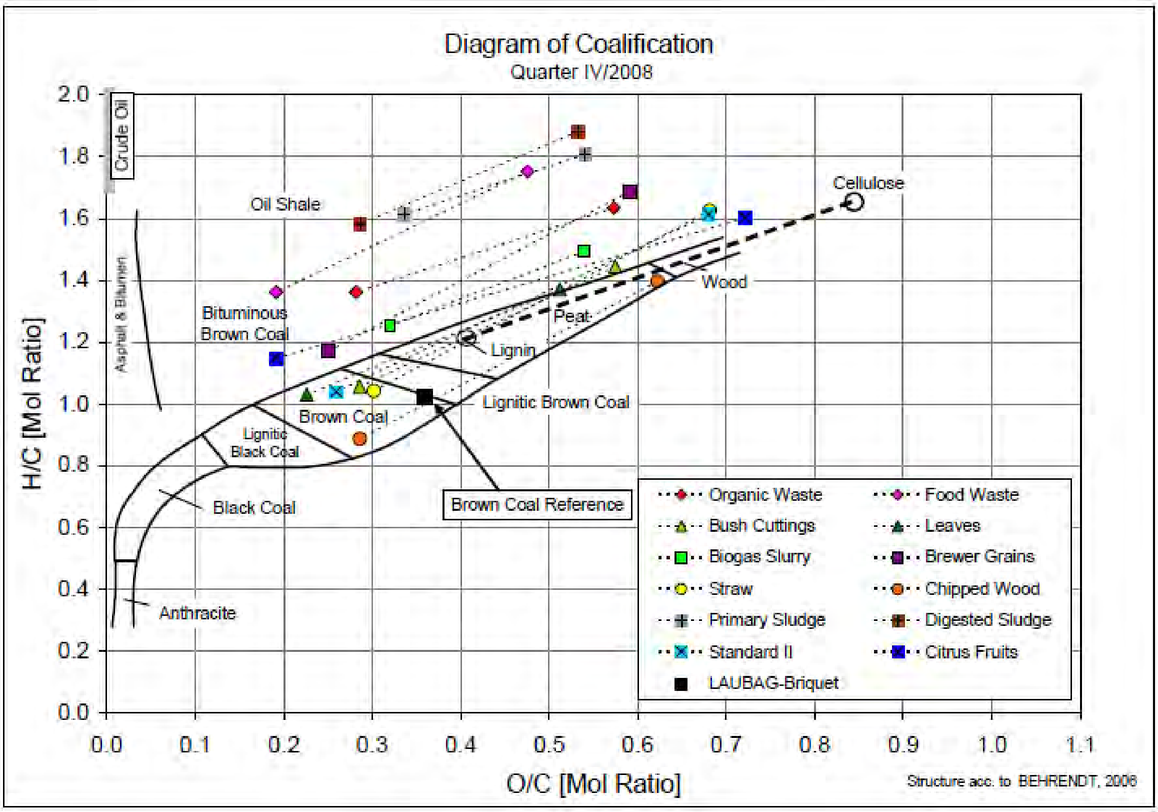

Figure 15: *Van Krevelen diagram (Ramke et al., 2009)*

In this diagram of coalification, the different substrates, before and after hydrothermal carbonization, are illustrated with the coal ranks (lower rank coals such as lignite and sub-bituminous coals and higher rank coals such as bituminous coal and anthracite) in order to have an easily comparison of HTC-coal with the physical, chemical and thermic properties of these type of coals. For example, the HTC-coal obtained from chipped wood is similar to the values of H/C and O/C of brown coal while the characteristics of HTC-coal of citrus fruits are more similar to bituminous-brown coal.

With regard to elemental composition, in particular to C-content, and calorific value, HTC-coal can be classified as being similar to brown coal *(Ramke et al., 2009).* More especially, an important linear correlation exists between the carbon content (C in %) and the higher calorific value (HHV in kJ/kg, also referred to as gross calorific value). In particular, the higher the degree of carbonization is, the higher carbon content and thus the higher the calorific value.

This correlation is shown in the following ***Figure 16***.

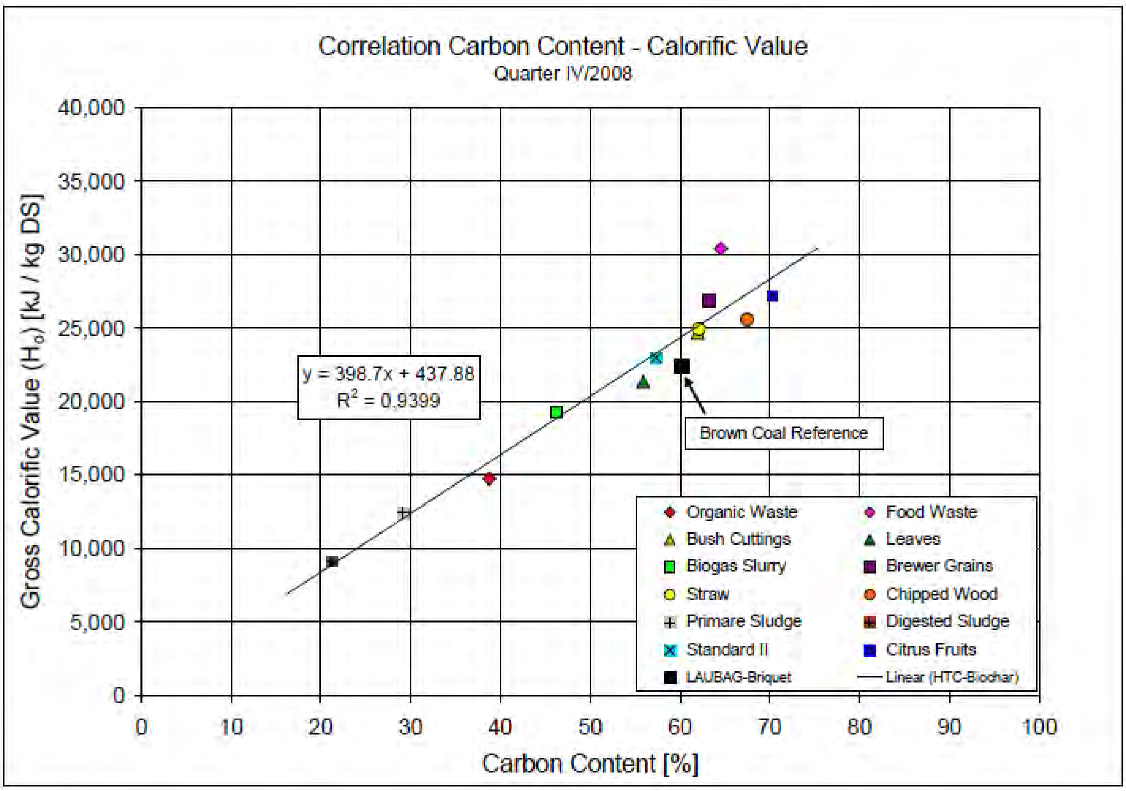

Figure 16: *Correlation carbon content and calorific value for different substrates (Ramke et al., 2009)*

In this representation, carbon content – calorific value diagram, the vectors, connecting input substrate to output substrate, would be directed from lower left to upper right, explanation of the increase of the carbon content and accordingly of the higher calorific value after the HTC-process *(Ramke et al., 2009)*.

The values of carbon content and calorific value depend on the type of feedstock and process parameters used during the reaction. In principle, the calorific value is determined by the concentration of C, H, O and N.

Another important characteristic of HTC-coal is that the elimination of hydroxyl and carboxyl groups during the HTC-process leads to a product with a lower hydrophilicity than the initial feedstock *(Funke et al., 2010)*, making the dewatering process of the HTC-coal easier as compared to the original biomass before the process.

3.6.2 Liquids

The liquid phase, usually called *process water*, is the liquid that remains after the filtration of the coal suspension produced through HTC of biomass.

In particular, compared with dry pyrolysis, HTC-process produces more soluble organic compounds; in fact, during the conversion, water is generated as a consequence of dehydration reaction. This means that more water that at onset is found at the end of the thermo-chemical process *(Ramke et al., 2009)*.

The process water has a high load of dissolved organic and also inorganic compounds, such as: sugar, organic acids, furans and phenols *(Funke et al., 2010)*.

3.6.2.1 Characteristics of process water

In different studies, the concentrations, after carbonization, of all components in the liquid phase result very high. In addition, also the values of conductivity are very high, revealing, thus, the presence of salts in the process water from diverse typologies of feedstock *(Berge et al., 2011)*.

The process water is, in most of the cases, acidic, which can be explained by the formation of a variety of organic acids that occur during the HTC-process; it has also a high COD (*Chemical Oxygen Demand*) level. The TOC (*Total Organic Carbon*) represents the dissolved carbon that could not stay bound to the HTC-coal.

The following ***Table 21*** compares the values from the analysis of the process water that was made by *Ramke et al. (2010)* for various substrates and by *Escala et al. (2012)* with sewage sludge.

	Values from Escala et al. (2012)	**Values from Ramke et al. (2010)**
pH	5.0 – 7.0	3.7 – 7.2
Phenole [mg/L]	292 – 666	NR
NH_4-N [mg/L]	1053 – 2187	3.4 – 4.1
NO_3-N [mg/L]	45 – 178	2.9 – 36
NO_2-N [mg/L]	0.22 – 1.35	NR
Total Nitrogen [mg/L]	2263 – 4720	NR
PO_4-P [mg/L]	4.8 – 148.7	0.2 – 550

Total Phosphorus [mg/L]	14.3 – 159.6	NR
COD [mg/L]	31 467 – 53 000	14 350 – 69 610
BOD$_5$ [mg/L]	NR	10 000 – 42 000
TOC [mg/L]	NR	9 045 – 27 840
NR: not reported		

Table 21: *Composition of the process water resulting from HTC (Adapted from Robbiani, 2013)*

However, other researches are need to better understand the presence of possible harmful substances as heavy metals in the process water, depending on the feedstock source.

3.6.3 Gases

During HTC-process, a small amount of gas is released, 2-5% weight, if compared to dry pyrolysis and gasification. The gas formed during hydrothermal carbonization consists essentially of carbon dioxide (CO_2), due to the process of decarboxylation, but other gases are present in minor fraction such as carbon monoxide (CO), methane (CH_4) and hydrogen (H_2).

The concentration of CO_2 in the gas phase lays between 70 − 90% depending on substrate and severity of reaction *(Ramke et al., 2009)*, even if a study by *Berge et al. (2011)* showed that the gas composition does not vary significantly with feedstock.

The amount of gases product increase with rising temperature, resulting in higher quantities of CH_4 and H_2 and less CO.

Usually, at the end of carbonization, the resulting gas is captured, in a such way that gas volume and carbon dioxide are measured in each tests. However, in this experimental research the gas phase was not analyzed.

Finally, as gas composition has not yet well explored or well reported in the scientific reviews, other researches on this subject are need with the aim to determine potential environmental impacts or any energy significance *(Berge et al., 2011)*.

3.7 Post-processing for solid and liquid products

At the end of the hydrothermal carbonization, the solid phase (HTC-coal) can easily be separated from the process water. In particular, in this work, for this operation, a simple thick and tightly woven cotton cloth was used and placed above a punctured container (like a colander) and another bucket, which permits, thus, to separate, in an easy way, the end-products.

Tests by *Ramke et al. (2009)* confirm that this separation of **hydrochar** from the process water can be easily carried out. By using a press, typical technique for sewage sludge dewatering, wet HTC-coal from different substrates is put under a constant pressure of 15 bar. The total volume of the discharge water is measured and related to the original mass of water. Then the corresponding total solids (TS) content is calculated over time. Comparisons between dewatering curves from sewage sludge before and after HTC indicate that dewatering properties are actually much better after HTC. These experiments suggest that the same properties can be expected from HTC-coal from other wastes with high moisture content. These tests on the dewatering properties are then accompanied with tests on the drying properties, for the determination of evaporation. In this way, the specific energy of HTC-coal can increase, thanks to a reduction of the water content and an increase of the heating value. Finally, if the HTC-coal is used as an energy carrier, it is necessary to convert the dust, low bulk density, into high density and energy concentrated fuel briquettes or pellets. This operation (densification) can be carried out, especially in developing countries, through a simple and cheap hand-operated piston press.

Unlike the HTC-coal, both process water and gas phase have a low economic interest. In addition, the **liquid phase** can cause some problems both within the process equipment and by discharging without any specific treatments. In fact, in order to lower the TOC and also other nutrients, the wastewater should be processed with aerobic or anaerobic treatment *(Fink, 2011; Funke, et al., 2010)*. On this subject, several tests by *Ramke et al. (2009)* confirmed the good biodegradability of the dissolved organic components in the liquid phase. The efficiency of COD degradation with aerobic treatment steps reached 85%. However, the post-treatment of process water remain an issue in developing countries because of the low or inexistent legislations regarding the wastewater and the lack presence of adequate treatment plant (WWTP).

3.8 Potential uses of HTC-coal

HTC-process permits therefore to convert different typologies of biomass into a coal-like product, i.e. HTC-coal. It has a higher energy density (i.e. the energy content of the hydrochar divided by the energy content of the biomass) than the initial feedstock and it is easier to transport, store and process.

Therefore, HTC-coal has various interesting applications such as *energy carrier*, *soil amendment*, *carbon sequestration*, *activated carbon adsorbents* and *other uses*.

However, the most interesting applications for HTC-coal in developing countries are the use as an energy source, a carbon sequester or a soil fertilizer.

Following, an overview of potential use of hydrochar are reported.

3.8.1 Renewable energy carrier

The most important application of HTC-coal is to use it as a combustible, seeing that it has a higher heating value and higher energy density (its specific energy content significantly increase after the thermochemical conversion), compared to the original feedstock, similar to natural coal.

As the CO_2 emitted during the combustion is balanced by the CO_2 captured during the biomass growth, it is so considered a carbon neutral energy source because it does not produce “new” CO_2.

There are numerous options in which HTC-coal can be used as a combustible for the energy production, replacing usual fossil fuels: combustion plants, combined heat and power plants, cement and steel factories, mono-combustion plants for sewage sludge, gasification.

In particular, in developing countries, HTC-coal can be consumed as cooking fuel replacing firewood or charcoal derived from wood, which could in consequence have a positive impact on deforestation.

3.8.2 Soil amendment

Another interesting application of HTC-coal is its use as water and ion binding component to improve soil quality *(Libra et al., 2011)*.

The use of charcoal as a soil conditioner, usually called biochar and obtained through the dry pyrolysis, is reported to have positive effects on soil properties (physicals and chemicals), soil fertility and thus crop productivity *(Duku et al., 2011)*.

Biochar has a high surface area due to its porous structure, i.e. it has a low density and high porosity, which improves the water retention (water holding capacity) when applied to the soil. Furthermore, it improves the nutrient retention capacity of the soil, which increases the nutrient supply for the plant and decreases the nutrient losses by leaching, which is a major problem in most rain forests.

It is likely that HTC-coal will have similar effects on the soils due to its similar physical and chemical properties. However, HTC-coal is produced at lower temperatures and may not have the same large internal surfaces as biochar *(Libra et al., 2011)*. In addition, investigations regarding the application of hydrochar in soil are still in its infancy.

Researchers often refer to "*Terra Preta*" soils, also known as "Amazonian Dark Earths" (ADEs) or "Indian black earth", to illustrate the improvement of soil after application of biochar on soil. Terra Preta (literally *black soil* in Portuguese) is a dark colored soil found in Brazilian Amazon Basin most likely created by pre-Columbian Indians 500-2500 years ago and abandoned after the invasions of Europeans *(Lilliestrale, 2007)*. However, many questions are still unanswered regarding the origin, distribution and properties of these dark earths.

Despite the humid tropical conditions and the rapid decomposition of organic matter due the high temperatures, these fertile soils have persisted and have been descripted in numerous countries of South America.

In particular, Terra Preta is characterized by higher soil organic matter (SOM) content, i.e. plant and animal material in various stages of decomposition, higher carbon content, higher moisture holding capacity, higher levels of nutrient holding capacity and nutrients such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), zinc (Zn), manganese (Mn) than in surrounding soils, as well as an intense microbial activity *(Glaser et al., 2001)*.

A key factor for this improved fertility in these lands, due to the higher SOM level, seems to be the high contents of anthropogenic charcoal found in the soil, originating from residues of incomplete combustion of organic material, mainly from cooking fires and indigenous land management *(Glaser et al., 2001; Lilliestrale, 2007).*

Therefore, the fertility of these lands is much higher than the surrounding soils, which is demonstrated through substantially greater crop yields. In particular, Terra Preta soils are mostly distinguished by a distinctive black coloration caused by elevated concentration (70 times higher than surrounding soils) of charred biomass *(Glaser et al., 2001).*

The following ***Figures 17a*** and ***17b*** show the differences in color and crop growth between a normal soil and Terra Preta soil.

Figure 17a – Figure 17b: *Comparison between normal soil and Terra Preta soil (Source: http://biochar.info/biochar.terra-preta.cfml and Biochar Engineering)*

In particular, the ***Figure 17a*** show the color's difference between normal soil, on the left, and Terra Preta soil, on the right; while the ***Figure 17b*** reveal the increase of soil fertility and so soil productivity in dark earths (on the right) compared with a normal soil (on the left).

For these reasons, the presence of hydrochar in soils, especially in the humid and tropical climates, could have positive effects on soil fertility and crop yields, thanks to its similar physical and chemical properties of biochar. Hence, it would be interesting to carry out other researches in order to understand the potential use of HTC-coal as a soil amelioration.

3.8.3 Carbon sequestration

Carbon sequestration is the capture and subsequent long-term storage of carbon to prevent it from being releases to the atmosphere in form of carbon dioxide (CO_2).

Large amounts of carbon in biochar may be sequestered in the soil for long periods, estimated to be hundreds to thousands of years.

Biomass is an efficient carbon converter, binding atmospheric CO_2 through photosynthesis but it is only a short-term carbon sink[18], as microbial decomposition of biomass liberates the amount of CO_2 that was bound in the plant material *(Titirici et al., 2007)*. It is assumed that carbon entering the soil, as biochar, is highly stable and can persist over centuries due to its chemical stability caused by the aromatic structure. Additionally this complex structure makes it resistant to microbial degradation *(Robbiani, 2013)*.

The following ***Figure 18*** shows the longer retention time of biochar compared to uncharred organic matter.

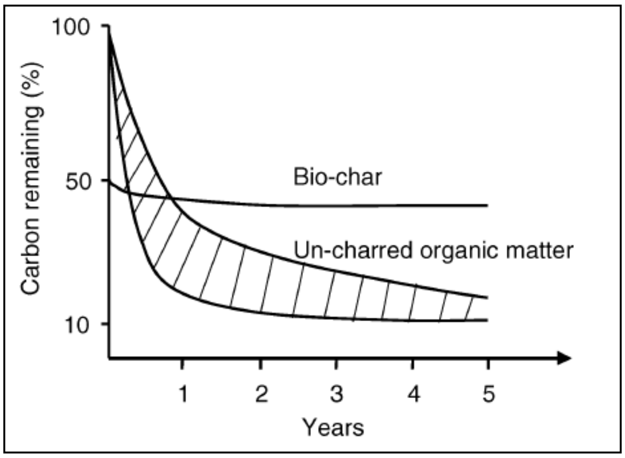

Figure 18: *Schematic representation of longer retention in soil of biochar (Lehmann et al., 2006)*

This long-term stability has been shown in Terra Preta soils, which are on average 500-2000 years old. Through hydrothermal carbonization of biomass, the carbon can be fixed into the coal product with a very high efficiency. Therefore C entering the soil as HTC-coal can act as a significant carbon sink for atmospheric CO_2.

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[18] The term “carbon sink” refers to any process, activity or mechanism that removes carbon from the atmosphere.

The result of this carbon sequestration in soil is a reduction in greenhouse gas (GHG) emissions and a decrease thereby of the atmospheric warming effect (mitigation of pollution). In fact, the natural decay of organic waste in municipal solid waste landfills releases, into the atmosphere, huge quantities of methane (CH_4), a potent greenhouse gas with a higher *Global Warming Potential*[19] (GWP equal to 23 over 100 years), contributing thus more to warming Earth. Therefore, HTC-process could be a solution in developing countries, where one to two thirds of the solid waste generated in urban areas are not collected.

3.8.4 Activated carbon adsorbents

Another one important traditional application for chars, especially for water purification purposes, is adsorption. Chars, after activation step, increase their surface area and pore size. Thanks to their increased sorption capacity, *activated carbons* can be used to adsorb a large variety of inorganic and organic contaminants from water (e.g. heavy metals, arsenates and others toxic substances).

Chars can be activated with two methods: physical and chemical activation. Physical activation is carried out with activating agents such as CO_2 or steam, while chemical activation is carried out by mixing the chars with chemical activating agents (potassium salts, sodium hydroxide, magnesium chloride, etc.) and heating the mixture at various temperatures in an inert environment. Sorbent materials for the removal of heavy metals from water have also been successfully produced using HTC without the need of an activating step *(Libra et al., 2011).*

3.8.5 Other applications

Recent research showed that HTC-process could be used for the generation of a variety of nanostructured carbonaceous material from biomass by choosing the type of feedstock

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[19] The “Global Warming Potential” of a greenhouse gas is defined as the ratio of the time-integrated radiative forcing from the instantaneous release of 1 kg of a trace substance relative to that of 1 kg of a reference gas. It thus a relative measure of how much heat a GHG traps in the atmosphere and it is calculated over a specific time interval, commonly 20, 100 or 500 years.

and the addition of certain compounds. The properties of these spherically shaped nanoparticles can be interesting for various applications such as production of *catalysts*, carbon fixation or the production of adsorbents *(Hu et al., 2008)*.

Furthermore, coal particles produced with HTC show promising potential for other various applications in the field of fuel cells, such as hydrogen storage, electrochemical energy storage with lithium-ion batteries or supercapacitors *(Libra et al., 2011)*.

3.9 Advantages of HTC

The most important advantage of HTC-process is that biomass can be converted into carbonaceous solids without an energy-intensive drying process before or during the thermochemical conversion. In this way, hydrothermal carbonization can extend, unlike the dry pyrolysis that restricts biomass with low water content (usually wood and crop residues), a variety of non-traditional wet biomass, from animal manures, human waste (i.e. faecal sludges) and sewage sludges to municipal biowaste. HTC, compared to dry pyrolysis, can thus be applied to a numerous biomass types with high moisture content, ranging from 75-90% or even higher. Moreover, HTC requires lower process temperature 180-250°C compared to 400°C-500°C for dry pyrolysis and to 800°C-1000°C for gasification. Although the out-products (i.e. solids, liquids and gases) are the same in dry pyrolysis and in HTC, different is their distribution. In fact, the main product of HTC-process is a carbon-rich solid, 50-80% weight, compared to about 20% weight for dry pyrolysis (average affected among slow – fast – flash pyrolysis).

In addition to this, carbonization of biomass offers other various advantages if compared with common biological treatments, like aerobic digestion, anaerobic digestion and alcoholic fermentation, which use enzymes, mushrooms and microorganisms to draw energy from biomass. In fact, HTC-reaction takes only hours (usually 1-12 hours) instead of days or also months required for biological processes, making them expensive and time consuming. Furthermore, in contrast with biochemical processing, the high temperatures of HTC can eliminate pathogens and inactivate other potential organic contaminants like pharmaceuticals, making thus the outputs products sterile and hygienic *(Libra et al., 2011)*.

Compared to other conversion processes that transform carbohydrates into products with higher carbon contents, HTC is in fact the most efficient. When biomass is composted, anaerobically digested or fermented, some of the original carbon in the substrate is converted into CO_2 and lost in the atmosphere. With HTC however, most of the original carbon present in the substrate stays bound in the final coal product; this means that the carbon efficiency (CE) of HTC-process is, in theory, close to 1 *(Titirici et al., 2007)*. Other technologies (such as biogas) have a lower carbon efficiency, thus HTC is the most efficient way to produce energy out of biomass. Moreover, HTC-coal requires less volume than biogas, according to *Rolf Krebs*, from the Institute for Environment and Natural Resources at the Zurich University for Applied Sciences in Wädenswil (ZHAW) - Switzerland, the stored volume of hydrochar for 1000 kWh amounts to 0.11 m^3, as opposed to biogas which requires 164 m^3. Finally, HTC is seen as an efficient process for carbon sequestration to mitigate climate change and also for soil amelioration.

A schematic comparison of HTC with fermentation and anaerobic digestion is shown in the following figure.

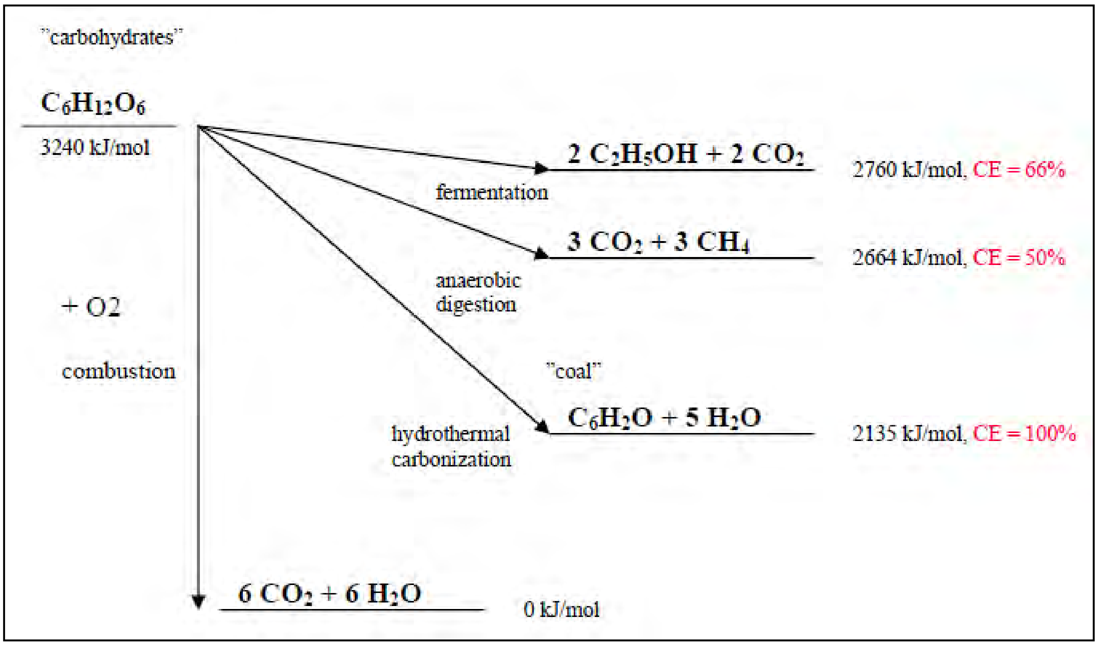

Figure 19: *Comparison of different energy and carbon exploitation schemes for carbohydrates (Lilliestrale, 2007 and Titirici et al., 2007)*

HTC is thus the most exothermic of the three common processes, it liberates up to a third of the combustion energy stored in the carbohydrate throughout dehydration, due to the high thermodynamic stability of water. It is then also the most efficient for carbon fixation, expressed by the carbon efficiency.

3.10 HTC-reactors: state of the art

Although, the HTC-process was already know for a long time (Bergius – 1913), it was not applied in industrial scale until very recently, precisely in the year 2010. In fact, in these last years, two important clean-tech companies, *AVA-CO2* and *TerraNova Energy*, based on the mechanism of the hydrothermal carbonization, are developed, mainly in Swiss and in Germany. However, in the following years, other companies, that use the principle of the HTC-process, are developed especially in Germany (for example SunCoal Industries from Königs Wusterhausen near Berlin).

Following an overview on the main existing industrial technologies is reported

3.10.1 AVA-CO2: Swiss Clean-tech Company

A pioneer and leader in the field of industrial implementation of hydrothermal carbonization (HTC) is a new and young Swiss clean-tech company, founded in 2009 and called ***AVA-CO2***, with its headquarters in Zug (Switzerland) and subsidiaries in Germany (Karlsruhe) and in Switzerland (Baden and Basel).

This company, thanks to the presence of many experts with different backgrounds and several years of experience, plans, implements and operates HTC-plants to offer, in this way, solutions to convert efficiently biomass into a sustainable source of energy (*AVA-cleancoal* for energy carrier and *AVA-biochar* for soil amelioration). In particular, the main difference between *AVA-cleancoal* and *AVA-biochar* is the level of coalification. For the first one, a complete carbonization of the biomass is important in order to guarantee the positive aspects such as high calorific value per ton; while for the second one, i.e. *AVA-biochar*, the coalification process should not be complete (shorter process time) in order to keep the positive characteristics (*AVA-CO2, 2010)*.

The HTC-process, as the partners of the company affirm, can be applied anywhere in the world, in particular, where large amounts of biomass (wet and dry) accrue and also where clean energy is required at the same time.

AVA-CO2 is the first company worldwide to develop successfully HTC to industrial maturity stage, passing from research into the industrial application of HTC technology and sending thus, a clear and important signal to the world of alternative energy generation. This technology permits not only to produce energy from biomass waste but also to reduce greenhouse gases, problem very discussed in our days because cause of serious climatic changes in the world, and finally enable a neutral CO_2 balance, reducing the impact on the environment *(Kläusli, 2010).*

This company has so built a demonstration plant, which is the world's first industrial-size HTC production plant *(HTC-0 in Karlsruhe - Germany)* into service in October **2010** and has realized the world's first commercial HTC plants *(HTC-1 in Relzow - Germany)* in October **2012**.

More precisely, at the end of October 2010, AVA-CO2 opened the first and largest industrial-scale HTC plant in **Karlsruhe**, in Germany, called **HTC-0**.

From a technical point of view, the plant has a total capacity of 14,400 liters and a processing capacity of 8,400 tons of biomass per year. The main characteristics of the HTC-plant are: pressure range 22-26 bar, temperature range 220-230°C, heat provided with steam (1.4 tons per batch), sensors of temperature and pressure (everything can be monitored in a separated room) and cost around 10-12 M€.

This HTC-plant in Karlsruhe consists essentially of three reactors operating in batch mode: the first is the mixing tank, in which the feedstock is preheated to 160°C with 10 bar (to the right in the ***Figure 22***), the second one, in the center, is the reactor, where the HTC-process (chemical reaction) takes place at about 220°C and at 22 bar and finally a buffer tank (to the left in the ***Figure 22***), where it is cooled down and its heat recovered to preheat the next batch. The product is then filtered and pressed for the production of HTC-coal *(Robbiani, 2013).*

Figure 20: *Picture of the HTC-plant in Karlsruhe*

(http://www.ava-co2.com)

HTC-0 is designed to use biowaste mainly from breweries, because enormous amount of brewer's grain and sludge arise during the production of beer.

This establishment permits to think about other similar areas of application, food manufacturers, for example in juice production, where huge amounts of orange peels accumulate or in sugar production.

The main application of the HTC-coal, in the form of coal dust or pellets[20] (the last one permits the simplest transportation and storage), produced with these industrial plants, is to use it as an energy carrier, for example in steel or cement factories, so in existing industrial furnace systems, or replacing dried sewage sludge in incineration plant.

The following ***Figure 23a*** shows the form of HTC-coal in pellets while the ***Figure 23b*** an example of its combustion.

Figure 21a – Figure 23b: *Picture of coal pellets and an example of their combustion (http://www.ava-co2.com)*

3.10.2 TerraNova Energy: German Clean-tech Company

Another clean-tech company that helps to develop the industrial realization of hydrothermal carbonization is ***TerraNova Energy***, situated in Dusseldorf - Germany.

Their systems are designed for decentralized-local installation and the capacity of these plants ranges from 1.200 tons to 12.000 tons biomass per year. The possible adjustment to the biomass available is realized through a combination of enlarging (scale up) and parallel

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[20] The coal in pellet form is also called with different names such as Green Coal or SunCoal Pellets, depending the company that produce it.

operation of relevant parts of the system. They usually have a modular design and are integrated in containers including chemicals storage area.

The structure of the TerraNova Energy plant consists in different steps: firstly, the biomass (original substance at 25% dry matter content) is placed in a receiver hopper then a high-pressure pump conveys it through a valve and a heat exchanger, which uses the waste heat of the finished reaction product for warming, in a continuously running stirred tank reactor. Secondly, catalysts and additives, which accelerate the chemical reaction, are added to the biomass into the reactor, which runs in the absence of air at a temperature of around 200°C and a pressure between 20-35 bar. After about 4 hours, the mixture is cooled down and the pressure is released from the biomass, before feeding it to a receiver tank. Finally, there are dewatering and drying systems for the solid end-product.

The next ***Figure 22*** shows the schematic structure of this TerraNova Energy plant.

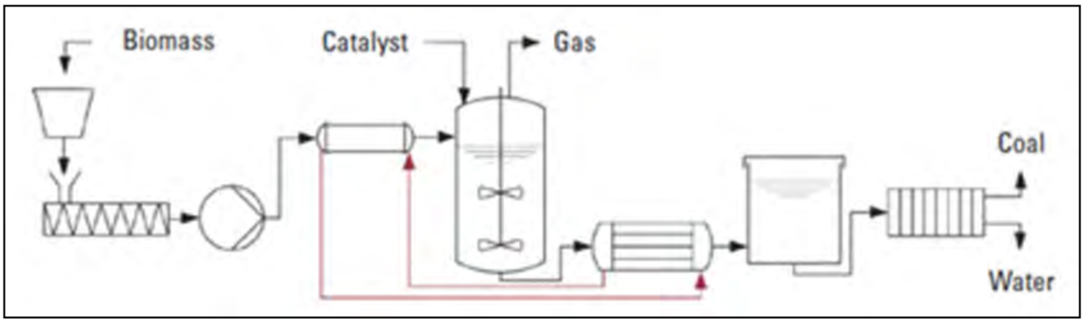

Figure 22: *Picture of the structure of TerraNova Energy plant (http://www.terranova-energy.com)*

In April 2010, sewage sludge is converted into a regenerative coal in the TerraNova Energy demonstration plant at the central sewage treatment plant in Kaiserslautern (Germany). The coal can be used as alternative fuel for heat and power generation.

Finally, the following ***Figure 23*** shows a picture of the automated TerraNova Energy plants in Kaiserslautern, with a modular design.

Figure 23: *Picture of TerraNova Energy plant in Kaiserslautern (http://www.terranova-energy.com)*

3.11 Feasibility and sustainability of HTC in developing countries

HTC is seen as a promising technology for conversion of any kind of organic waste with high water contents (typically around 75-90%) and also for treatment of problematic biomass streams like biowaste, faecal sludge, sewage sludge or industrial waste, where, especially in developing countries, they represent a serious issue for both environmental level and human well-being. In fact, hydrothermal carbonization, as regards sustainable sanitation in developing countries, allows to obtain, thanks to the high temperatures reached during the reaction, a stable and sterile product, destroying the eventual presence of pathogens agents or organic contaminants (for example pharmaceutically active compounds) and improving, at the same time, the hygienic conditions of people, as well as transform .

On this subject, there is a research and project in the rural areas of Kagera, in Tanzania, called *"Carbonization as Sanitation – CaSa"* and financed by Heidedhof Stiftung. The aim of this project is to assure sanitation, energy supply and soil fertility in one of the poorest regions in Tanzania. This system, as ***Figure 24*** shows, is a new concept of sanitation with integrated carbonization process; in fact, it consists of a small-scale biogas digester, a urine diverting dehydrating toilet (UDDT) and a hydrothermal carbonization (HTC) unit *(Krause, 2010)*.

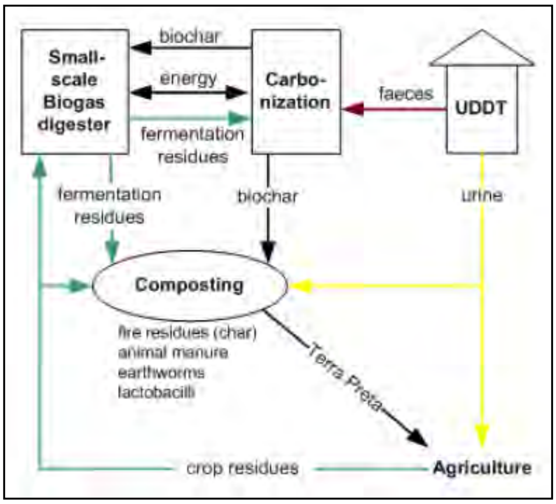

Figure 24: *Picture of project "CaSa" in Tanzania (Krause, 2010)*

However, further research are needed regarding the energy supply for the pilot HTC plant and the technical linkage with a small-scale biogas digester, as well as the impacts of the system on soil fertility and structure.

In addition to this, *Escala et al. (2012)* conducted another experimental study regarding the feasibility of HTC-process on sewage sludge (residue of wastewater treatment plants), stabilized and non-stabilized, effected in a laboratory-scale batch reactor *(Grenolmatik 25, Grenol GmbH, Germany)* in Zurich University of Applied Sciences (ZHAW[21]). This research was born for understanding if, through the HTC-process, the final product from sewage sludge satisfies the stringent regulations, which aim to protect the environment and human health, to favor and to increase its use in agriculture. This because, even though sewage sludge has an useful agronomic properties (for example supply of phosphorous and nitrogen), it is often contaminated with heavy metals, microorganisms and a variety of dangerous organic substances, which can pose a serious threat for the soil, vegetation, animals and humans. These experiments show the feasibility of the HTC-process for this type of feedstock, even if the values for H/C and O/C in HTC-coal were shown to be higher than in natural coal and rather close to typical values for cellulose and also a lower carbon efficiency[22] (CE), between 60-73%. For this reason, other experiments and studies are needed to optimize the process-parameters, especially temperature and residence time, to understand, at the same time, their influence on the variation of the composition of the HTC-coal and the process water, followed by an efficient process water treatment. All this is necessary to guarantee a minimal environmental impact, lower energy requirements and greater potential energy recovery.

However, even though, to date, the implementation of this technology seems to be restricted to high cost and high-tech solutions suitable only for industrialized countries, the wide field of applications and potential benefits of HTC-coal are attractive for its use also in developing countries; since, through HTC process, food waste and faecal sludge (main problems in low and middle income countries) can be transformed in a valuable energy carrier (substituting traditional firewood and avoiding thus deforestation) allowing to improve, at the same time, the hygienic conditions of people.

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[21] The “ZHAW” is the acronym of Zurich University of Applied Sciences, Institute of Natural Resource Sciences, Campus Grüental, CH-8820 Wädenswil (Switzerland). The exact name in German is: Zürcher Hochschule für Angewandte Wissenschaften, Institut für Umwelt und Natürliche Ressourcen.

[22] The “carbon efficiency” is defined as the relative amount of carbon from the starting product bound in the final product.

4 MATERIALS AND METHODS

The following chapter contains detailed information on equipment and analytical techniques used during all the stage in *Eawag/Sandec*[23], Switzerland, from March to May 2013.

In particular, after a brief indication regarding the Federal Swiss Institute, the HTC prototype, for experimental purposes for developing countries, will be described with the execution procedures of the tests and the relative analytical techniques.

4.1 General information about Eawag – Sandec

Sandec is the Department of Water and Sanitation in Developing Countries at the Swiss Federal Institute of Aquatic Science and Technology (*Eawag*), one of the most important aquatic research institutes to the world, with head office in Dübendorf (ZH).

The next ***Figures 25a*** and ***25b*** show the Eawag's building.

Figure 25a – Figure 25b: *Eawag's building (http://www.eawag.ch/about/nachhaltig/fc/dl/architektur/index)*

The principal aims of this department are to develop and to make easier the implementation of new concepts and technologies in developing countries, concerning,

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[23] Eawag/Sandec: Swiss Federal Institute of Aquatic Science and Technology – Department of Water and Sanitation in Developing Countries (Überlandstrasse 133, P.O. Box 611, 8600 Dübendorf, Switzerland). More specifically, the name "Eawag" was originally a German acronym, standing for "Eidgenössische Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz" (Federal Institute of Water Supply, Wastewater Treatment and Water Pollution Control) and this designation is still used in legal documents.

especially, the water supply and the solid waste management, as well as the improvement of sanitation conditions.

Their work is so divided into the following five complementary research fields:

1) ***Strategic environmental sanitation planning:*** its goal is to improve hygienic conditions through strategies and solutions socially and culturally adequate in low- and middle incomes;
2) ***Municipal solid waste management:*** its objective is to develop appropriate treatment of the organic fraction in order to minimize the risk to human health and avoid environmental degradation;
3) ***Excreta and wastewater management:*** this research field concentrates on optimization of treatment technologies, innovation in resource recovery and method for sustainable systems level implementation;
4) ***Water supply and treatment:*** its purpose is to develop sustainable treatments, improving drinking water quality;
5) ***SODIS (Solar Water Disinfection Process) reference center:*** its goal is to spread this efficient method for the treatment of water in developing countries, which uses the solar light to purify the water from bacterium and virus (pathogens agents are thus destroyed). SODIS is recommended by the World Health Organization (WHO) and it won the *"Energy Globe Award 2004"* and also the *"Prize for the special humanitarian actions 2006"* of the Red Cross Switzerland (RCS).

The following ***Figure 26*** shows these five research fields at Sandec.

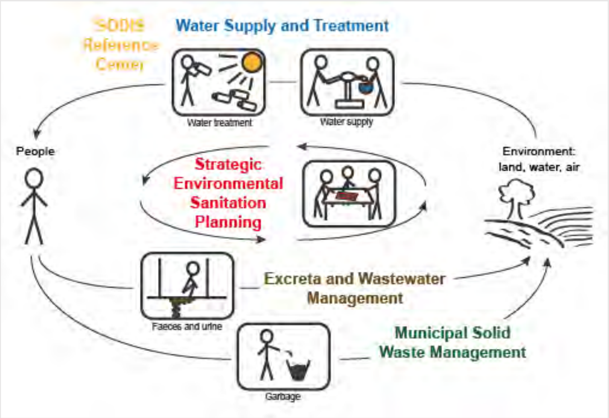

Figure 26: *Schema of the research fields at Sandec (http://www.eawag.ch/forschung/sandec/gruppen/index_EN)*

4.2 Description of the HTC reactor

The HTC prototype reactor, planned for experiments purposes and adapted to conditions in developing countries, has been designed by *Robbiani Zeno*, for his Master Thesis in Mechanical Engineering. Its real construction has been carried out by the apparatus manufacturing company Calorifer AG in Elgg (ZH) and the conformity assessment according to European Directives were carried out by a third party called Swiss TS in Wallisellen (ZH).

The design selection and construction of the HTC reactor has been done following determined criteria, in such a way that this technology is, as much as possible, suits for the developing countries for biowaste/faecal sludge treatment. Therefore, the main criteria followed for its applications in these poor areas are: low cost, low level of technology (i.e. easily reproducible and constructed), use of materials available in low- and middle-income countries, ease of handling (i.e. no complex infrastructure or expert knowledge) and high durability (i.e. no frequent troubleshooting) and security (i.e. safe operation).

The constructed **HTC reactor** is built in stainless steel, since it is in contact with water and should be resistant to acidic conditions of process water. It is a simple cylindrical pipe (with an inner diameter of 200 mm (DN200), long 600 mm and with volume of 21.8 L) close to one end with a vessel dished end (curved shape), which operates in a batch-feeding mode, without stirrer, and heated with the help of an external electric heating mantle (maximum power of 2500 W and maximum temperature of 300°C) that surrounds the vessel.

The top is equipped with a flange and closed with a lid that can be screwed (with 12 screws before by hand and then with the use of two simple wrenches and finally with a torque wrench) to the flange, allowing the inside of the reactor to be accessed without difficulty. A graphite-sealing ring, between flange and lid, allows the reactor to be hermetically sealed. Moreover, the reactor is fixed with two lateral rods on a frame with bearings from which it can rotate; this rotating system allows the high-pressure vessel to be easily opened, filled and tightly closed. In this way, after every reaction, the contents, HTC-coal and process water, are easily emptied and separated, facilitating thus also the final cleaning of the reactor. In particular, a removable transversal bar, fixed to the inferior rod at the bottom of the reactor, allows that the rotation can be blocked when needed, especially during the phase of emptying and cleaning of the reactor at the end of each reaction.

Above the lid, the sensors are positioned for the survey of the inner temperature and inner pressure during the HTC-conversion. There are also an overpressure valve and a drain valve. The first one, overpressure valve, allows releasing the pressure outside, when it exceeds the maximum allowable pressure of 30 bar, through a stainless steel pipe and the second one, drain valve, allows releasing the residual pressure and gases, at the end of each reaction and after letting the reactor cooling down, through a simple plastic pipe (this particular plastic pipe is connected to the drain valve only the next day after the HTC-reaction, when the reactor is cold, with inner temperature below 40°C). Moreover, the external temperature of the heating mantle is controlled with a regulator connected to the heating mantle and an energy meter is connected to the heating mantle to measure the energy consumed during the reaction. The physical parameters (inner temperature, inner pressure and energy consumption) are continually recorded on a computer during the whole reaction.

Furthermore, an additional hole, in the lid, is also provided, allowing thus the possibility to change the disposition of the measuring instruments (for example inner temperature measured at the side rather than in the middle) or to add a new device (pH-meter, second overpressure valve, stirrer) *(Robbiani, 2013).*

The next ***Figure 27*** show the schema of the HTC prototype reactor.

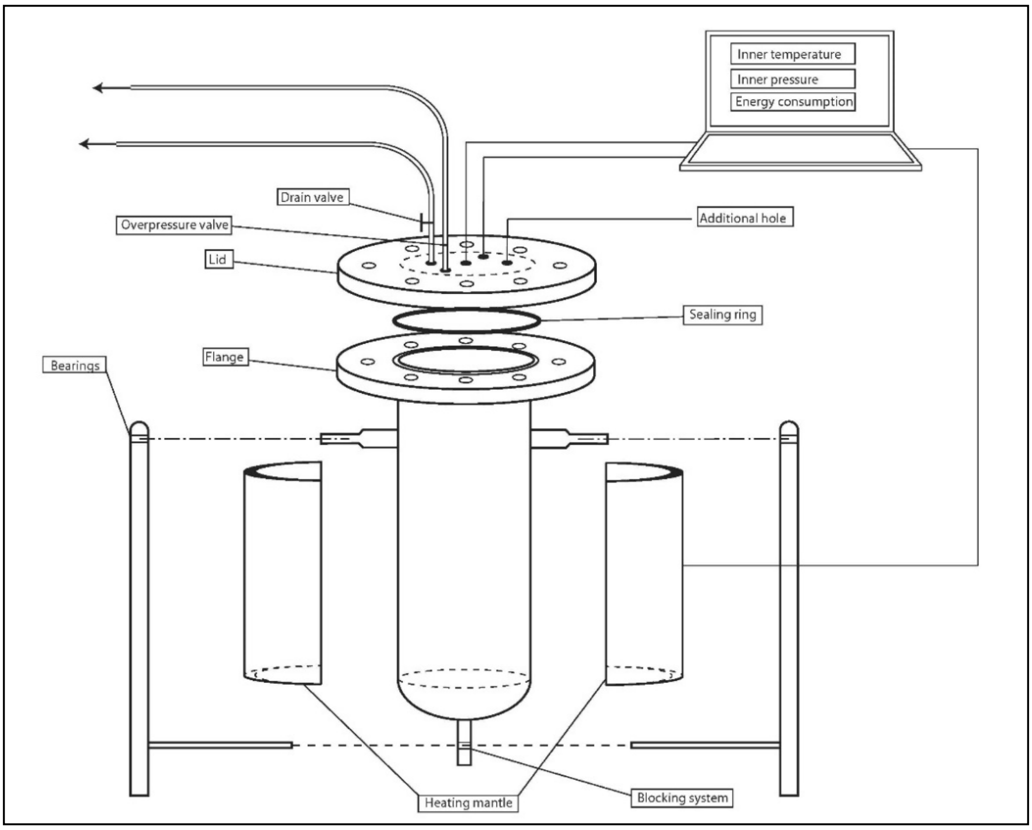

Figure 27: *Schema of the HTC prototype reactor (Robbiani, 2013)*

Once the reactor built, a hydraulic pressure test was carried out to test its correct functionality and to receive, only after passed it, the certification of the system. The reactor was thus marked with a CE-label with its relative characteristics (range of pressure, range of temperature, etc.). In this way, the reactor, with this certification, is safe and conforms to the requirements (regarding design, materials and welding work) of the EC directives *(Robbiani, 2013)*.

The next ***Table 22*** summarizes some characteristics, certification and relative costs of the reactor.

Component	**Specifications**	**Cost [24] [CHF] and [€]**
Reactor	Material: stainless steel (DN200)	**5700 CHF/ (~ 4660 €)**
	Total weight: 68 kg (regarding all the different parts)	
	Volume: 21.8 L	
	Temperature range: 180 - 220°C	
	Max. allowable temperature: 300°C	
	Pressure range: 10 - 25 bar	
	Max. allowable pressure: 30 bar	
	Max. number of load cycles: 1000	
Certification	Applied regulation: PED 97/23 EC - AD2000	**6000 CHF/ (~ 4906 €)**
	Fluid group: 1 (inflammable)	
	Category: III	
Total		**11'700 CHF/ (~9566 €)**

Table 22: *Costs and specifications of HTC reactor (Adapted from Robbiani, 2013)*

It is possible, therefore, to notice that the cost of certification is higher than the cost of the same reactor, without the additional equipment (overpressure valve, drain valve and heating mantle) and measuring instruments (temperature sensor, pressure sensor and energy meter).

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[24] The conversion Swiss Franc (CHF) to Euro (€) is: 1 CHF = 0.8176 € (using currency rates of 06/12/2013).

The description of these additional equipment and measuring instruments are following reported.

As regards the additional equipment:

- **Overpressure valve:** is the security valve, which releases the pressure only when the maximal allowable pressure (30 bar), recorded inside the reactor, is reached. It is so connected to a stainless steel pipe for the possible exhaustion of the steam released. In particular, for the first six experiments (2 tests with rice and the first 4 tests with biowaste) we used a valve able to bear pressures up to **25 bar**. Then, for the other tests *(see the next chapter)*, this overpressure valve was replaced with one from **30 bar**. In addition, this valve is used, during each experiments, as a safety device and not as a pressure regulation device, this means that it needs to regulate the temperature of the heating mantle, through the external temperature sensor, to check and to maintain the pressure below the maximal allowable pressure (30 bar);
- **Drain valve:** is a valve that release the residual pressure, inside the reactor, once the reaction is over, i.e. only when the reactor is cooled down (below 40°C). In this way, the draining pipe is not exposed to high temperature steam and can be directed to the outside with a simple plastic pipe. At the end of the reaction, usually the day after, this valve is slowly opened to release the residual pressure until the pressure, inside the reactor, is below 1 bar. In no way, this type of valve should be opened during the reaction;
- **Heating mantle:** is an isolated electric mantle (to avoid the dissipation of energy in the surrounding environment) with internal temperature sensor and regulator that surrounds the reactor. Heat is produced through Joule effect when an electric current passes through the resistors; while a simple thermostat fixes the temperature (Robbiani, 2013).

The next ***Table 23*** resumes the additional equipment with their relative characteristics and cost.

	Designation	Characteristics	Cost [CHF] and [€]
Additional equipment	*Overpressure valve* *SV510* *Spyrax Sarco AG* 	Connection: G1/2'' Max T: 280°C Max P: 30 bar	**600 CHF/** **(~ 491 €)**
	Drain valve *AV243* *Spyrax Sarco AG* 	Connection G1/2'' Max T: 400°C Max P: 300 bar	**220 CHF/** **(~ 180 €)**
	Heating mantle *HFT and* *Temperature regulator* *HT42—30P* *Hillesheim Gmbh* 	Diameter: 219 mm Length: 500 mm Max T: 300°C Max Power: 2500 W	**1570 CHF/** **(~1284 €)**

Table 23: *List of additional equipment (adapted from Robbiani, 2013)*

Since the maximum allowable temperature of the overpressure valve is 280°C, the maximum allowable temperature of the reactor has also been set to 280°C (instead of 300°C).

While as regards the measuring instruments:

- **Temperature sensor:** is an inner temperature sensor connected to a display from which the data can be transferred to a computer via USB cable. The temperature sensor is positioned in the middle of the lid (values recorded each 20 seconds);
- **Digital manometer:** is an inner pressure sensor from which the data can be transferred to a computer via USB cable (values recorded each 20 seconds);

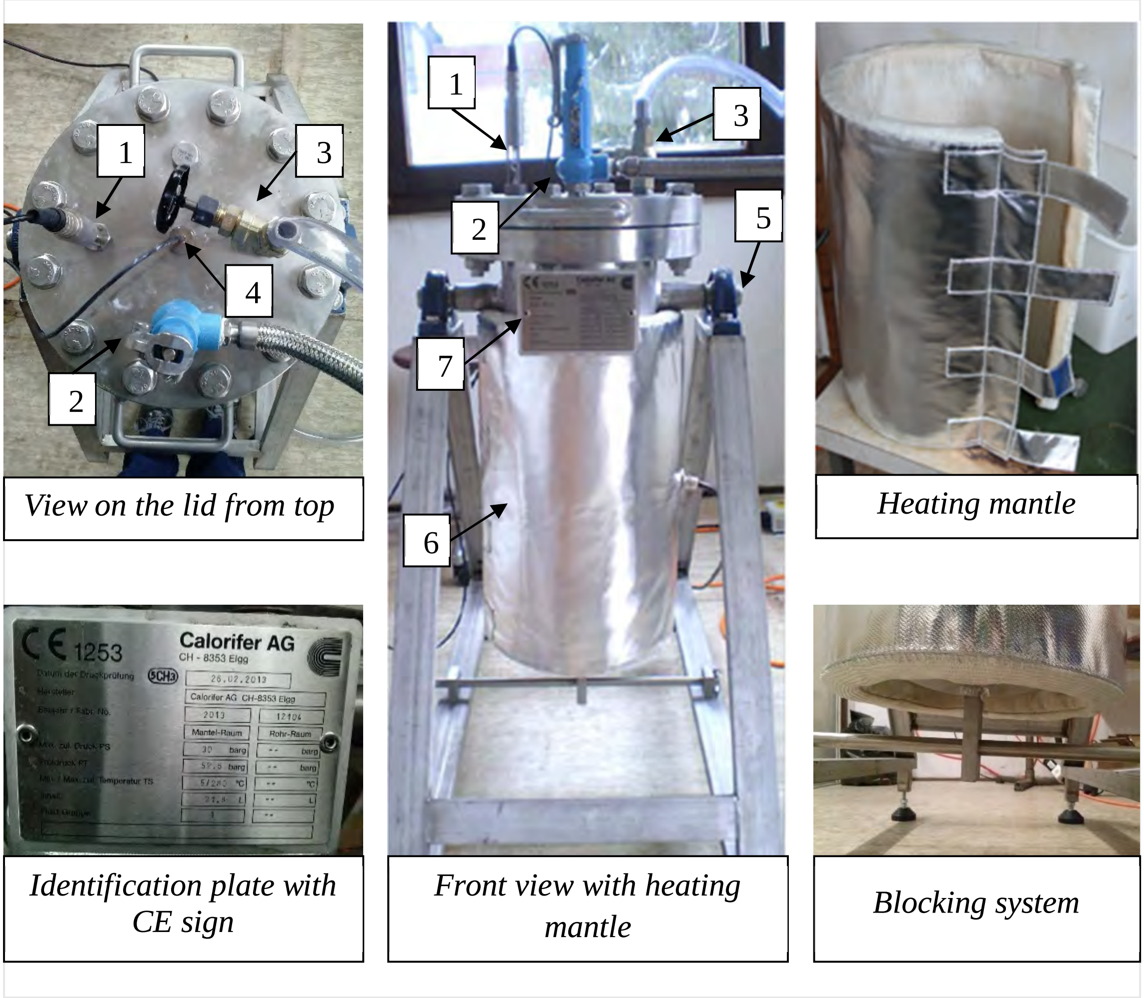
- **Energy meter:** is the energy consumption logger and the data transmission happens through USB radio stick (values recorded each 3 seconds).

The next ***Table 24*** resumes the measuring instruments with their relative characteristics and cost.

	Designation	Characteristics	Cost [CHF] and [€]
Measuring Instruments	*Temperature sensor W120.3L and Display ACS 13A Roth + CO. AG* 	Connection: G1/2'' Sensor type: PT 100 Sensor length: 250 mm	**920 CHF/ (~ 753 €)**
	Digital manometer Leo Record Keller AG 	Connection: G1/2'' Pressure range: 0-31 bar T range: 20-300°C	**1680 CHF/ (~ 1374 €)**
	Energy meter VSM-120 	Current range: 0-80 A	**340 CHF/ (~ 278 €)**

Table 24: *List of measuring instrument (Adapted from Robbiani, 2013)*

The following pictures, assembled in ***Figure 28***, show the HTC reactor with the different measurement sensors and valve, as well as the heating mantle. Moreover, the frame with rotating system and bearings, including the blocking system are also reported.



View on the lid from top

Heating mantle

Identification plate with CE sign

Front view with heating mantle

Blocking system

Figure 28: *Pictures of the HTC reactor – 1*
(1: Pressure sensor, 2: Overpressure valve, 3: Drain valve, 4: Temperature sensor, 5: Bearing, 6: Heating mantle, 7: Identification plate with CE label)

The HTC-reactor has been positioned inside a small container, endowed with two windows to have a greater airing during the phase of opening. The day after the reaction, and obviously closed through a door to avoid so the entry of non-authorized people.

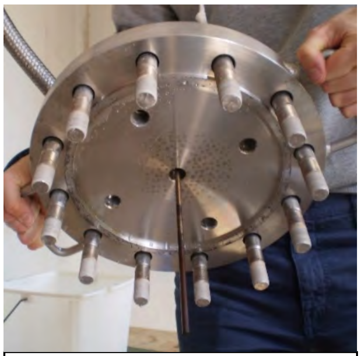
The final location of the HTC prototype, especially in the developing countries, must be takes in serious consideration because of the high temperature and pressure reached during the reaction, avoiding thus crowded places where people and particularly children spend the most part of the time. For this reason, it is opportune to put the batch reactor in a closed place but well aired, where only the authorized person can easily complete all the phases (filling, closing, opening and emptying). The reactor is designed with a limited size and weight, such that one single person can operate it.

The following pictures, assembled in ***Figure 29***, show other details of the HTC prototype reactor used in this experimental work.

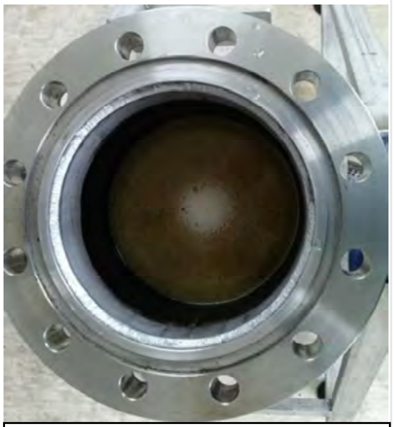
General view with stainless steel pipe for exhaustion of steam from overpressure valve

Panoramic view of reactor with heating mantle and the different sensors above the lid

Lateral view without lid



Inferior part of the lid with temperature sensor and screws



Reactor before HTC

Figure 29: *Pictures of the HTC reactor* **-** *2*

4.2.1 Total cost

As the following ***Table 25*** shows, the total cost of the HTC prototype, including the additional equipment and the measuring devices, is 17˙000 CHF (around 14˙000 €).

Item	Cost [CHF] and [€]
Reactor	5˙700 CHF/ (~ 4˙660 €)
Certification	6˙000 CHF/ (~ 4˙906 €)
Additional equipment	2˙400 CHF/ (~ 1˙955 €)
Measuring instruments	2˙900 CHF/ (~ 2˙405 €)
TOTAL	**17˙000 CHF/ (~14˙000 €)**

Table 25: *Total cost of prototype HTC reactor (Adapted from Robbiani, 2013)*

As already says, the cost of the certification exceeded the cost of the actual reactor and it represents 35% of the final cost. However, it guarantees that the reactor is safe and obeys to strict regulations, *European Pressure Equipment Directives*, for all the pressure-vessels.

The total cost of this HTC prototype, if compared with other existing HTC technologies, in particular with that of the ZHAW reactor (Grenolmatik 25 by Grenol GmbH, Germany), which is similar in size, is results surely be inferior, nearly six times lower than its cost (around 100˙000 CHF). This elevated cost, for the ZHAW reactor, is main due to its stirring unit and its fully automated thermal oil heating mantle system; factors that do not affect, at this scale, the carbonization process *(Sandec News, 2013)*.

Moreover, according to *Robbiani (2013)*, three types of stirrer are possible to use: magnetic agitator (20˙000.- euro), magnetic coupled stirrer (40˙000.-) and stirrer with a (rotating) mechanical shaft-seal (no information could be obtained about the exact price but at least 10’000.- is estimated for such a device). Therefore, since such these systems involve high costs and significantly increased overall technological complexity of the reactor, it was decided, for this reason, to build the HTC prototype without a stirrer.

Therefore, the developed HTC prototype, in comparison to other HTC experimental reactors of a similar volume, is a simple system with a low cost (further reduction cost is not possible) and complexity. However, the final cost of this prototype remains high and surely represents a great obstacle to use and spread this technology in developing countries.

4.3 Experimental set-up and monitoring of parameters

During each tests, the inner pressure [bar] and the inner temperature [°C], as well as the energy consumption [KWh] of the heating mantle, are recorded for the whole process, using two computers, through the connection of the USB ports.

In particular, the external temperature (T_ext) is imposed and controlled with the regulation device connected to the heating mantle and an energy meter is connected to the heating mantle to measure the energy consumed during the reaction. Moreover, the inner temperature (T) is measured at the center of the reactor for all the experiments carried out in this work.

The next ***Figure 30*** shows the complete experimental set-up:

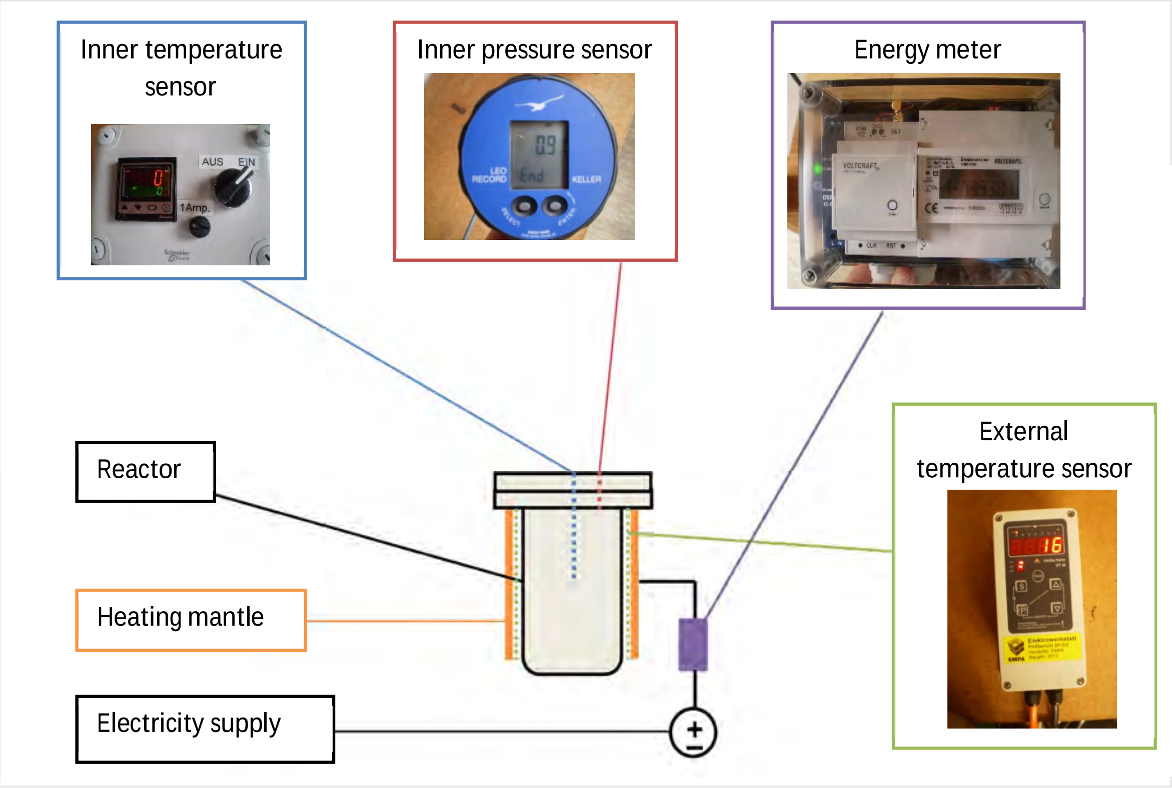


Figure 30: *Experimental set-up (Robbiani, 2013)*

The monitoring of the physical parameters (inner temperature, inner pressure and energy consumption of the heating mantle with the external temperature imposed) are recorded in continuous during the whole reaction.

The following ***Table 26*** summarizes these parameters monitored with their relative characteristics.

PARAMETER	EXPERIMENTAL SET-UP	FREQUENCY OF MONITORING	POSITION	MAXIMUM VALUE
Inner Temperature [°C]	inner temperature sensor	in continuous (values recorded each 20 seconds)	above the lid (at the center of the reactor)	280°C
Inner Pressure [bar]	inner pressure sensor	in continuous (values recorded each 20 seconds)	above the lid (next to the inner temperature)	30 bar
Energy Consumption [kWh] and Average Power Consumption [W]	energy meter	in continuous (values recorded each 3 seconds)	connected to the heating mantle	2500 W (maximum power for the heating mantle)

Table 26: *List of parameters monitored during HTC-reaction*

In particular, during the execution of each HTC-reaction, it is necessary to control these parameters every hour in order to adjust, in the event that pressure or inner temperature increase very fast, the external temperature of the heating mantle (maximum temperature of 300°C) with the external temperature sensor. Another important thing to keep in mind during the HTC-reaction is that the overpressure valve is used only as a safety device and not as a pressure regulation device; therefore, it should be avoided to reach the maximal pressure of it (30 bar).

4.4 Execution procedures of all the tests

During this experimental research, different tests were carried out with raw rice (called *"preliminary tests"* in chapter 5) and then with food waste (called *"tests with biowaste"* in chapter 5) from the canteen "Aqa" of Eawag.

In particular:

a) Preliminary tests: consist of 3 experiments, the first one was carried out without substrate, so using only water (namely tap water), while the second and third ones were tested, expending raw rice, at different solid loads (TS=2.6% and TS=5.2%, respectively). The objective of these experiments was to test only the correct functionality of the reactor in accordance with technical requirements;

b) Tests with biowaste: consist, in total, of 10 tests, with the purpose to analyze and compare the end-products obtained and to assess what are the optimal operational parameters, in terms of carbonization temperature and residence time, but especially the maximum amount of waste per batch, for this HTC-reactor, to be treated to have thus a final positive energy balance. These 10 tests were subdivided in two different series, as it follows:

- 6 tests increasing the TS in each batch (TS [%]=2.5; TS [%]=4.9; TS [%]=7.4; TS [%]=9.4; TS [%]=12.8 and TS [%]=15.2);
- 4 tests with the same TS = 4.9% but varying the inner temperature, reached inside the reactor (200°C; 190°C; 180°C and 170°C).

This experimental part is preceded by a phase of collection and preparation of the biomass choice, in such a way to have an only champion on which to effect the elementary analysis (in terms percentages of C, H, O and N) and the measure of the higher heating value (HHV).

The use of the HTC prototype reactor, as the execution procedures, regardless of the type of the biomass, is always the same in all the tests.

In particular, the main steps for using the reactor (standard procedure) can be divided into these following eight points (see the *“Manual for using HTC-reactor”* with its relative photo-documentation in the appendix):

1) Collection and preparation of biomass;

2) Preparation of reactor before starting the reaction;

3) Closing the lid of reactor, following a precise procedure;

4) Switching-on all the programs and starting the reaction;

5) Control of the parameters (mainly T and P) every hour;

6) Switching-off the reactor and saving the results of all the parameters;

7) Opening the reactor the day after, following a precise procedure;

8) Cleaning the reactor at the end, after separation of coal from process water.

So, the experimental procedure of the tests consists, briefly, in: <u>preparation of reactor before starting the reaction</u> (i.e. addition of the necessary amount of the biowaste and water inside the reactor, followed by its closing), <u>real execution of the HTC-reaction</u> (i.e. switching-on all the programs, control of the parameters and switching-off the reactor) and finally <u>opening the reactor the day after</u> (i.e. emptying procedures and cleaning the reactor).

4.4.1 Collection and preparation of biowaste

Before proceeding with the collection of the organic waste from the canteen, we previously esteemed the necessary total amount to perform two different series of experiments. The first one, as already mentioned, constituted by 6 tests, with an increase, in each test, of the Total Solids (TS[%]=2.5; TS[%]=4.9; TS[%]=7.4; TS[%]=9.4; TS[%]=12.8 and TS[%]=15.2), i.e. increasing the amount of the biowaste (keeping constant the volume, biowaste + water, of 17L). The second one, constituted by 4 tests, keeping constant the TS (TS[%]=4.9) but varying the inner temperature (200°C; 190°C; 180°C; 170°C) for 4 hours.

Therefore, to perform these 10 tests, we estimated in total, for safety, around **60 kg** of biowaste.

Only at this point, we proceeded with the collection, in large bins, of the food waste produced by the canteen and then we continued with its preparation (pre-treatment), which consisted in the blending of all the amount of biomass collected, through a professional blender, to obtain, in this way, a homogenous mixture.

The next ***Figure 31*** shows the professional blender used in this pre-treatment of food waste (any information regarding the model and the power).

Figure 31: *Blender used in pre-treatment of food waste*

More especially, the typology of waste present in the biowaste collected was very various and mainly contained: white rice, pasta, soup, meat (raw and cooked), bread, different vegetables (beans, salad, carrots, etc.) and peels of assorted typologies of fruit (orange, pineapple, avocado, banana, etc.).

In this phase, we did not evaluate the exact amount, in kilograms, of each typology of food waste (waste composition) present in the bins but we considered only the total amount of biowaste.

Some pictures, before the blending, of food waste collected from the canteen are reported in the next ***Figure 32a – 32b*** and ***32c***.

Figure 32a – 32b -32c: *Examples of biowaste collected before the blending*

The blending phase (without the addition of water) has been performed on the whole amount of biowaste collected, through a professional cooking blender, subdividing the organic fraction in a small portion (about 2-3 kg), into buckets, in order to obtain a homogenous mixture, like a thick soup.

The next pictures in ***Figure 33a*** **–** ***33b*** and ***33c*** show the food waste collected before, during and after the blending phase.

Figure 33a – 33b – 33c: *Biowaste before, during and after the blending*

After having blended the whole amount of biowaste collected, we put the mixture into a big bin and mixed everything again with a simple stick, to have, in this way, a mixture the more possible homogenous.

At this point, a small champion (44.3 g) of this blend (called *Original Biowaste* in the next chapter 5) is taken and put inside a beaker to determine the Total Solids (TS), through a drying oven at 105°C for 24 hours. On the dry champion of biowaste, also the elementary analysis (C, H, O and N), with methodical UNI EN 15104:2011, is performed, to allow thus a comparison with the final HTC-coal, obtained in the different tests.

The purpose is to note the increase of carbon content in the hydrochar compared to the original feedstock, namely the initial biowaste.

Then, all the mixture of food waste is put into small buckets and placed in the freezer, in a such way that elementary composition did not change during the whole ten experiments.

The next pictures in ***Figure 34a*** **–** ***34b*** and ***34c*** show these three phases: final mixing of food waste, champion of biowaste and final location of the mixture obtained after blending.

Figure 34a – 34b – 34c: *Final mixing after blending, champion of biowaste for TS and placing it in the freezer*

The measure of TS of the original biowaste is resulted equal to **22.60%** (moisture content of 77.40%) while the elementary analysis of food waste is reported in the next ***Table 27***.

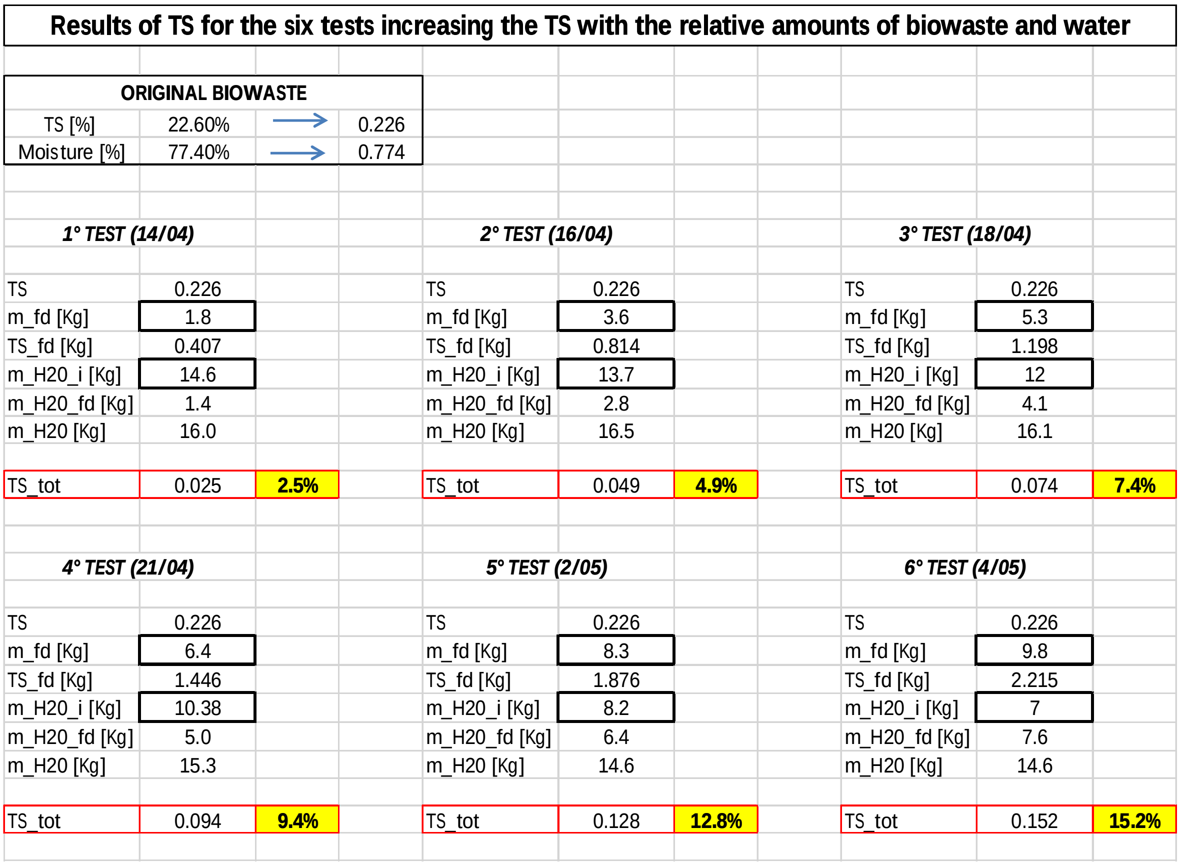
Organic Substrate	***TS [%]***	***HHV [MJ/kg$_{db}$]***	***C [%$_{db}$]***	***H [%$_{db}$]***	***O [%$_{db}$]***	***N [%$_{db}$]***
Original biowaste	22.60	19.3	46.2	6.5	43.7	2.2
HHV = Higher Heating Value; db = dry basis.						

Table 27: *Characteristics of biowaste before the HTC-reaction*

After that, the Total Solids are calculated for each test, namely the relative amounts of biowaste (m_fd [kg] = mass of food waste) and tap water (m_H2O_i [kg] = mass of water initial) are estimated, in order to fill the HTC-reactor with a gradual increase of the final TS.

These calculations have been effected considering that the maximum volume to be filled is of **17 L**, namely three quarter of the reactor's volume. This because, it's necessary to leave a free space (13-18 cm), from the water level (mixture) to the reactor's edge, since the water density decreases significantly, during the HTC process, at high temperatures resulting in a higher volume which can exceed the reactor's volume (21.8 L).

The next ***Figure 35*** shows these calculations for each tests.



Results of TS for the six tests increasing the TS with the relative amounts of biowaste and water

ORIGINAL BIOWASTE			
TS [%]	22.60%	→	0.226
Moisture [%]	77.40%	→	0.774

1° TEST (14/04)			***2° TEST (16/04)***			***3° TEST (18/04)***		
TS	0.226		TS	0.226		TS	0.226	
m_fd [Kg]	1.8		m_fd [Kg]	3.6		m_fd [Kg]	5.3	
TS_fd [Kg]	0.407		TS_fd [Kg]	0.814		TS_fd [Kg]	1.198	
m_H20_i [Kg]	14.6		m_H20_i [Kg]	13.7		m_H20_i [Kg]	12	
m_H20_fd [Kg]	1.4		m_H20_fd [Kg]	2.8		m_H20_fd [Kg]	4.1	
m_H20 [Kg]	16.0		m_H20 [Kg]	16.5		m_H20 [Kg]	16.1	
TS_tot	0.025	**2.5%**	TS_tot	0.049	**4.9%**	TS_tot	0.074	**7.4%**

4° TEST (21/04)			***5° TEST (2/05)***			***6° TEST (4/05)***		
TS	0.226		TS	0.226		TS	0.226	
m_fd [Kg]	6.4		m_fd [Kg]	8.3		m_fd [Kg]	9.8	
TS_fd [Kg]	1.446		TS_fd [Kg]	1.876		TS_fd [Kg]	2.215	
m_H20_i [Kg]	10.38		m_H20_i [Kg]	8.2		m_H20_i [Kg]	7	
m_H20_fd [Kg]	5.0		m_H20_fd [Kg]	6.4		m_H20_fd [Kg]	7.6	
m_H20 [Kg]	15.3		m_H20 [Kg]	14.6		m_H20 [Kg]	14.6	
TS_tot	0.094	**9.4%**	TS_tot	0.128	**12.8%**	TS_tot	0.152	**15.2%**

Figure 35: *Calculations for each test of the Total Solids*

The relative percentages of the TS for each experiments are in yellow and in bold, obtained varying the amounts of biowaste and water; more precisely increasing the organic fraction and decreasing the liquid phase (water), keeping constant the volume of 17 L.

4.4.2 Preparation procedure of the reactor: filling and closing

Once the relative amounts of biowaste and water are known, to pour in the reactor for each test, it is possible to proceed with the real experimental part.

Therefore, after having defrosted the mixture of biowaste **(1)**, one or two days before doing the experiment, the exact amount of biomass with a simple digital balance is weighed **(2)** and the water, needed for the reaction, is collected with a little tank **(3)**. Only at this point, it is possible to add into the reactor four/five liters of water collected **(4)**, with a graduated cylinder (measuring cup 1L), followed by the addition of the biowaste weighted using a ladle **(5)**. Finally, after having poured the whole mixture of biowaste, the remaining necessary water **(6)**, for the hydrothermal carbonization, is spilled into the reactor (filling volume about 17 liters) and all the mixture (biowaste and water) is mixed using a steel rod **(7)**, before closing the HTC-prototype.

The following pictures, assembled in ***Figure 36***, show this described preparation procedure.

Figure 36: *Filling procedure of the reactor*

After having completed the filling phase, it is possible to continue with the closing of the reactor's lid, on which the different sensors are positioned, as already described previously.

Firstly, the lid is carefully raised and placed on the reactor **(1)**, after checked the state of the graphite-sealing disc. Then all the 12 screws are tighten before by hand **(2)** and subsequently with the use of two simple wrenches **(3)** and finally with a torque wrench **(4)**, using different strength, 42 Nm and 84 Nm, **(4a)**.

Finally, the heating mantle is positioned and tighten as much as possible around the cylindrical pipe of the reactor **(5)**.

The following pictures, assembled in ***Figure 37***, show this described closing procedure.

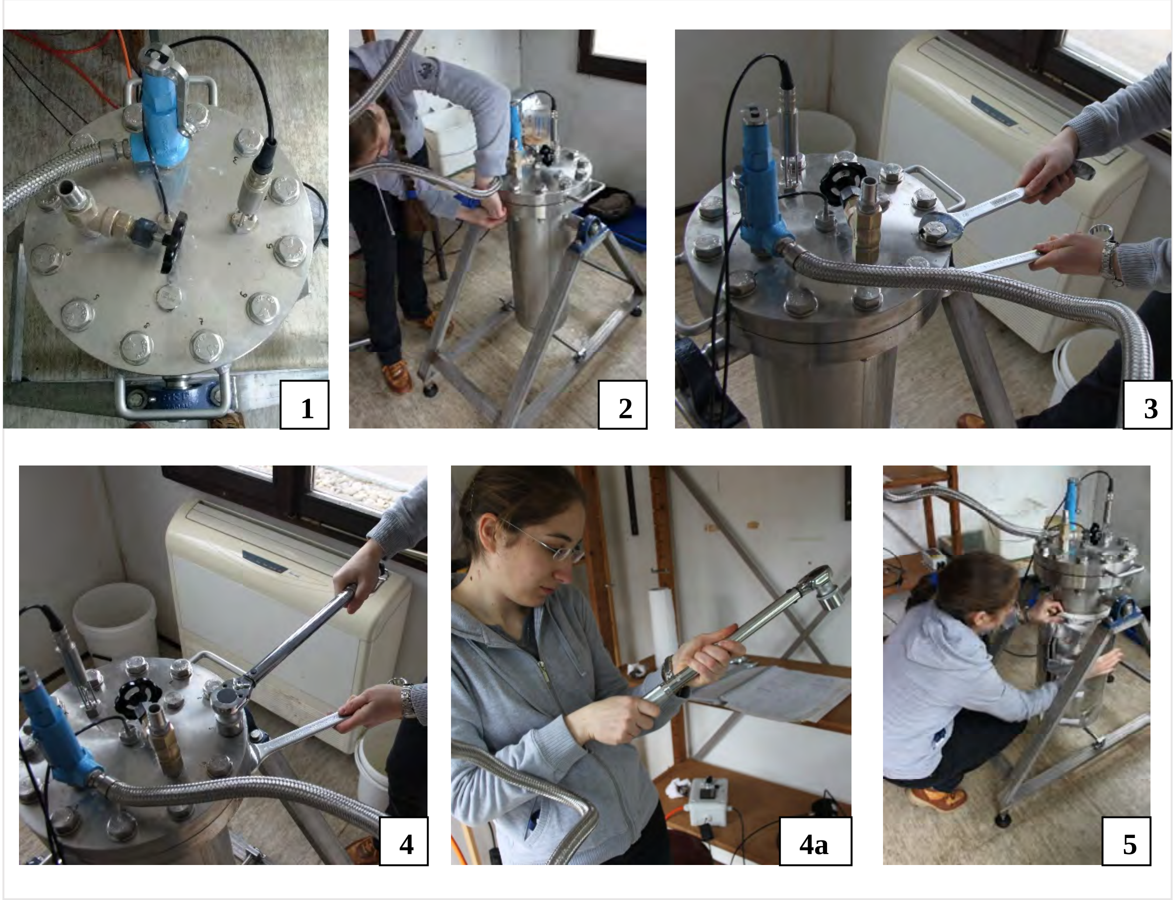


Figure 37: *Closing procedure of the reactor*

4.4.3 Execution HTC-reaction

After the closing phase, it is so possible to start the HTC-reaction, switching-on the two computers and the relative programs, which they permit to record in continuous the following parameters: temperature *(program SWS-ACS 13A)*, pressure *(program CCS-30)* and energy consumption *(program VSM-101 Voltcraft)*.

Therefore, it is necessary to connect the USB-cables **(1)** and the USB radio stick to the computers and then turn on the relative digital instruments **(2)**, visualizing in this way the initial values of temperature [°C], pressure [bar] and energy consumption [KWh] and at this point the programs **(3)**.

After this, it is possible to impose the external temperature (T_ext) with the regulation device of the heating mantle, giving so the real beginning of the HTC-reaction. From this moment, the heat is applied approximately for 10 hours (from the turning-on to the turning-off of the heating mantle through its temperature regulator), considering that the mixture generally employs about 6 hours to reach the inner temperature of 180°C, temperature from which, according to the literature, the hydrothermal carbonization starts.

During this period, it is indispensable to effect frequent controls, every hour, to monitor constantly the parameters, mainly temperature and pressure. In particular, in the event that pressure or temperature increase very fast, the temperature of the heating mantle have to be adjust, with its relative regulator, since the overpressure valve is used only a safety device and not as a pressure regulation device.

The next pictures, ***Figure 38a*** **–** ***38b*** and ***38c***, show the switching-on of the digital devices and relative programs

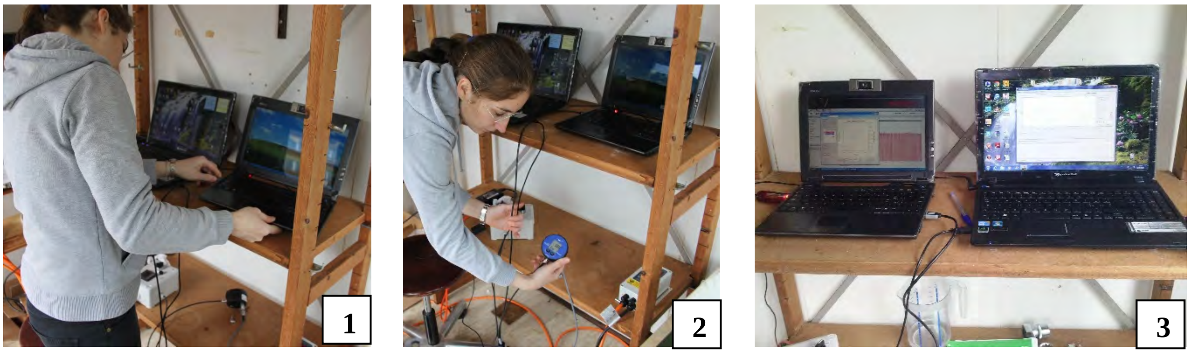


Figure 38a – 38b – 38c: *Switching-on of the digital devices and relative programs*

After this total reaction time (time during which heat is supplied to the reactor), the reaction is switched-off through the external temperature sensor and then, before switching-off the two computers, the recorded parameters of temperature, pressure and energy consumption are saved in a folder. Finally, the heating mantle is carefully removed, in such way that the reactor is let to cool down more quickly during the night.

4.4.4 Opening reactor and emptying procedure

The next day after the reaction, it is possible to proceed with the opening of the reactor, followed by its emptying procedure.

Firstly, the inner temperature sensor and the inner pressure sensor are switched-on **(1)**. Then, the residual pressure is released through the drain valve with the respective transparent tube, until the pressure reaches pressures below 1 bar **(2)**. This valve is used only to drain the remaining pressure when the reactor is cold, below 40°C, and in no way it should be opened during the reaction (the gas phase is not analyzed in this research).

After this, it is possible to continue with the opening of the reactor. The screw are so opened with the torque wrench at 42 Nm **(3)**, following always the cross pattern and then the screw's rings are removed manually **(4)**. Before to lift up the lid, paying attention to the length of temperature sensor, it is indispensable to wear the protection mask, glasses and gloves since compounds, like phenols, which vaporise are harmful to the eyes, the skin and the respiratory tract, have been measured and found in the process water.

The next pictures, ***Figure 39a*** **-** ***39b*** **-** ***39c*** and ***39d*** show some steps of the opening reactor

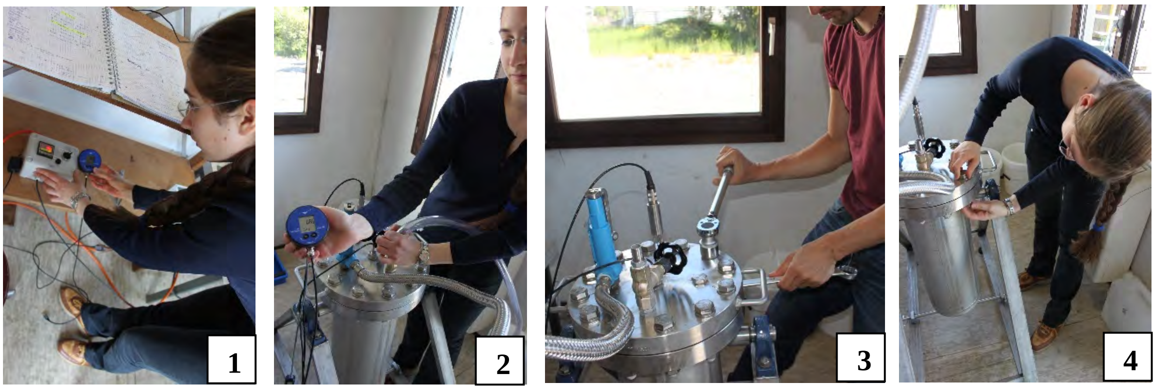


Figure 39a - 39b - 39c - 39d: *Opening procedure reactor*

After that the lid is lifted up **(5)**, cleaned the temperature sensor with a paper towel and subsequently placed the lid on top of a bucket **(6)**, the emptying procedure can begin **(7-8)**, using a thick and tightly woven cotton cloth, placed above a punctured container (like a colander) and another bucket, which permits to separate **(9)** the end-products: the solid phase **(10)**, i.e. HTC-coal, and the liquid phase **(11)**, i.e. process water.

The following pictures, assembled in ***Figure 40***, show this described emptying procedure.

Figure 40: *Emptying procedure reactor*

After completed this emptying phase, the HTC-coal is pressed with the cloth and put it into another clean bucket to later on know the exact amount [kg] of hydro-char obtained, through a simple digital balance **(12)**. Then a sample of this coal **(13)** is took for the measure of Total Solids (TS) and is put, with the rest HTC-coal, in the oven at 105°C for 24 hours **(14)**. The dry coal **(15a)** and the dry sample of coal **(15b)** is subsequently used for the measure of the calorific value (HHV) and the elementary analysis (C, H, O, and N).

It also necessary to take two samples of the process water **(16)** to make afterward the analysis of pH, electrical conductivity (EC) and Total Organic Carbon (TOC). The total liquid and solids input and output are as well weighed before and after the reaction.

The remaining process water is brought in another laboratory where it is adequately treated (post-processing) before being disposed in the environment (this section regarding the treatment of the process water is not dealt in this research).

The following pictures, assembled in ***Figure 41***, show the final operation regarding the HTC-coal and process water.

Figure 41: *Samples of HTC-coal and process water after reaction*

4.4.5 Cleaning procedure of the reactor

At the end, after the separation of HTC-coal from the process water, it is necessary to clean well the reactor with water and sponge to remove the eventual coal inside of it.

It is also important to wash the woven cotton cloth with just water and then leave to dry it to the air before the next experiment.

4.5 Analytical techniques

After each experiments, one sample is taken from solids and liquids to allow determination of the respective measurements. In particular, elementary analysis (C, H, O and N), Total Solids (TS) and higher heating value (HHV) are performed for HTC-coal while pH, electro-conductivity (EC) and Total Organic Carbon (TOC) are carried out for process water.

More specifically, the measurements regarding the elemental analysis and the higher heating value, of all the solid products obtained in this research, are carried out at Zurich University of Applied Sciences, Institute of Natural Resource Sciences (ZHAW).

Following, a briefly description of the analysis concerning the process water are reported.

- ✓ **pH:** is the measure of the acidity (values less than 7) of the process water and it is mathematically defined as the negative logarithm of the hydrogen ion concentration. It is measured with a portable multi-parameter digital meter (HQ40d, HACH LANGE), based on Standard Method (4500-H+B, ASTM Method D1293-B4 and USEPA Method 150.1). For each sample of liquid phase, three measurements of pH are carried out in order to do the average to consider in the final characteristics of the end-products (this analysis of pH is done by myself). Once a week, the calibration of pH meter and electrode is also done, using standard solutions (pH 4, 7 and 10).
- ✓ **Electro-conductivity (EC):** is the measure of the ability of process water (dissolved material) to conduct an electric current, its units are [µS/cm].It is measured with a portable multi-parameter digital meter (HQ40d, HACH LANGE), based on Standard Method 2510-B. For each sample of liquid phase, three measurements of EC are carried out in order to do the average to consider in the final characteristics of the end-products (this analysis of EC is done by myself).
- ✓ **Total organic carbon (TOC):** is the amount of carbon bound in an organic compound present in the process water. It is measured in laboratory at Eawag, following the Standard Method 415.1. However, the method used to measure

TOC at Eawag through *Shimadzu TOC-L, 720°C catalytic combustion* is incorrect to do the final carbon mass balance, because of too high amount of suspended particles in the process water. The correct analysis method is that used at ZHAW, through *Photometer Lange DR3800, Test LCK 386*; in this case, the process water is centrifuged for 10 minutes at 4000-4400 rpm. Without this photometric analysis method the carbon mass balance could not be done, so, in the next research, it is important to keep in mind this particular technique in order to calculate the TOC of process water and accordingly the carbon mass balance.

Following, a briefly description of the analysis concerning the HTC-coal are reported.

- ✓ **Total solids (TS):** is the matter that remains as residue upon evaporation and drying, in an oven, at 105°C for 24 hours. This measure followed the Standard Methods 2540D (this analysis of TS is done by myself). The following formula allows determination of TS:

$$\boxed{TS\ [\%\ by\ weight] = \frac{A-C}{B-C} * 100}$$

Where:

A = weight of dried residue plus dish [mg]
B = weight of wet residue plus dish [mg]
C = weight of dish [mg]

- ✓ **Higher heating value (HHV):** represent the amount of heat produced during complete combustion and it serves to determine how efficient and effective the HTC-coal is. HHV takes into account the latent heat of vaporization of water in the combustion products. It is measured at ZHAW (some values of HHV are carried out by myself) through a bomb calorimeter, *Calorimeter IKA C200*, following the method described in federal Standard EN 14918.
- ✓ **Elementary analysis (C, H, O and N):** allows the determination of the mass fraction of carbon, hydrogen, oxygen and nitrogen of HTC-coal and of original

food waste. It is measured, following Standard method ASTM, at ZHAW through *Elemental analyzer LECO Truspec CHN+O.*

The next ***Table 28*** summarizes the different measurements and methods used to analyze the output products: liquids, i.e. process water and solids, i.e. HTC-coal.

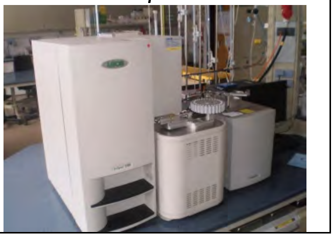
	Measurement parameter	Unit	Description	Measuring instrument or method
Liquids	*pH*	*[-]*	*Measure of the acidity of the process water after the reaction*	*Eawag: Hach-Lange HQ D40* 
	EC	*[µS/cm]*	*Measure of the electrical conductivity of the process water after the reaction*	*Eawag: Hach-Lange HQ D40* 
	TOC	*[mg/l]*	*Measure of the Total Organic Carbon present in the process water after the reaction*	*Eawag: Shimadzu TOC-L 720°C catalytic combustion*
Solids	*TS*	*[%]*	*Measure of the total solids of the HTC-coal and of the original substrate*	*Eawag: 24 hours in 105°C drying chamber*
	Calorific value	*[J/g]*	*Measure of the higher heating value of the dried HTC-coal and of the original substrate*	*ZHAW: Calorimeter IKA C200* 
	Elementary analysis (C,H,O and N)	*[% by weight]*	*Measure of the C, H, O and N contents of the dried HTC-coal and of the original substrate*	*ZHAW: Elemental analyzer LECO Truspec CHN+O* 

Table 28: *Measurements methods (Adapted from Robbiani, 2013*

5 TESTING OF THE REACTOR AND RESULTS

Before to test, by myself, the HTC-reactor with biowaste from the canteen of Eawag, three experiments were carried out with *Robbiani Zeno*, who has planned for experiments purposes and adapted to conditions in developing countries this HTC prototype reactor, using raw rice as a model organic substrate. For this reason, in this chapter, the description of all the experiments done will be separated in two parts: preliminary tests (including a water test and two tests with rice) and tests carried out with food waste (in total 10 tests, subdivided in two different series: 6 tests increasing the Total Solids (TS) and the last 4 tests varying the inner temperature recorded during the HTC-reaction).

5.1 Preliminary tests

The aim of these three initial experiments was to test and to ensure the proper functionality and safe operation of the designed HTC-reactor in accordance with technical requirements. For this reason, these results are then compared with the values previously obtained by *Robbiani Zeno*, using the same substrate (i.e. same type of rice *"Carolina"*) and carbonization conditions[25] in another similar HTC reactor, called *Grenolmatik 25* (Grenol GmbH, Germany), at ZHAW[26] (Wädenswil – Switzerland). More specifically, this reactor, used to compare the results, is however a bit different from the HTC-reactor discussed in this report. In fact, it is composed, firstly, of a double wall pressure (digital and analog) vessel, made of stainless steel, with a detachable container of 25 Liters capacity; it has a stirring device and a built-in heating mantle working with a thermal oil. Finally, the system of *Grenolmatik 25* is fully automatic (i.e. the parameters of temperature and pressure are recorded automatically with a programmable controller).

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[25] The comparison is carried out with the average of the results from the two experiments conducted without the use of stirrer by *Robbiani Zeno*. In particular, he made these two tests with 1.13 kg of the same rice and 15.8 liters of water (TS = 6.2%). The heat (total residence time) was applied during approximately 10 hours and the inner temperature was stabilized at around 205°C during minimum 4 hours.

[26] The "ZHAW" is the acronym of Zurich University of Applied Sciences, Institute of Natural Resource Sciences, Campus Grüental, CH-8820 Wädenswil (Switzerland). The exact name in German is: Zürcher Hochschule für Angewandte Wissenschaften, Institut für Umwelt und Natürliche Ressourcen.

In particular, these preliminary tests consist of three experiments: the first one was carried out without substrate, so using only water (namely tap water), while the second and third ones were tested, expending raw rice, at different solid loads.

Rice is a model substrate that can be easily carbonized under standard conditions, namely total residence time of 10 hours with temperature above 180°C (temperature at the start of the carbonization) for minimum 4 hours. It is a convenient feedstock to use for testing as it can be easily obtained and is homogenous with regard to Total Solid (TS) and elemental composition (C, H, O, and N).

These initial characteristics of raw rice, used for the second and third tests, are reported in the next ***Table 29***. Then, these values are compared with the values of the HTC-coal obtained after the HTC-reactions.

Organic Substrate	***TS [%]***	***HHV [MJ/kg$_{db}$]***	***C [%$_{db}$]***	***H [%$_{db}$]***	***O [%$_{db}$]***	***N [%$_{db}$]***
Original rice	88.15	17.7	44.1	6.5	49.4	1.2
HHV = Higher Heating Value; db = dry basis.						

Table 29: *Characteristics of rice before the HTC-reaction*

Finally, in the following ***Table 30***, these preliminary tests are summarized with the relative information, regarding the date and time of their execution and a brief description.

Preliminary test	***Beginning (Date - Time)***	***End (Date - Time)***	***Description***
1	29.03.2013 - 11:01	29.03.2013 - 17:58	*Only water* (17L)
2	02.04.2013 - 10:40	02.04.2013 - 20:55	*Rice 1* with **TS = 2.6%** (0.5kg)
3	04.04.2013 - 10:09	04.04.2013 - 20:23	*Rice 2* with **TS = 5.2%** (1kg)

Table 30: *Preliminary tests of HTC-reactor*

5.1.1 Test only water

For the first test carried out without substrate, the reactor was filled with **17** Liters of water, closed and heated at different temperatures.

The objective of this experiment was to get to know how the internal temperature [°C] and pressure [bar] reacted when the external temperature (T_ext), imposed with the regulation device of the heating mantle, is increased progressively (only for this experiment, the energy consumption was not recorded and the energy supply was applied until the achievement of 180°C for a total residence time, lower than 10 hours, unlike the others experiments).

The next ***Figure 42*** shows the graphic[27] of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction, on varying of the external temperature (green line).

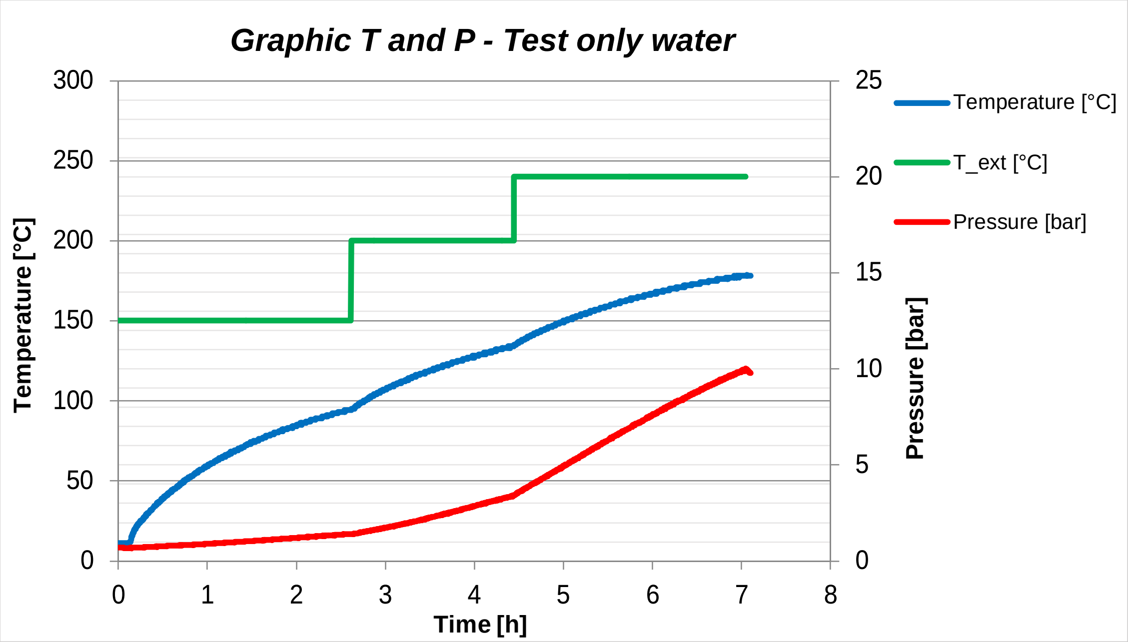

Figure 42: *Graph of temperature and pressure for the test with only water*

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[27] For all the experiments, the graphic T and P presents the principal vertical axis, temperature [°C], and the secondary vertical axis, pressure [bar], plotted against the time [h]. In particular, the maximum value of the principal vertical axis, 300°C, is determined by the maximum admissible temperature of the heating mantle; while the maximum value of the secondary vertical axis, 25 bar, is due to the maximal allowable pressure of the overpressure valve (this security valve was replaced with one from 30 bar during the experiments carried out with biowaste).

The external temperature of the heating mantle was increased stepwise: 150°C – 200°C and 240°C. The internal temperature rose slowly and reached the maximum temperature of 180°C after 7 hours. The pressure rose very gradually for the first 4 hours with values around 4 bar, then it increased up to reach, at the end of the test, the maximum value of 10 bar. As soon as the inner temperature reached the 180°C, we switched off the energy supply of the heating mantle, recording, for few minutes, the drop of the temperature (178°C) and pressure (9.7 bar). It was then decided to apply, at the beginning of the following experiment, an external temperature of 240°C.

5.1.2 Rice 1 with TS = 2.6%

This first test with raw rice was conducted using **0.5 kg** of rice and **16.8 L** of water (TS = 2.6%). The heat was applied during approximately 10 hours (condition kept both for the experiments with rice and biowaste), in such way to be been able to compare, subsequently, the results with those already obtained with the reactor at ZHAW.

The next ***Figure 43*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction.

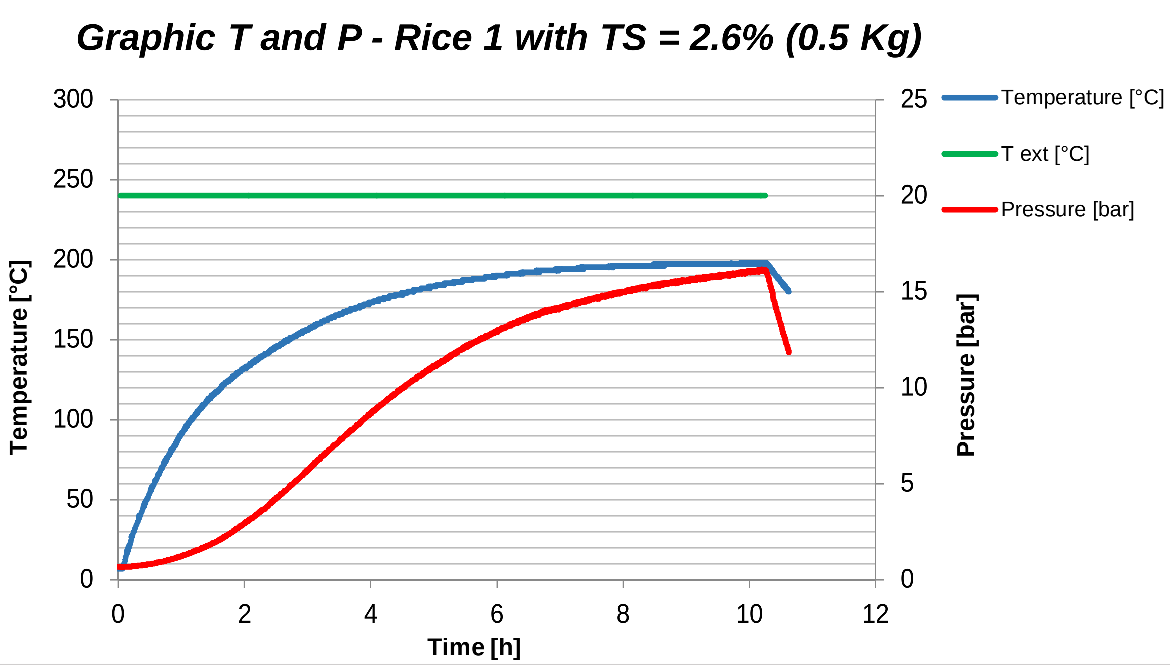

Figure 43: *Graph of temperature and pressure for test Rice 1 with TS = 2.6%*

The inner temperature stabilized around 198°C, without exceeding 200°C, with the external temperature of the heating mantle kept stable at 240°C. The pressure reached the maximum value of 16 bars after 9 hours from the beginning of the HTC-reaction.

The carbonization time, i.e. total time above 180°C, was in all 6 hours, started after 4.6 hours from the beginning of the reaction. At the end of the reaction, we switched off the energy supply of the heating mantle, recording the initial drop of the inner temperature until it reached 180°C with relative pressure of 11.8 bar.

As the experiments at ZHAW were conducted with an internal temperature of 205°C during minimum 4 hours, it was decided to use a higher external temperature (260°C) for the next batch in order to reach comparable carbonization conditions.

The main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction, are summarized in the following ***Table 31***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	12.4
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1263
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.2
Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.0

Table 31: *Energy consumption and duration of Rice 1 with TS = 2.6% (Adapted from Robbiani, 2013)*

5.1.3 Rice 2 with TS = 5.2%

The second and last experiment with raw rice of the preliminary tests was conducted using **1 kg** of rice and **16.6 L** of water (TS = 5.2%). The heat of the heating mantle was applied for approximately 10 hours. The objective of this test was to reach the internal temperature around 200°C in such way to attain similar carbonization conditions to the experiment conducted at ZHAW; for this reason the external temperature was imposed, right from the beginning of the HTC-reaction, at 260°C.

The next ***Figure 44*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction.

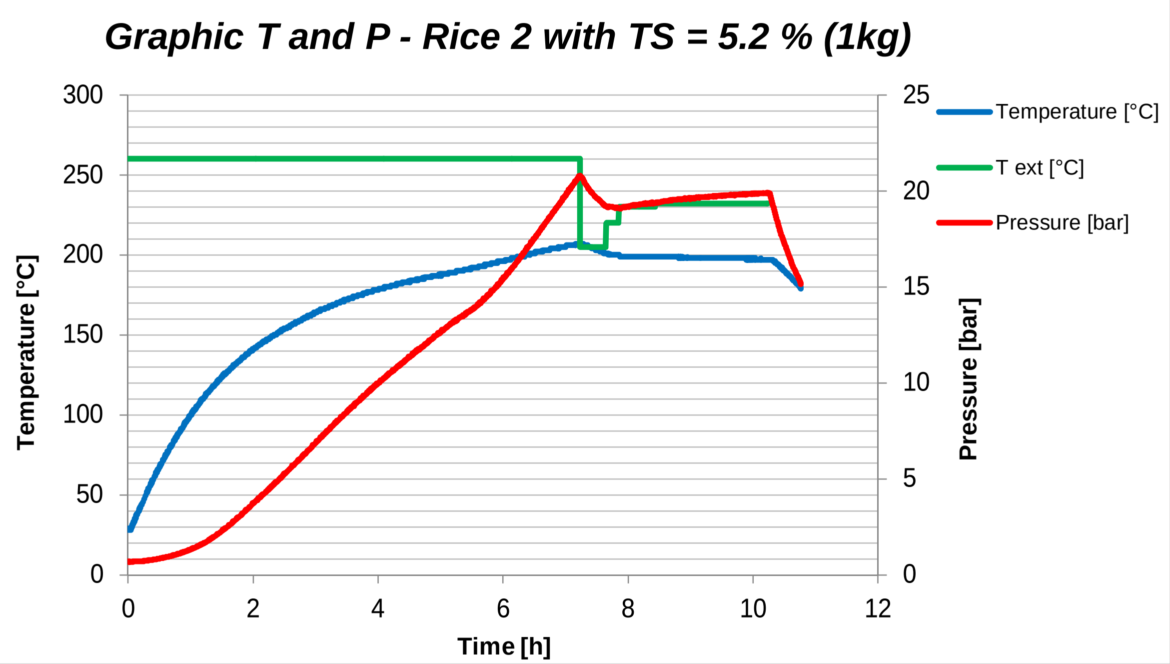

Figure 44: *Graph of temperature and pressure for test Rice 1 with TS = 2.6%*

The inner temperature increased to 207°C (maximum temperature recorded) while the pressure went up to 20.8 bar (maximum pressure recorded), after around 7 hours from the beginning of the HTC-reaction. After which, the external temperature was decreased, through the regulation device of the heating mantle, to 205°C and then increased stepwise up to 232°C. In this way, the internal temperature stabilized around 200°C during the remaining time (4.2 hours). At the end of the reaction, the energy supply of the heating mantle was switched off and the initial drop of the inner temperature was recorded until it reached 180°C with relative pressure of 15.2 bar.

The main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 32***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	11.8
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1219

Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.2
Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.7

Table 32: *Energy consumption and duration of Rice 2 with TS = 5.2 % (Adapted from Robbiani, 2013)*

5.1.4 Outputs measurements and analysis

For all the outputs obtained from the two tests with raw rice, namely HTC-coal and process water, we did the respective measurements. In particular, for the solid product: total solids (TS), higher heating value (HHV) and elementary analysis; for the liquid product: pH, electro-conductivity (EC) and total organic carbon (TOC), as described in the preceding chapter *(see ch. 4.5).*

The results of these measurements and analysis are summarized in the next ***Table 33***, in comparison with the characteristics of the original rice and with the results from ZHAW reactor.

		Original rice	**Rice 1 with TS=2.6%**	**Rice 2 with TS=5.2%**	Rice with TS=6.2% from ZHAW
In	Feedstock [kg]	-	**0.5**	**1**	1.1
	Water [L]	-	**16.8**	**16.6**	15.8
Out	HTC-coal (wet) [kg]	-	**0.9**	**1.9**	2.3
	Process water [L]	-	**15.8**	**15.1**	15.1
Solids	TS output [%]	-	**10.8**	**18.1**	18.4
	HHV [MJ/kg dry basis]	17.7	**23.0**	**26.9**	27.7
	C [% dry basis]	44.1	**56.6**	**66.9**	69.4
	H [% dry basis]	6.5	**5.9**	**4.9**	5.2
	O [% dry basis]	49.4	**32.1**	**23.8**	22.7
	N [% dry basis]	1.2	**2.4**	**1.9**	2.2
Liquids	pH [-]	-	**3.6**	**2.7**	3.2
	EC [µS/cm]	-	**599**	**1083**	1038
	TOC [mg/L]	-	**4677**	**7764**	4933

Table 33: *Results of the measurements for Rice 1 with TS=2.6% and Rice 2 with TS=5.2% in comparison with results from ZHAW reactor (Adapted from Robbiani, 2013)*

With the tests *Rice 1 with TS=2.6%* and *Rice 2 with TS=5.2%*, both the higher heating value and the carbon content of the original substrate are significantly increased while the hydrogen content and oxygen content are decreased. More especially, the calorific value is passed from 17.7 MJ/kg to **23.0 MJ/kg** for the first one and to **26.9 MJ/kg** for the second one. Whereas the initial hydrogen and oxygen contents, 6.5% and 49.4% respectively, are decreased to 5.9% and 32.1% for *Rice 1* and to 4.9% and 23.8% for *Rice 2*.

The amount of wet HTC-coal, obtained from the two experiments with rice, is naturally increased with the increase of the initial organic substrate, put inside the reactor before the hydrothermal carbonization. In particular, the weight of hydro-char (wet) is 0.9 kg for *Rice 1* and 1.9 kg for *Rice 2*; this second value is comparable to the one gotten at ZHAW reactor, 2.3 kg, using nevertheless 1.1 kg of rice instead of 1 kg of the same rice in the second test.

The higher heating value and carbon content of the HTC-coal from the first test are a bit lower than the ones from the experiments at ZHAW. This can be explained by looking at the severity of the reactions. During the first test, the inner temperature never exceeded 200°C whereas for the experiment at ZHAW, the temperature was stabilized at around 205°C during more than 4 hours. For the second test, carbonization conditions similar to the one used at ZHAW are reached. In any case, the measurements from the output products of both experiments give comparable results. In particular, the higher heating value and carbon content of both HTC-coals are relatively close to each other.

As regards the results of pH and EC of process water are all similar; that is, there is not a great differences between the second test and the experiment at ZHAW. There is only a big difference between the values from the two reactors regarding the TOC of process water, 7764 mg/L and 4933 mg/L respectively. This discrepancy of values is due to different methods used to measure TOC in the process water (at Eawag: *Shimadzu TOC-L, 720°C catalytic combustion* and at ZHAW: *Photometer Lange DR3800, Test LCK 386*) *(see ch. 4.5)*. This implies that the TOC-analyses conducted at Eawag are higher compared to the one done by ZHAW.

From these measurements of outputs, it was possible to calculate other parameters (data processing), which further characterized the HTC-reaction. These results are thus summarized in the following ***Table 34***.

Parameters		**Calculation**	**HTC-coal from Rice 1**	**HTC-coal from Rice 2**	**HTC-coal at ZHAW**
Carbon mass balance	*C in solids [%]*	$\frac{C_{HTC-coal} * TS_{HTC-coal} * m_{HTC-coal}}{C_{rice} * TS_{rice} * m_{rice}}$	**26.9**	**58.4**	65.4
	C in liquids [%]	$\frac{TOC\,[g/l] * V_{PW}[l]}{C_{rice} * TS_{rice} * m_{rice}[g]}$	**38.0**	**30.2**	18.8
	C in gases [%]	$1 - C_{solids} - C_{liquids}$	**35.1**	**11.4**	15.8
Solid yield [% dry basis]		$\frac{TS_{HTC-coal} * m_{HTC-coal}}{TS_{rice} * m_{rice}}$	**21.0**	**38.5**	42.5
Reaction severity [-]		$f = 50 * t^{0.2} * e^{\frac{-3500}{T}}$	**0.22**	**0.26**	NA
Energy content of HTC-coal [kWh]		$\frac{TS_{HTC-coal} * m_{HTC-coal}\,[g] * HHV\,[J/g]}{3'600'000[J/kWh]}$	**0.6**	**2.5**	3.2
Energy consumed [kWh]		**(measured)**	**12.4**	**11.8**	NA
NA = Not Available.					

Table 34: *Results of analysis from measurements of the outputs of Rice 1 with TS=2.6% and Rice 2 with TS=5.2% in comparison with results from ZHAW reactor (Adapted from Robbiani, 2013)*

As the ***Table 34*** shows, the first test, *Rice 1*, gives particularly low solid yield, only 21.0% in comparison to 38.5% for Rice 2 and 42.5% for ZHAW reactor, as well as low C in solids, often called carbon efficiency[28] (CE), of 26.9%. The second test, *Rice 2*, gives better results but values remain a bit lower than the ones from the experiments at ZHAW.

Regarding the carbon mass balance, the values of C in liquids is very higher in comparison with the one obtained at ZHAW, the reason of this great difference is always due, as already said formerly, to different methods used to measure TOC in the process water.

The reaction severity is a bit increased in the second test (0.25) compared to the first one (0.22), due to higher temperature reached during the reaction (maximum temperature = 207°C); this also explains the higher carbon content of the HTC-coal produced in the second experiment.

The HTC-coal produced in the second test has a total energy content of around **2.5 kWh**, which is about one fifth of the energy required for the reaction, 11.8 kWh. From this

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[28] The "carbon efficiency" is defined as the relative amount of carbon from starting product bound in the final product.

result, it can be extrapolated that the HTC-coal produced from a rice input around 5 times bigger represents a comparable amount of energy than the amount needed for the reaction.

5.2 Tests with biowaste

Once finished the preliminary tests, it was decided to continue the following experiments using as biomass the organic fraction (biowaste), collected from the canteen “Aqua” of Eawag *(see ch. 4.4 for the procedure of food waste before HTC).*

These experiments carried out with biowaste consist, in total, of 10 tests, subdivided in two different series, as it follows:

1) **6 tests** increasing the TS in each batch (i.e. increasing the initial amount of biowaste put into the reactor, keeping constant the maximum volume of 17L). In particular: TS [%]=2.5; TS [%]=4.9; TS [%]=7.4; TS [%]=9.4; TS [%]=12.8 and TS [%]=15.2;
2) **4 tests**[29] with the same TS = 4.9% but varying the inner temperature, reached inside the reactor, in particular: 200°C; 190°C; 180°C and 170°C.

The carbonization conditions followed for the first series were: total reaction time approximately 10 hours and minimum 4 hours with temperature above 180°C, whereas, for the second series the main operative condition was: about 4 hours with the respective inner temperature, trying to stabilize it in that range of temperature.

Moreover, the objective of this second experimental part was to test, for the first time, this particular thermochemical conversion, with biowaste from the canteen and then to analyze and compare the end-products obtained. In this way, it was possible to assess, through a series of experiments with different solid load, what are the optimal operational parameters, in terms of carbonization temperature and residence time, but especially the

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[29] The second series of experiments with biowaste was decided to carry out after having already commenced the first four tests of the first series. Therefore, we chose, according to the available amount of food waste (collected once time at the beginning of all the tests to have the same characteristics) to perform other 4 experiments with TS=4.9% (3.6kg), referring thus to the second test of the first series, varying for each batch the inner temperature.

maximum amount of waste per batch, for this HTC-reactor, to be treated to have thus a final positive energy balance.

The initial characteristics of food waste (i.e. total solids, heating value and elemental analysis), collected from the canteen and used for all the following experiments, are reported in the next ***Table 35***. Then, these values are compared with the values of the HTC-coal obtained after the HTC-reactions.

Organic Substrate	***TS [%]***	***HHV [MJ/kg$_{db}$]***	***C [%$_{db}$]***	***H [%$_{db}$]***	***O [%$_{db}$]***	***N [%$_{db}$]***
Original biowaste	22.60	19.3	46.2	6.5	43.7	2.2
HHV = Higher Heating Value; db = dry basis.						

Table 35: *Characteristics of biowaste before the HTC-reaction*

5.2.1 Tests increasing the TS

This first series of tests consist of 6 experiments carried out with biowaste, increasing for each batch the Total Solids (TS).

For all the performed tests, we tried to maintain the same operative conditions; this means that the heat was applied approximately 10 hours with temperature around 200°C.

In the following ***Table 36***, these six tests with increase of TS are all summarized with the relative information, regarding the date and time of their execution and a brief description.

Tests of biowaste	***Beginning (Date - Time)***	***End (Date - Time)***	***Description***
1	14.04.2013 – 11:51	14.04.2013 – 22:43	*Biowaste 1* with **TS = 2.5%** (1.8kg)
2	16.04.2013 – 10:31	16.04.2013 – 20:35	*Biowaste 2* with **TS = 4.9%** (3.6kg)
3	18.04.2013 – 11:10	18.04.2013 – 21:21	*Biowaste 3* with **TS = 7.4%** (5.3kg)
4	21.04.2013 – 12:17	21.04.2013 – 22:47	*Biowaste 4* with **TS = 9.4%** (6.4kg)

5	02.05.2013 – 11:06	02.05.2013 – 21:30	*Biowaste 5* with **TS = 12.8%** (8.3kg)
6	06.05.2013 – 10:39	06.05.2013 – 21:27	*Biowaste 6* with **TS = 15.2%** (9.8kg)

Table 36: *Tests carried out with biowaste increasing the TS*

5.2.1.1 Biowaste 1 with TS = 2.5%

This first experiment with biowaste was conducted using **1.8 kg** of food waste, opportunely pre-treated *(see ch. 4.4)*, and **14.6 L** of water, with a final TS equal to 2.5%.

We began the tests with low TS because we used for the first time a new organic substrate for HTC, so the reactor should not be filled with a too high amount of feedstock, since the resulting pressure can increase very fast, depending on the nature of the substrate. The low value of TS allowed thus a better control of the pressure during the reaction.

The next ***Figure 45*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction.

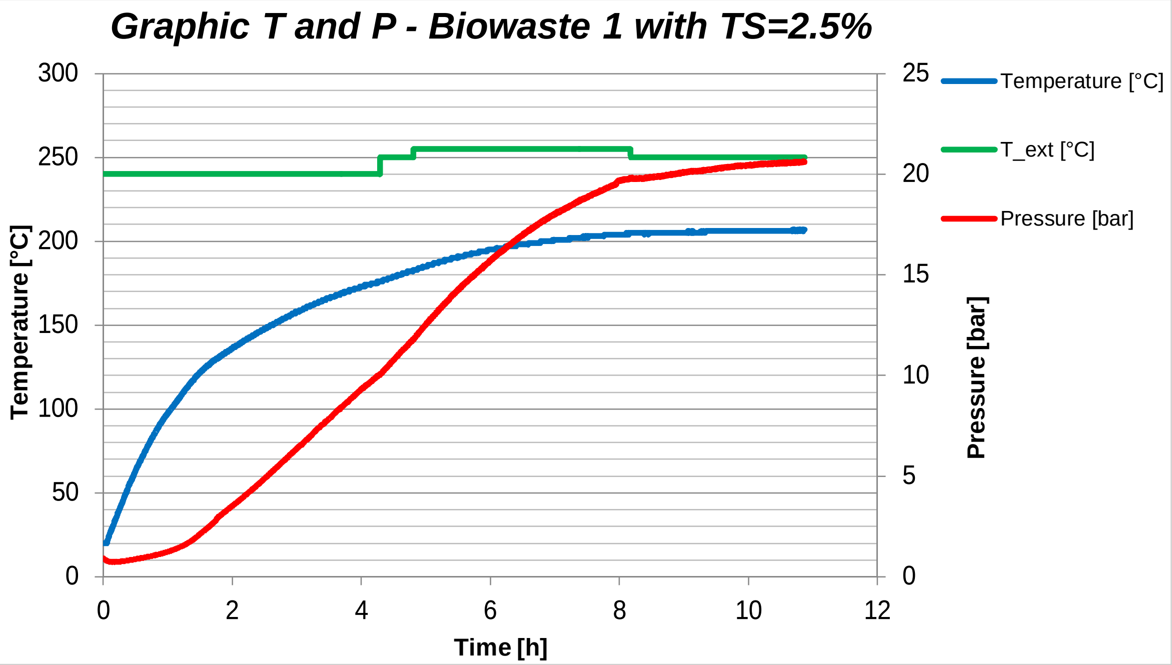

Figure 45: *Graph of temperature and pressure for test Biowaste 1 with TS = 2.5%*

The inner temperature stabilized around 205°C after about 8 hours from the beginning of the HTC-reaction while the external temperature, imposed at first to 240°C, was increased stepwise to 250°C and to 255°C. Finally, the external temperature was decreased to 250°C to keep the inner temperature below 110°C and to respect, in this way, the relative condition of internal temperature around 200°C.

In particular, the maximum temperature reached was 207°C at 10.7 hours and the respective pressure was 20.64 bar, that it was also the maximum value of pressure reached during the whole reaction.

The carbonization time, i.e. total time above 180°C, was more than 6 hours, started after 4.5 hours from the beginning of the reaction. In addition to this, the time with temperature above 200°C was about 4 hours, recorded after 6.8 hours from the beginning.

The main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 37***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	13.4
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1231
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.8
Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.3

Table 37: *Energy consumption and duration of Biowaste 1 with TS = 2.5%*

5.2.1.2 Biowaste 2 with TS = 4.9%

This experiment was carried out using **3.6 kg** of biowaste (amount doubled compared to previously test) and **13.7 L** of water, obtaining a TS equal to 4.9%.

The next ***Figure 46*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded during the hydrothermal carbonization.

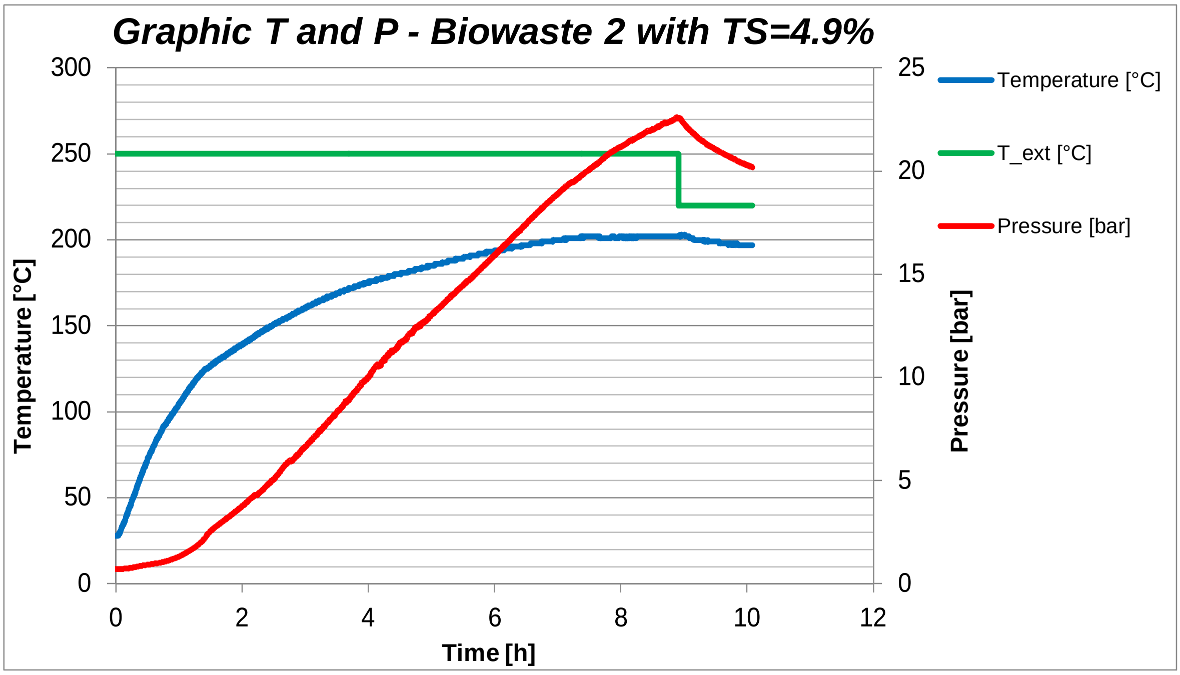

Figure 46: *Graph of temperature and pressure for test Biowaste 2 with TS = 4.9%*

The external temperature was imposed right from the beginning of the reaction at 250°C and it was subsequently decreased at 220°C as soon as the pressure reached the maximum value of 22.6 bar, after 8.9 hours, with temperature stabilized around 200°C (maximum temperature reached was 203°C). At the end of the HTC-reaction, with the external temperature at 220°C, the inner temperature slightly decreased to 197°C and also the pressure fell at 20.2 bar, in the last 1.2 hours. The carbonization time, i.e. total time above 180°C, was about 5.7 hours, started after 4.4 hours from the beginning of the reaction, whereas, the time with temperature around 200°C was about 3.6 hours, recorded after 6.4 hours from the beginning.

Finally, the main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 38***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	11.8
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1167
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.1

Reaction Time	[h]	*Total time with inner temperature above 180°C*	5.7

Table 38: *Energy consumption and duration of Biowaste 2 with TS = 4.9%*

5.2.1.3 Biowaste 3 with TS = 7.4%

The third test carried out with food waste was performed using **5.3 kg** of organic fraction and **12 L** of water, with a final TS equal to 7.4%.

The next ***Figure 47*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded during the hydrothermal carbonization.

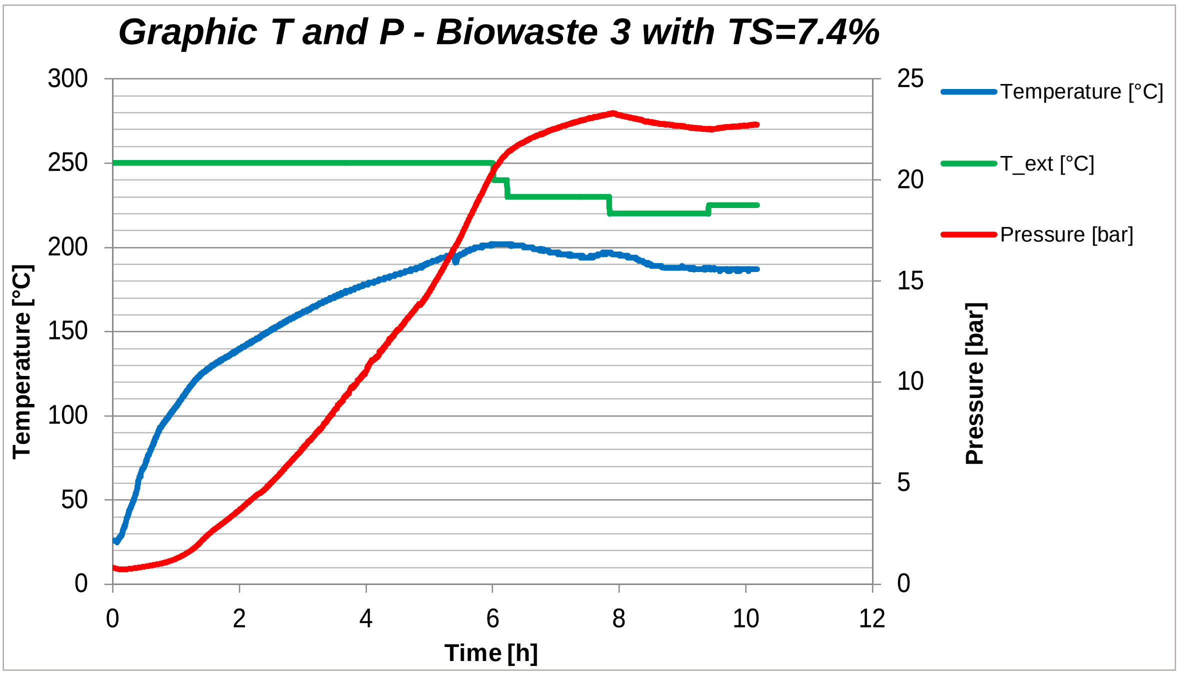

Figure 47: *Graph of temperature and pressure for test Biowaste 3 with TS = 7.4%*

The external temperature was again imposed at 250°C right from the beginning of the reaction (condition kept also for the following experiments) and it was subsequently decreased stepwise (240°C - 230°C - 220°C and 225°C) to try to prevent that pressure reaches the maximal allowable pressure of the overpressure valve, namely 25 bar. This because the overpressure valve was used as a safety device and not as a pressure regulation device; therefore, we tried to regulate the external temperature of the heating mantle in order to keep the internal temperature below this value (25 bar).

The inner temperature reached the maximum value of 202°C after about 6 hours with relative pressure around 20 bar. Although the external temperature of the heating mantle was decreased at 230°C, the internal pressure increased up to 23.3 bar (maximum value of pressure recorded) anyway. For this reason, the external temperature was slightly decreased to try to stabilize the pressure around 22 bar and to maintain, at the same time, an inner temperature inside the range of 190-200°C.

At the end of the reaction (total reaction time of 10.2 h), the final temperature reached was 187°C with the relative pressure was 22.7 bar.

The carbonization time, i.e. total time above 180°C, was about 6 hours, started after 4.1 hours from the beginning of the reaction, whereas the time with temperature above 200°C was less than 1 hour because of the necessary decrease of external temperature.

The main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 39***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	11
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1075
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.2
Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.0

Table 39: *Energy consumption and duration of Biowaste 3 with TS = 7.4%*

5.2.1.4 Biowaste 4 with TS = 9.4%

This experiment was conducted using **6.8 kg** of food waste and **11 L** of water, getting in this way a TS equal to 9.4%.

The next ***Figure 48*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction.

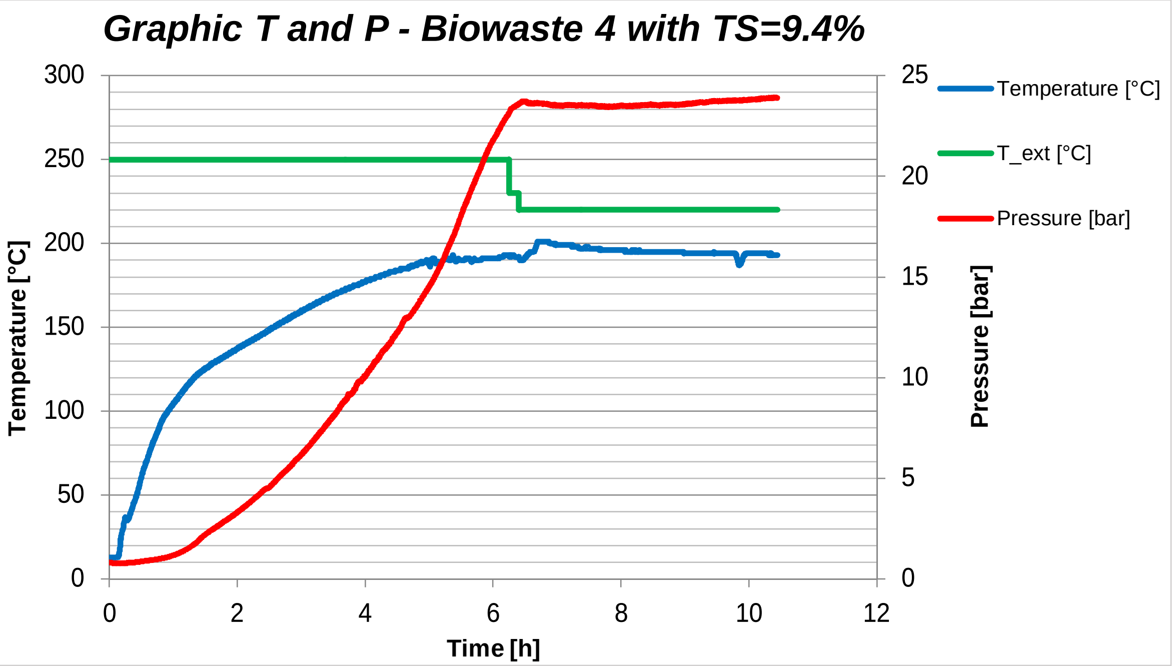

Figure 48: *Graph of temperature and pressure for test Biowaste 4 with TS = 9.4%*

The inner temperature stabilized around 195°C with external temperature decreased at 220°C in the last 4.3 hours. The pressure increased very fast, for these reason, at 6.3 hours from the beginning of the reaction, was decreased before at 230°C and then at 220°C, in this way, the internal pressure increased anyway but very slowly, reaching the maximum value of 23.9 bar at the end of the reaction (10.4 h) when the inner temperature was equal to 193°C.

The inner temperature still exceeded the threshold of 200°C but only for a small lapse of time, exactly for just 0.3 hours, this means less than 20 minutes. However, the carbonization time, i.e. total time above 180°C, was about 6.3 hours, started after 4.2 hours from the beginning of the reaction, similar to the values gotten in the previous performed tests carried out with biowaste.

The main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 40***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	11.6
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1104
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.4

Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.3

Table 40: *Energy consumption and duration of Biowaste 4 with TS = 9.4%*

5.2.1.5 Biowaste 5 with TS = 12.8%

This penultimate test of the first series, concerning to the increase of TS for each batch, was conducted using **8.3 kg** of biowaste and **8.2 L** of water, getting a TS equal to 12.8%.

Before beginning this experiment, the overpressure valve able to bear pressure up to 25 bar was necessarily replaced with one from 30 bar (maximum allowable pressure for this HTC prototype reactor) because during the execution of tests, called *Biowaste 3 with TS=7.4%* and *Biowaste 4 with TS=9.4%*, elevated pressures, around 22-23 bar, were reached inside the reactor when the inner temperature was not reached 200°C yet (condition that we tried to achieve in all the performed tests).

The next ***Figure 49*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction.

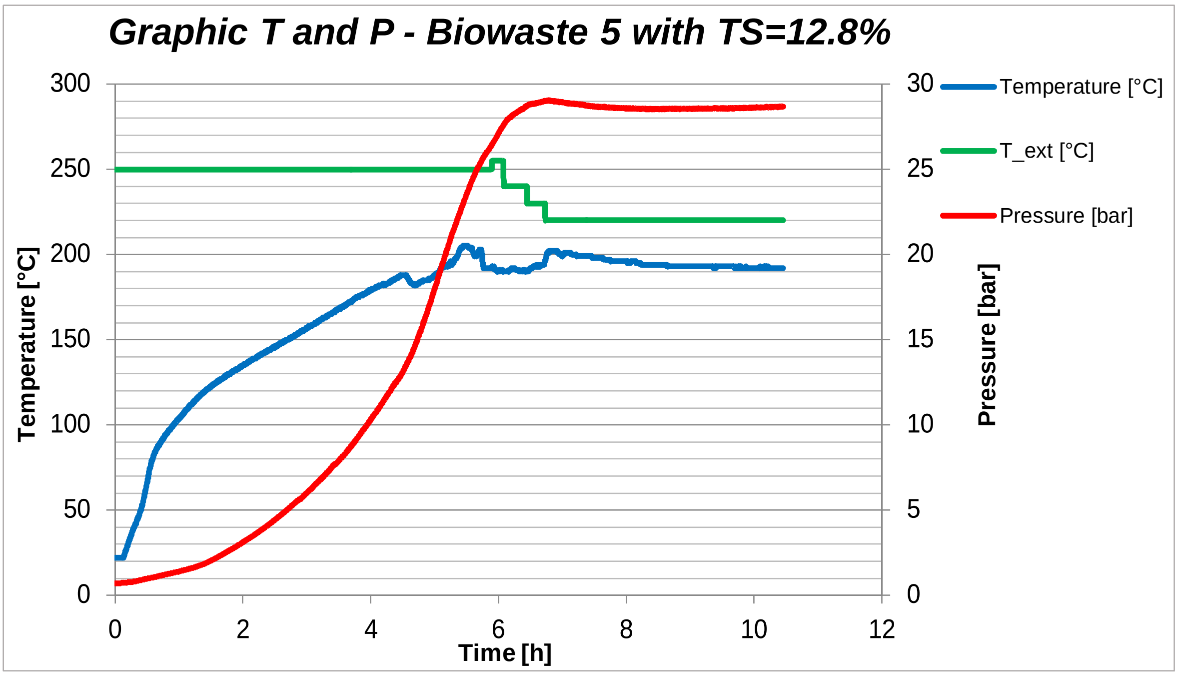

Figure 49: *Graph of temperature and pressure for test Biowaste 5 with TS = 12.8%*

The external temperature was decreased stepwise from 250°C to 220°C because the pressure increased very quickly, reaching the maximum value of 29.06 bar, after 6.8 hours from the beginning of the process, with the corresponding temperature of 202°C. However, the external temperature was beforehand slightly increased at 255°C, since the internal temperature fell from above 205°C (maximum temperature reached during the HTC-reaction) to 192°C but this regulation was kept only for about 11 minutes, as the pressure increased continually, in this short lapse of time, from 26.4 bar to 27.6 bar.

The inner temperature, after having underwent a drop around 190°C, increased again above 200°C, stabilizing itself then around 194°C in the last 3 hours. It is important to notice that even though the external temperature was decreased of 30°C (from 250°C to 220°C) the internal pressure did not decrease a lot (only drop of 0.5 bar) but it stabilized at 28.6 bar with a final inner temperature recorded of 192°C.

In particular, the carbonization time, i.e. total time above 180°C, was about 6.4 hours, started after 4 hours from the beginning of the reaction, while the time with temperature above 200°C was about 0.8 hours. Considering temperatures around 200°C (range 197-205°C) instead, the total time was about 1.4 hours.

The main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 41***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	10.5
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	998
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.5
Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.4

Table 41: *Energy consumption and duration of Biowaste 5 with TS = 12.8%*

5.2.1.6 Biowaste 6 with TS = 15.2%

This last test of the first series, regarding the increase of TS for each batch, was conducted using **9.8 kg** of biowaste and **7 L** of water, getting a TS equal to 15.2%.

The next ***Figure 50*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded for the whole length of the reaction.

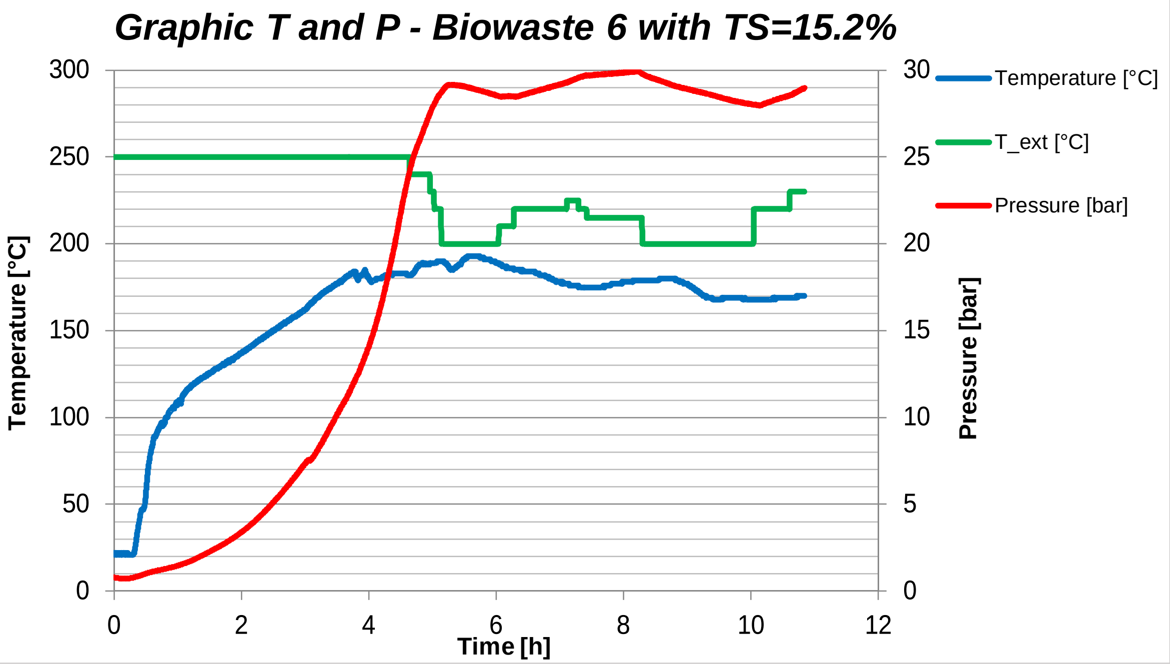

Figure 50: *Graph of temperature and pressure for test Biowaste 6 with TS = 15.2%*

The external temperature of the heating mantle was varied many times to try to keep high values of pressure, reached during the HTC-reaction, below 30 bar. The purpose of all these regulations of external temperature, through the regulator temperature, was to avoid that the overpressure valve opened during the HTC-process. For this reason, the inner temperature never exceeded 200°C and it underwent many variations, without having a stable trend for a long time. In particular, the external temperature was decreased stepwise from 250°C to 200°C, after 5.1 hours from the beginning of the reaction, when the pressure reached the value of 28.7 bar with the respective inner temperature equal to 190°C. In this lapse of time, with T_ext = 200°C, the inner temperature slightly increased anyway, reaching the maximum value, recorded during the whole HTC-process, of 193°C for about 10 minutes while the pressure weakly decreased from 28.7 bar to 28.5 bar.

As the internal temperature subsequently dropped below 190°C, the external temperature was gradually increased at 225°C to try to rise it. However, the inner temperature continually went down, reaching values around 175°C, after 7 hours from the beginning of the reaction with pressure above 29 bar. In order to drop the pressure inside the reactor, the external temperature was again decreased at 215°C but it reached all the same the maximum value of 29.9 bar, when the internal temperature was only 179°C.

Therefore, the temperature of the heating mantle was immediately imposed at 200°C to avoid thus the opening of the overpressure valve. In fact, in this way, the trend of pressure decreased quite quickly, reaching values around 28 bar but internal temperature below 170°C. In the last 50 minutes, we tried to rise the inner temperature through an increase of the external temperature but without succeed in this feat. At the end of the reaction, in fact, the inner temperature stabilized around 170°C whereas the pressure reached 28.9 bar. However, the carbonization time, i.e. total time above 180°C, was about 3.4 hours, started after 4 hours from the beginning of the reaction, without exceed 200°C, unlike the other experiments carried out with biowaste previously.

This experiment has allowed us to understand what the maximum admissible amount of biowaste is for this HTC prototype reactor, namely 9.8 kg of food waste (for this type of organic fraction) with TS equal to 15.2%. This is a consequence of the quickly pressure's growth with values very close to the maximal allowable pressure, that is 30 bar.

Finally, the main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 42***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	10
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	916
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	10.8
Reaction Time	[h]	*Total time with inner temperature above 180°C*	3.4

Table 42: *Energy consumption and duration of Biowaste 6 with TS = 15.2%*

5.2.1.7 Outputs measurements and analysis

One sample was taken from solids (HTC-coal) and liquids (process water) after each experiments carried out with food waste, for this first series of tests with the increase of TS, to do subsequently the relative measurements and analysis.

The results of these measurements and analysis, for all the six tests done, are thus summarized in the next ***Table 43***, in comparison with the characteristics of the original biowaste.

		Original biowaste	Biowaste1 **TS=2.5%**	Biowaste2 **TS=4.9%**	Biowaste3 **TS=7.4%**	Biowaste4 **TS=9.4%**	Biowast5 **TS=12.8%**	Biowast6 **TS=15.2%**
In	Feedstock [kg]	-	1.8	3.6	5.3	6.8	8.3	9.8
	Water [L]	-	14.6	13.7	12	11	8.2	7
Out	HTC-coal (wet) [kg]	-	0.4	1.6	2.8	3.8	4.5	5.9
	Process water [L]	-	16.2	15.3	14	12.8	11.2	9.7
Solids	TS output [%]	-	33.8	20.6	21.3	19.8	22.9	23.4
	HHV [MJ/kg$_{db}$]	**19.3**	30.0	29.3	29.0	28.3	28.9	29.2
	C [%$_{db}$]	**46.2**	68.5	67.2	66.8	66.2	66.8	65
	H [%$_{db}$]	**6.5**	6.8	6.6	6.6	6.8	6.7	6.8
	O [%$_{db}$]	**43.7**	23.2	24.7	24.4	24.7	24.4	26
	N [%$_{db}$]	**2.2**	2.6	2.8	3.1	3	3	3
	H/C [Mol Ratio]	**1.689**	1.198	1.176	1.181	1.232	1.210	1.260
	O/C [Mol Ratio]	**0.709**	0.254	0.276	0.273	0.280	0.274	0.300
Liquids	pH [-]	-	3.5	3.5	3.5	3.5	3.5	3.4
	EC [µS/cm]	-	2615	4439	6233	7840	9446	10577
	TOC [mg/L]	-	5037	8381	9818	13542	18784	17430

Table 43: *Results of the measurements for all the tests carried out with the increase of TS (db = dry basis)*

In all the experiments both the higher heating value and the carbon content of the original substrate are significantly increased after the hydrothermal carbonization. In fact, the calorific value is passed from 19.3 MJ/kg to **29.1 MJ/kg** on average (with an increase of 50.8%), while the carbon content from 46.2% to 66.7% on average (with an increase of 20.5%). In general, the results of both higher heating value and carbon content of all HTC-coals are very close to each other. In particular, these values respect the linear correlation between the carbon content (C in %) and the gross calorific value, namely, the higher the degree of carbonization is, the higher carbon content and thus the higher the calorific value, as the next ***Figure 51*** shows.

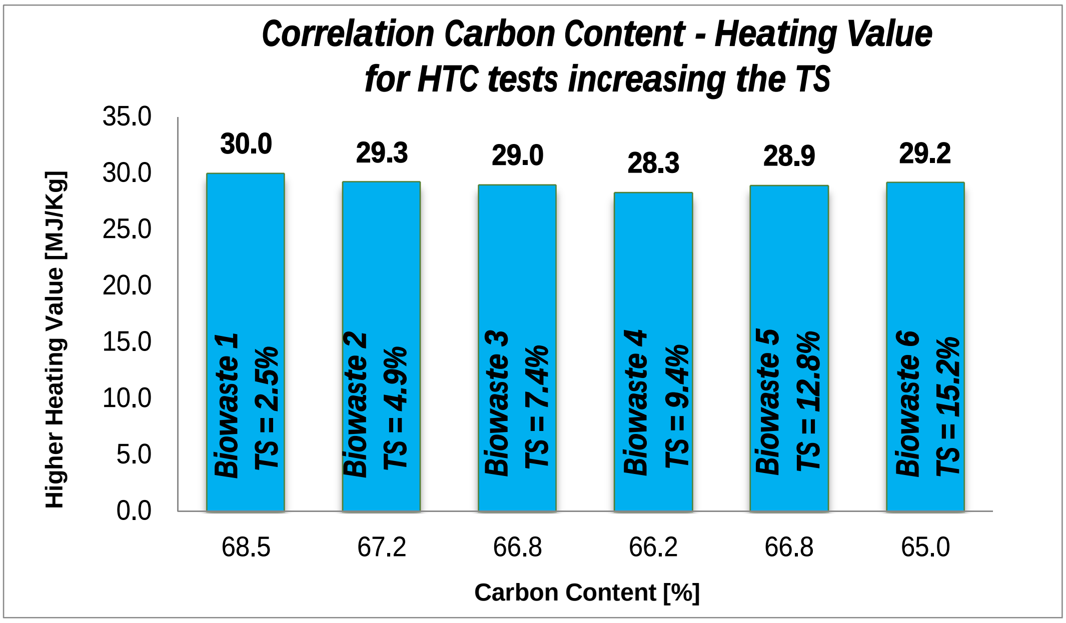

Figure 51: *Correlation carbon content and calorific value for all the tests with biowaste increasing the TS*

Only in the last experiment with *TS = 15.2%* this correlation is not followed since even though the carbon content is lower (65.0%) than the other values, due to the lower temperature (below 180°C) because of high pressure reached during the reaction, the final calorific value of HTC-coal is higher (29.2 MJ/kg) compared to tests with *TS=9.4%* (28.3 MJ/kg) and *TS=12.8%* (28.9 MJ/kg).

Moreover, only the oxygen content is decreased from 43.7% for the original biowaste to 24.5% on average for the HTC-coal produced (with a decrease of 19.2%) while, unlike the experiments with rice and in general with the literature, the hydrogen content is not decreased but it rose a little, from 6.5% to 6.7% on average. Nevertheless, the carbonization caused, for all the experiments, a decrease in the atomic ratios of H/C and O/C, as the literature reports. In particular, the initial H/C and O/C ratios were 1.69 and 0.71, respectively before the HTC-reaction, while at the end of the process 1.21 and 0.28 on average, respectively.

The amount of wet HTC-coal, obtained from each tests with food waste, is naturally increased with the increase of the Total Solids (TS), from the minimum amount of 0.4 kg for the first test with TS equal to 2.5% to the maximum amount of 5.9 kg for the last one with TS equal to 15.2%. These values confirm that raising the solid load increased as a result the solid product, i.e. large parts of the dissolved organic fraction as solid material.

As regards the results of pH of process water are all similar among these experiments, ranging from 3.4 to 3.5 (acid conditions), while the values regarding the EC (electro conductivity) and TOC (Total Organic Carbon) are increased a lot with the rise of TS in each tests, ranging from 2615 µS/cm to 10577 µS/cm for EC (these high values reveal the presence of salts in all samples of process water) and ranging from 5037 mg/L to 17430 mg/L for TOC.

In particular, the trend of these values of TOC, for all the performed tests, is depicted in the following ***Figure 52***.

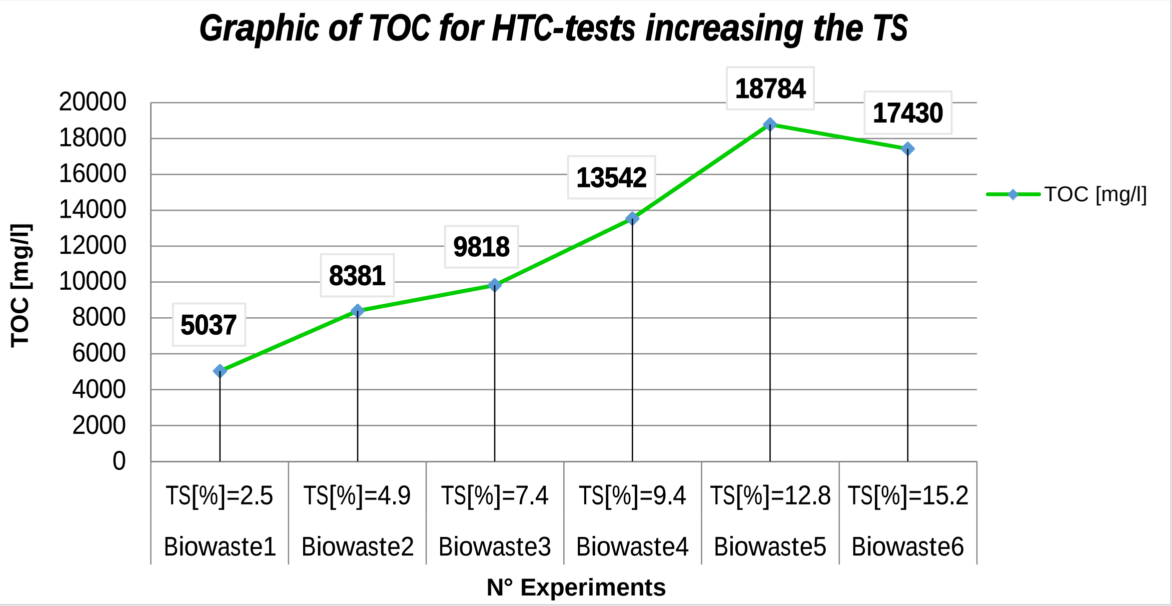

Figure 52: *Graph of TOC for all the tests carried out with biowaste increasing the TS*

However, these values of TOC are extremely higher compared to the ones done by ZHAW obtained with rice, this because the TOC-analyses conducted at Eawag (*Shimadzu TOC-L, 720°C catalytic combustion)* utilize a different method without centrifugation, pre-treatment method need to calculate the correct TOC analysis of the process water *(see ch. 4 in analytical techniques)*. This procedure, unfortunately, is not correct for doing the carbon mass balance because of the high amount of suspended particle in the liquid after HTC-process. For this reason, for all the tests carried out with biowaste, it was not possible to calculate, unlike the experiments performed with raw rice (in that case, even though we used the same TOC-analyses at Eawag, the carbon mass balance is made only because the distribution of carbon in liquid permitted however the balance among the three phases), the distribution of the carbon in the liquid and gases phases, after HTC-process. We have discover the difference of methods for TOC only at the end of experiments because the elemental analysis (C, H, O and N) was done, for all the tests, when the analysis of TOC are already been measured. Therefore, only when we tried to calculate the relative mass carbon balance in each experiments, we realized that the elevated values of TOC did not allow having a correct balance *(see in appendix the analysis of outputs where these calculations, regarding the carbon mass balance, are however reported for completeness)*.

However, from these measurements of outputs, it was possible to calculate other parameters (data processing), which further characterized the HTC-reaction. These results are thus summarized in the following ***Table 44*** *(see the relative formulae in the previous Table 34)*.

Parameters	**Biowaste1 TS=2.5%**	**Biowaste2 TS=4.9%**	**Biowaste3 TS=7.4%**	**Biowaste4 TS=9.4%**	**Biowaste5 TS=12.8%**	**Biowaste6 TS=15.2%**
Solid yield [% dry basis]	30.6	39.8	50.3	49.2	55.5	62.9
Reaction severity [-]	0.25	0.23	0.23	0.23	0.25	0.18
Carbon efficiency (CE) [%]	45.4	57.9	72.7	70.4	80.2	88.3
Carbonization time (above 180°C) [h]	6.3	5.7	6.0	6.3	6.4	3.4
Energy content of HTC-coal [kWh]	1.0	2.6	4.9	5.9	8.4	11.3
Energy consumed [kWh]	13.4	11.8	11	11.6	10.5	10

Table 44: *Results of analysis from measurements of the outputs of tests with the increase of TS*

As the ***Table 44*** shows, the first and second tests, *Biowaste 1 with TS=2.5%* and *Biowaste 2 with TS=4.9%*, give especially low solid yield, only 30.6% for the first one and 39.8% for the second one, in comparison to the others results, as well as low carbon efficiency (CE), of 45.4% and 57.9% respectively.

In general, the experiments carried out with high values of TS, gives better results in terms of carbon efficiency (ranging from 70.4% to 88.3%) and solid yield (ranging from 49.2% to 62.9%), but especially give values very close to them.

The reaction severity, depending on temperature and residence time, is quite stable around 0.23 for all the tests, only the last experiment has a low reaction severity, 0.18, due to the low temperature reached during the reaction and short time with temperature above 180°C, therefore it has also a low energy consumed compared to the other tests.

The HTC-coal produced has a total energy content that increase in each test, ranging from **1.0 kWh** for the first one to **11.3 kWh** for the last one whereas the energy consumed varied from 13.4 kWh to 10 kWh. From these results, it is possible to notice that only with the last test *Biowaste 6 with TS=15.2%* the energy content of HTC-coal is larger (11.3 kWh) than the energy consumed (10 kWh). This it means that the last experiment, unlike the preceding tests, permits to reach a positive energy balance and also represents the maximum amount of biowaste per batch to be treated (9.8 kg of food waste from canteen) for this HTC prototype reactor, with maximal pressure allowable of 30 bar.

5.2.2 Tests with the same TS on varying of the inner temperature

This second series of tests consist of 4 experiments carried out always with the same biowaste, i.e. same initial characteristics of the original organic fraction *(see the prior* ***Table 35****)*, on varying, in each batch, of the inner temperature (200°C – 190°C – 180°C and 170°C) recorded inside the HTC-reactor but using the same TS equal to 4.9%.

More especially, the amounts of biowaste (3.6 kg) and water (13.7 L), used for all these four experiments, are the same of the preceding test *Biowaste 2* carried out *with TS=4.9%*.

The objective of these tests was to understand how the characteristics of HTC-coal could change on varying of the inner temperature reached during the reaction, as to discover, in this way, the optimal operational conditions (carbonization temperature and residence time) to impose subsequently in other future researches on this HTC prototype reactor.

The carbonization condition followed for all these experiments was to keep the internal temperature for about **4 hours** with temperature of **200°C** for the first test, **190°C** for the second one, **180°C** for the third one and finally **170°C** for the last one. As soon as the inner temperature was kept for that duration with the respective temperature previously listed, the heat of the heating mantle was switched-off. This means that the total residence time is different for each experiments: longer residence time for higher temperature.

In the following ***Table 45***, these four tests with the same TS are all summarized with the relative information, regarding the date and time of their execution and a brief description.

Tests of biowaste	***Beginning (Date - Time)***	***End (Date - Time)***	***Description***
7	13.05.2013 – 09:45	13.05.2013 – 23:10	*Test 1* ***- T1=200°C*** with TS = 4.9% (3.6kg)
8	21.05.2013 – 10:32	21.05.2013 – 21:55	*Test 2* ***- T2=190°C*** with TS = 4.9% (3.6kg)
9	23.05.2013 – 11:09	23.05.2013 – 21:05	*Test 3* ***- T3=180°C*** with TS = 4.9% (3.6kg)
10	27.05.2013 – 11:18	27.05.2013 – 19:30	*Test 4* ***- T4=170°C*** with TS = 4.9% (3.6Kg)

Table 45: *Tests carried out with biowaste varying the temperature with the same TS*

5.2.2.1 Test 1 with T1 = 200°C

This test of the second series of experiments carried out with food waste consisted to keep the inner temperature for approximately 4 hours at around **200°C**; in other words, this particular trial foresaw the repetition of test called *Biowaste 2 with TS=4.9%* previously described, which it worked with the same conditions.

The next ***Figure 53*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded during the hydrothermal carbonization.

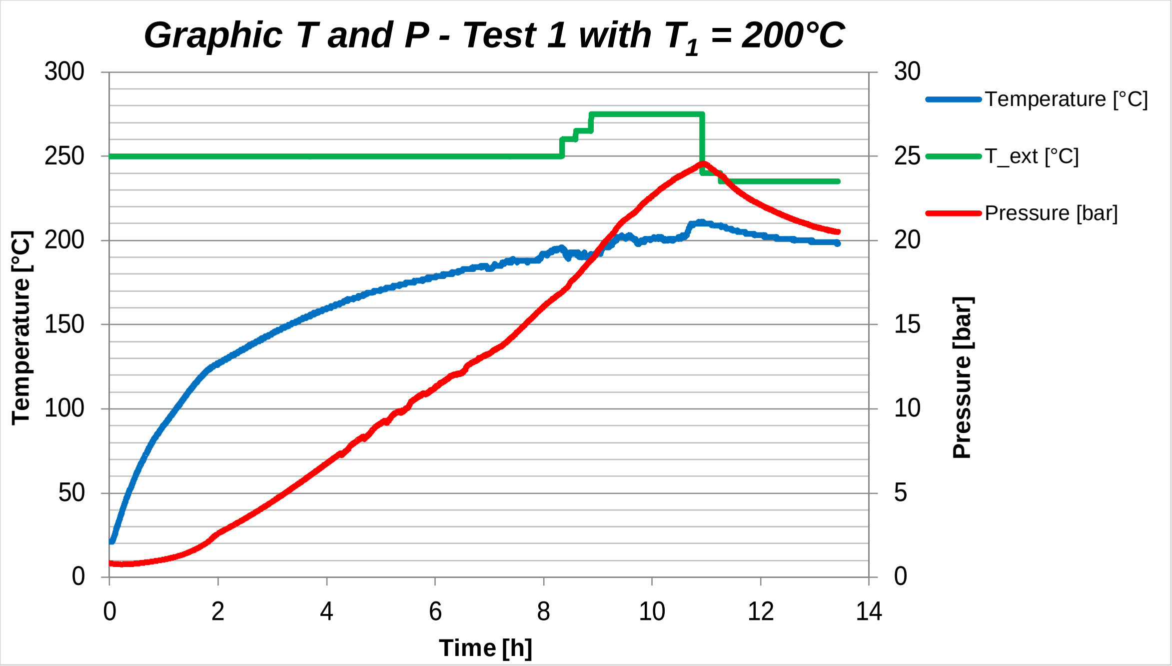

Figure 53: *Graph of temperature and pressure for Test 1 with T_1 = 200°C and TS = 4.9%*

The external temperature was imposed right from the beginning of the reaction at 250°C and then it was increased stepwise, as the inner temperature rose very slowly, up to 275°C, after about 9 hours from the start with temperature around 190°C. In this way, both internal temperature and pressure are increased, reaching the maximum value of 211°C for first one and 24.6 bar for pressure, after about 11 hours from the beginning of the HTC-process.

Then, the external temperature of the heating mantle was decreased at 235°C in order to slightly fall the inner temperature and to stabilize it around 200°C for the last 2.5 hours of the HTC-reaction (in total the internal temperature was around 200°C for approximately 4 hours). At the end of the process, more precisely after 13.4 hours, the inner temperature was 198°C while the pressure was 20.5 bar.

The carbonization time, i.e. total time above 180°C, was really long, 7.3 hours, started after 4.4 hours from the beginning of the reaction, unlike the test *Biowaste 2 with TS=4.9%* of 5.7 hours; whereas, the time with temperature around 200°C was approximately 4.2 hours, recorded after 9.3 hours from the beginning of the reaction.

Although this test worked with the same initial conditions, i.e. same TS and same external temperature imposed at the beginning of the reaction (250°C), presents some difference if compared to the previous test *Biowaste 2 with TS=4.9%*. In fact, both inner temperature and pressure of this *Test 1 with* T_1*=200°C* are increased very slowly during the reaction, reaching the temperature of 180°C only at 6.1 hours, unlike of 4.4 hours for *Biowaste 2*.

Therefore, this disparity in terms of temperature and pressure, between these two experiments is shown in the next ***Figure 54***.

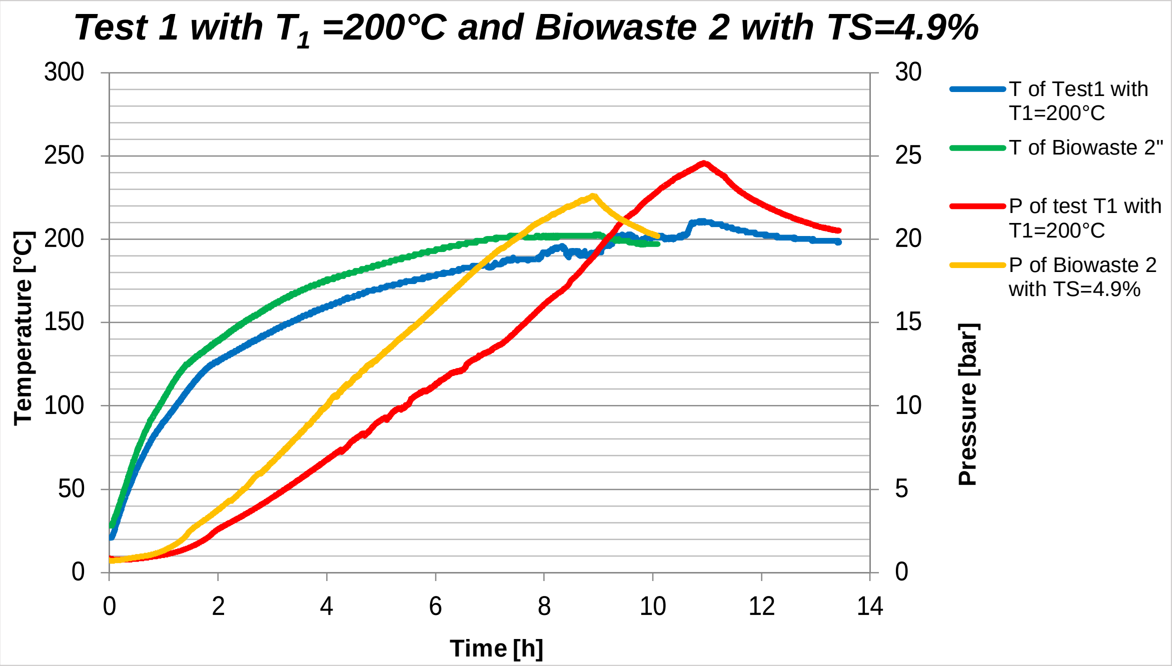

Figure 54: *Comparison between Test 1 with* T_1 *= 200°C (TS = 4.9%) and Biowaste 2 with TS = 4.9%*

From this graph it is possible to notice that the trend of inner temperature and pressure of *Test with* T_1*=200°C* is increased more slowly compared to what is occurred in the precedent experiment. This is probably due to a bad operation of heating mantle, because of dissipation of energy in the surrounding environment or its non-correct position around the reactor.

Anyway, their trend are quite similar but only moved lower down for internal temperature and a bit to the right for pressure, with about 2 hours' difference between *Test with T_1=200°C* and *Biowaste 2 with TS=4.9%* (the results of these two experiments are at the end compared in the outputs measurement and analysis).

In conclusion, the main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 46***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	13.4*
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1116*
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	13.4
Reaction Time	[h]	*Total time with inner temperature above 180°C*	7.3

Table 46: *Energy consumption and duration of Test 1 with T_1 = 200°C*

*(*these values are the results got only up to 12 hours then the energy program is automatically switched-off, so there are not the real and total consumptions for the whole length of this HTC-reaction)*

5.2.2.2 Test 2 with T2 = 190°C

This experiment, carried out with always TS equal to 4.9%, consisted to decrease the inner temperature, compared to previously test, at **190°C** and to keep this range of temperature for approximately 4 hours.

The next ***Figure 55*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded during the hydrothermal carbonization.

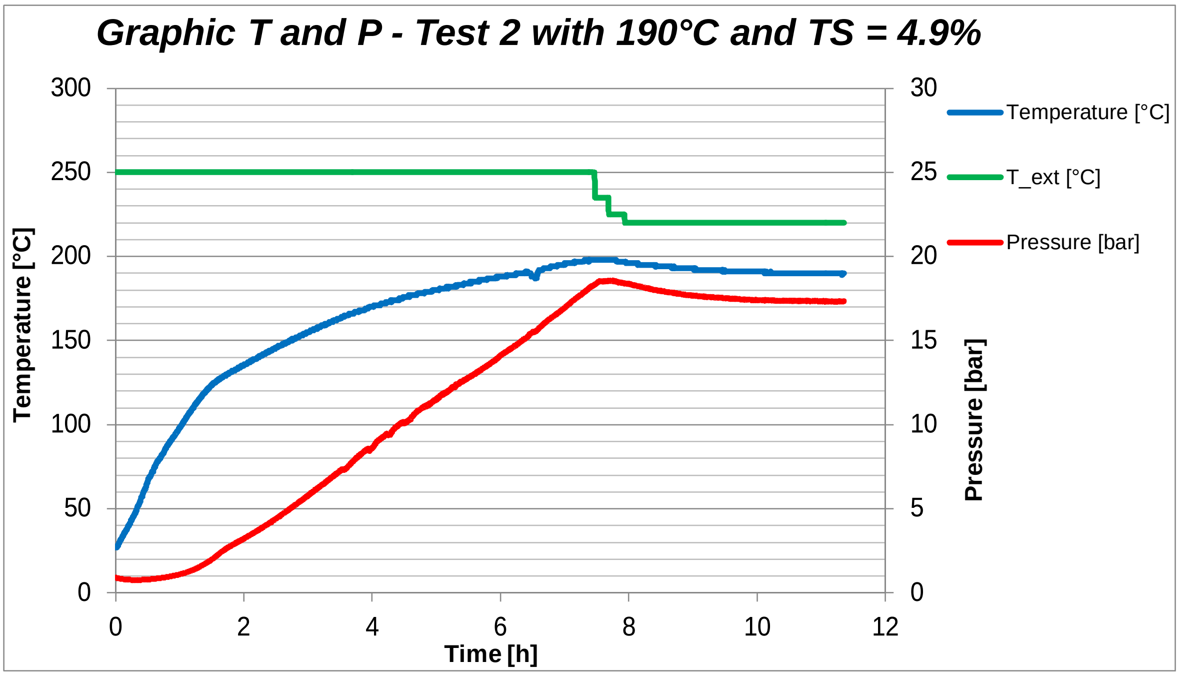

***Figure 55:** Graph of temperature and pressure for Test 2 with T_2 = 190°C and TS = 4.9%*

The inner temperature reached 190°C, for the first time, after 6.2 hours from the beginning of the HTC-reaction with the corresponding pressure of 14.7 bar. Subsequently, it decreased a bit, dropping up to 187°C for a smaller lapse of time of 6 minutes, although the external temperature was always imposed at 250°C and the pressure continually increased.

This reduction of internal temperature is probably due to the start of carbonization around the temperature sensor, caused by an inhomogeneous carbonization conditions inside the reactor, possible consequence of the absence of a stirring device, costly equipment that it was decided not to implement in this HTC prototype reactor, reducing as much as possible the total costs.

After this slightly decrease, the internal temperature rose up to 198°C (maximum temperature reached during the whole reaction) after 7.3 hours from the beginning of the HTC-process, with values of pressure around 18 bar (maximum pressure reached of 18.6 bar). At this moment, the external temperature of the heating mantle was reduced stepwise from 250°C to 220°C in order to keep the inner temperature below 200°C (never exceed it) and especially around the range of 190°C (condition imposed for this experiment).

In this way, both temperature and pressure gradually decreased and in particular, the internal temperature stabilized in that range until the end of the reaction. The final temperature recorded was 190°C while the relative final pressure was 17.3 bar.

The carbonization time, i.e. total time above 180°C, was 6.4 hours, started after 4.9 hours from the beginning of the HTC-reaction. In addition to this, the time with temperature around 190°C was approximately 4 hours, reached for the first time after 6.2 hours from the beginning.

Finally, the main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 47***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	12
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1132
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	11.3
Reaction Time	[h]	*Total time with inner temperature above 180°C*	6.4

Table 47: *Energy consumption and duration of Test 2 with* $T_2 = 190°C$

5.2.2.3 Test 3 with T3 = 180°C

This experiment consisted to further decrease the inner temperature at **180°C** and to keep this range of temperature for approximately 4 hours.

The next ***Figure 56*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded during the hydrothermal carbonization.

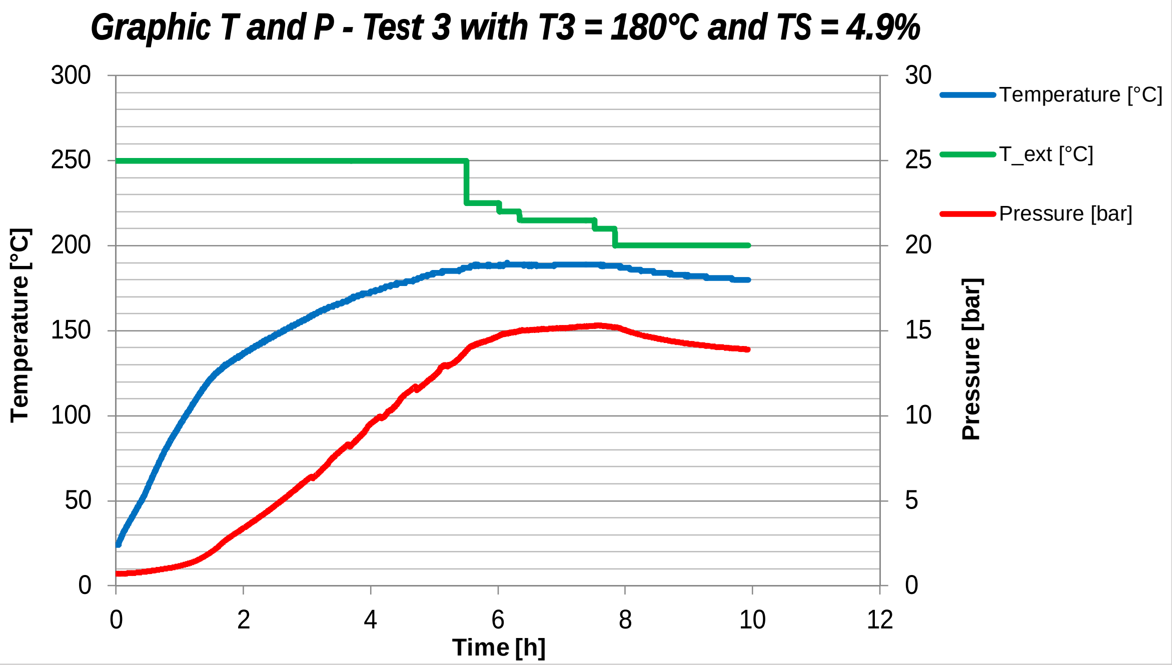

***Figure 56:** Graph of temperature and pressure for Test 3 with T_3 = 180°C and TS = 4.9%*

The external temperature of the heating mantle was reduced, for the first time, from 250°C to 225°C, after 5.5 hours from the beginning of the HTC-reaction, when the inner temperature reached the value of 187°C and the pressure was around 14 bar.

However, the internal temperature continually increased, reaching the maximum value of 189°C at 6 hours; for this reason, the external temperature was again decreased stepwise to 220°C and then to 215°C to try to keep the temperature below 190°C (never exceed this value) and to fall it around 180°C. Nevertheless, the internal temperature, instead of to drop, stabilized around 187°C for about 2.6 hours. In this experiment, it was not easy to adjust the external temperature of the electric heating mantle to control the temperature inside the reactor because the system is all manually regulated and especially its regulation is not directly with the inner temperature of the reactor.

Therefore, after 7.8 hours from the start of the HTC-process, the external temperature was finally reduced to 200°C for the last 2 hours, when the inner temperature was always around 187°C and the pressure was around 15 bar (maximum value reached of 15.3 bar after 7.6 hours). Only in this way, both internal temperature and pressure slightly decreased, reaching the final values of 180°C and 13.8 bar respectively, after 9.9 hours (total residence time).

More precisely, the carbonization time, i.e. total time above 180°C, was 5.3 hours, reached after 4.7 hours from the beginning of the reaction while the duration with temperature around 180°C, considering the range 178°C and 187°C, was only 3.2 hours.

In this case, the inner temperature reached values a bit higher compared to the condition of 180°C but it did not exceed the threshold of 190°C, ranging from 180°C to 189°C anyway.

Finally, the main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 48***.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	11.4
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1140
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	9.9
Reaction Time	[h]	*Total time with inner temperature above 180°C*	5.3

Table 48: *Energy consumption and duration of Test 3 with* T_3 *= 180°C*

5.2.2.4 Test 4 with T4 = 170°C

This last experiment of the second series of experimental tests consisted of decreasing the inner temperature at **170°C**, below the usual carbonization temperature fixed at 180°C, and keeping this range for approximately 4 hours.

In particular, the aim of this experiment was to discover if lower temperature could permit to have similar characteristics of HTC-coal in comparison with the previously tests carried out with the same TS, equal to 4.9%, and with the same carbonization condition, 4 hours with the respective temperatures.

The next ***Figure 57*** shows the graphic of the inner temperature (blue line) and pressure (red line), recorded during the hydrothermal carbonization.

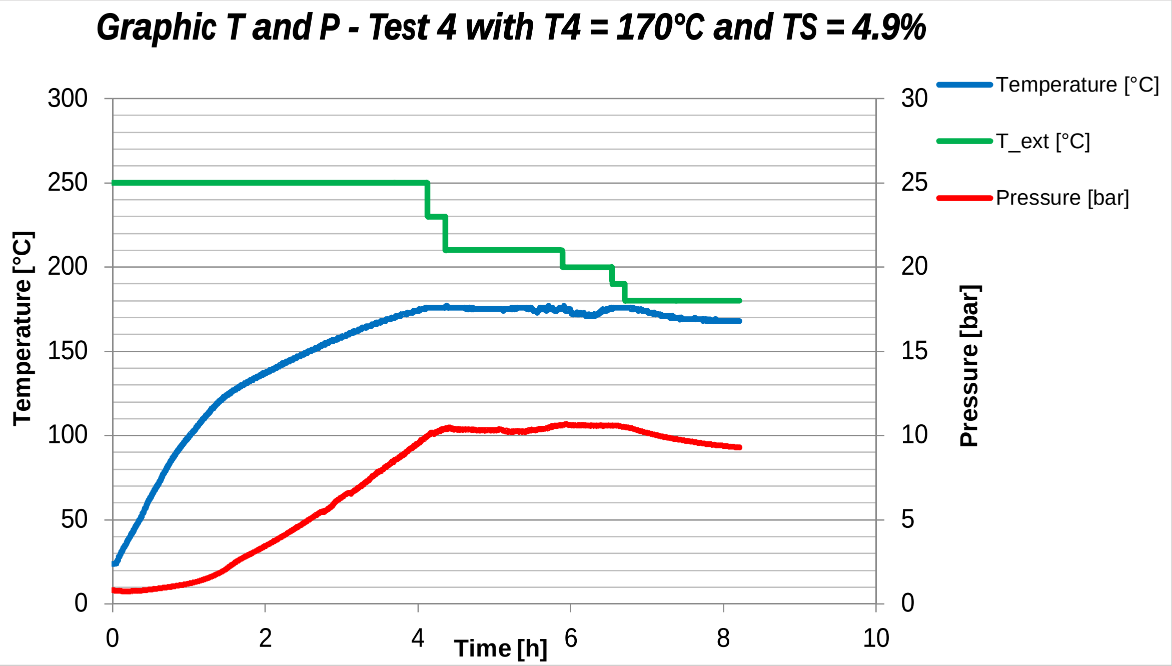

Figure 57: *Graph of temperature and pressure for Test 4 with* T_4 *= 170°C and TS = 4.9%*

The external temperature was decreased many times from 250°C to 180°C to try to keep the temperature inside the reactor around 170°C.

In particular, the inner temperature reached 170°C after only 3.6 hours from the beginning of the HTC-reaction, when the pressure was around 8 bar and the external temperature was imposed at 250°C. From this moment, the internal temperature slightly increased, reaching the maximum value of 177°C, after about 4 hours with the corresponding pressure of 10.4 bar. The temperature inside the reactor stabilized around this range for 1.6 hours, although the external temperature was decreased at 210°C. Therefore, in order to fall the inner temperature at values next to 170°C, the external temperature of the heating mantle was again reduced stepwise from 210°C to 180°C. During this time, the temperature firstly decreased around 170°C while the pressure increased, reaching the maximum value of 10.7 bar. Subsequently the inner temperature increased over again, reaching values around 176°C and pressure went up to 10.7 bar that it was also the maximum pressure reached during the whole HTC-reaction. Then, the trend of both temperature and pressure decreased, reaching the final values of 168°C and 9.3 bar respectively.

So, the internal temperature, as the ***Figure 57*** shows, stabilized around 175°C for approximately 3.8 hours, without never exceeding 180°C, while the pressure became stable around 10 bar for about 3 hours.

Finally, the main parameters of energy and power consumption of the heating mantle, as well as the duration of this HTC-reaction are summarized in the following ***Table 49***. In particular, unlike the other experiments carried out up to now, the inner temperature has never exceeded the threshold of 180°C, for this reason, the total time with inner temperature above 170°C was added in the table.

PARAMETER	UNIT	DESCRIPTION	VALUE
Energy Consumption	[kWh]	*Total electrical energy consumed by the heating mantle*	8.8
Average Power Consumption	[W]	*Average power consumed by the heating mantle*	1064
Total Experiment Time	[h]	*Time during which heat is supplied to the reactor*	8.21
Reaction Time	[h]	*Total time with inner temperature above 180°C*	0
Reaction Time 170°C	[h]	*Total time with inner temperature above 170°C*	3.8

Table 49: *Energy consumption and duration of Test 4 with* $T_4 = 170°C$

5.2.2.5 Outputs measurements and analysis

At the end of each experiments, carried out with biowaste on varying the inner temperature, one sample was taken from solids (HTC-coal) and liquids (process water) to analyze them, as in the preceding tests.

Therefore, the results of these measurements and analysis, for all these four tests, are thus summarized in the next ***Table 50***, in comparison with the characteristics of the original biowaste. In addition to this, in that table, it also reported the results of *Biowaste 2* with *TS* equal to *4.9%* in order to compare with those obtained from *Test 1 with* $T_1 = 200°C$, since these two experiments have followed the same carbonization conditions, approximately 4 hours with temperature around 200°C.

		Original biowaste	Biowaste2 **TS=4.9%**	Test 1 **T1=200°C** (TS=4.9%)	Test 2 **T1=190°C** (TS=4.9%)	Test 3 **T1=180°C** (TS=4.9%)	Test 4 **T1=170°C** (TS=4.9%)
In	Feedstock [kg]	-	3.6	3.6	3.6	3.6	3.6
	Water [L]	-	13.7	13.7	13.7	13.7	13.7
Out	HTC-coal (wet) [kg]	-	1.6	1.6	1.3	1.4	1.1
	Process water [L]	-	15.3	14.4	14.9	14.8	15.6
Solids	TS output [%]	-	20.6	21.6	27.6	23.4	26.7
	HHV [MJ/kg_{db}]	**19.3**	29.3	29.5	29.6	29.0	28.9
	C [$\%_{db}$]	**46.2**	67.2	67.8	68.3	67.4	65.0
	H [$\%_{db}$]	**6.5**	6.6	6.8	6.9	6.9	7.5
	O [$\%_{db}$]	**43.7**	24.7	20.8	23.4	25.3	28.3
	N [$\%_{db}$]	**2.2**	2.8	3.2	3.1	3.2	3.2
	H/C [Mol Ratio]	**1.689**	1.176	1.208	1.215	1.222	1.390
	O/C [Mol Ratio]	**0.709**	0.276	0.231	0.257	0.281	0.326
Liquids	pH [-]	-	3.5	3.6	3.8	3.6	3.6
	EC [µS/cm]	-	4439	5077	4983	2003	4953
	TOC [mg/L]	-	8381	9934	10254	11187	15860

Table 50: *Results of the measurements for all the tests carried out with the same TS on varying the inner temperature (db = dry basis)*

Firstly, it is important to notice that also in these experiments, as in the previous test, both the higher heating value and the carbon content of the original substrate are significantly increased after the hydrothermal carbonization. In fact, the calorific value is passed from 19.3 MJ/kg to **29.2 MJ/kg** on average (with an increase of 51.3%), while the carbon content from 46.2% to 67.1% on average (with an increase of 20.9%). The results, in general, of both higher heating value and carbon content of HTC-coals are very close to each other.

However, the values of HHV and C content for the second test with $T_2 = 190°C$ are slightly higher, 29.6 MJ/kg and 68.3% respectively, than the results of the first test performed with $T_1 = 200°C$, 29.5 MJ/kg and 67.8%. This slight difference between these two tests, it is unusual because high temperatures (in this case 200°C) should lead to higher reaction rates and so an increase of carbon content, compared to low temperatures (in this case 190°C).

The possible reason of these values, if we watch the respective trends of inner temperature carefully *(Figures 56 and 58)*, is that in test with $T_2 = 190°C$ the inner temperature stabilized around 190°C without undergoing noticeable variations during the HTC-reaction, whereas in test with $T_1 = 200°C$ the internal temperature increased and decreased continuously to reach only at the end temperature around 200°C. This means that not only the achievement of high temperatures influence the product's characteristics but also the way which these high temperatures are established inside the reactor.

In particular, the linear correlation between carbon content (C in %) and higher heating value (HHV in MJ/kg), for all the four tests, is shown in the next ***Figure 58***.

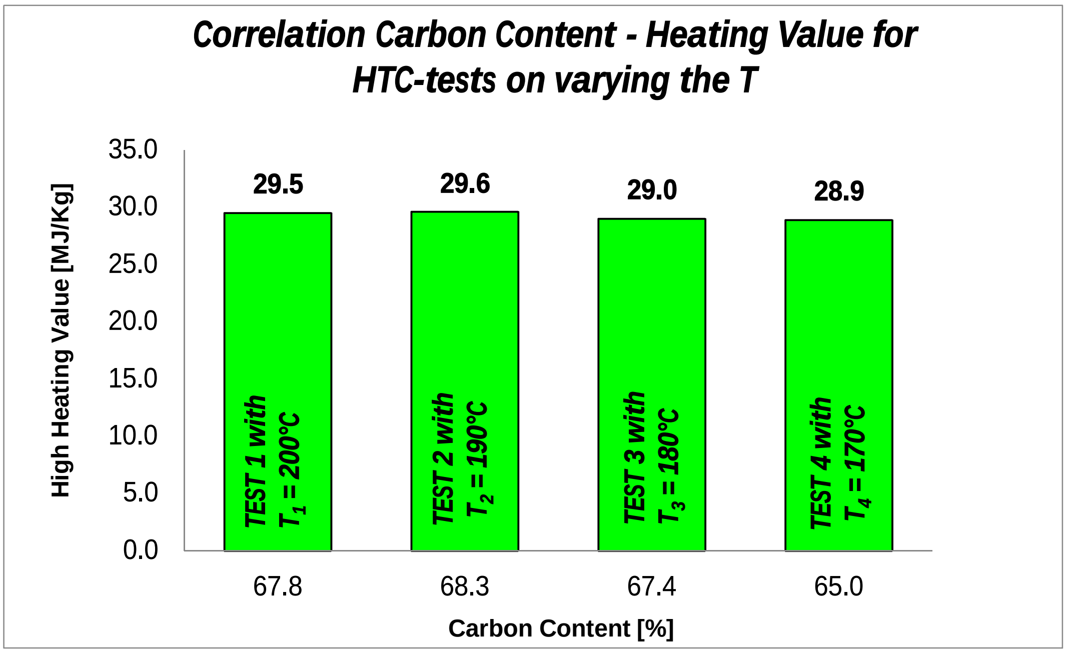

Figure 58: *Correlation carbon content and calorific value for the four tests carried out with biowaste on varying the inner temperature with the same TS=4.9%*

Moreover, also in this second series of experiments, as for the six preceding test carried out with food waste, only the oxygen content is decreased from 43.7% for the original biowaste to 24.4%, on average, for the HTC-coals produced (with a decrease of 19.3%) while, unlike the experiments with rice and in general with the literature, the hydrogen content is not decreased but it rose a little, from 6.5% to 7% on average.

Nevertheless, the hydrothermal carbonization caused, for all these four experiments, a decrease in the atomic ratios of H/C and O/C, as the literature reports, due to the dehydration and decarboxylation reactions during the process. In particular, the initial H/C and O/C ratios were 1.69 and 0.71 respectively before the HTC-reaction, while at the end of the process on average 1.23 and 0.27. In particular, the values of H/C and O/C ratios increase with decreasing of internal temperature, as the literature reports in the scientific revues.

As regards the N content is a bit increased if compared to the value of original biowaste but it is almost constant in all the experiments, about 3.2% for all the HTC-coals produced.

In particular, these values of H/C and O/C ratios are represented through a dot in the following coalification diagram, called also *Van Krevelen diagram*, ***Figure 59***.

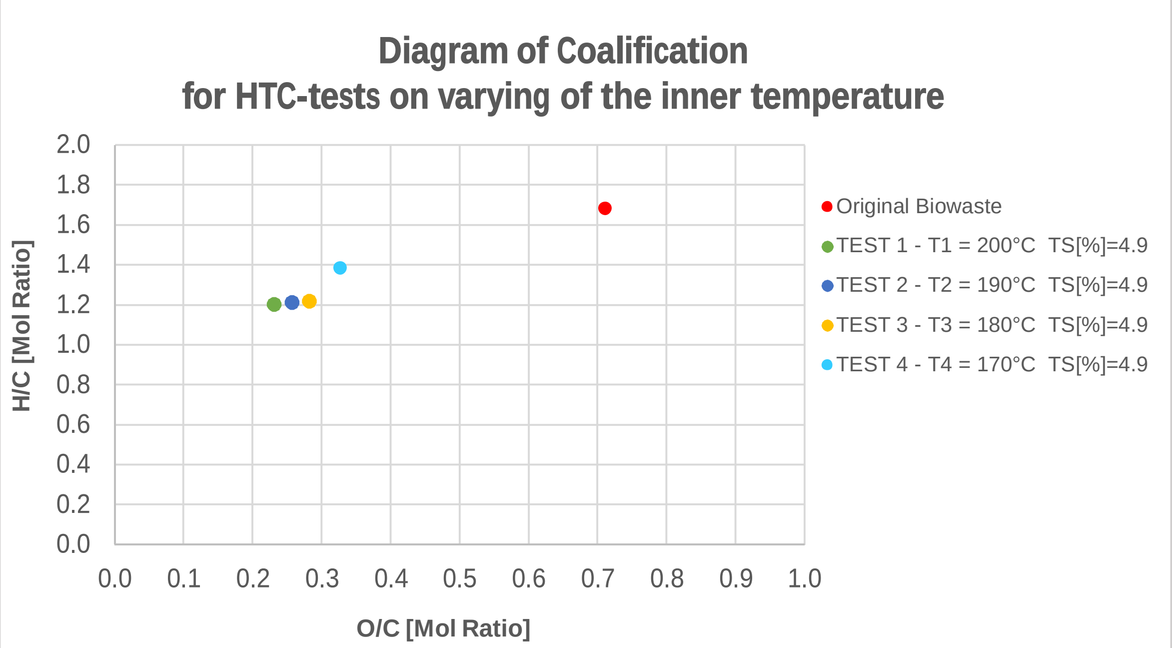

Figure 59: *Coalification diagram for the four tests carried out with biowaste on varying the inner temperature with the same TS=4.9%*

This diagram shows that both H/C and O/C ratios, for all the four tests, are decreased during the course of HTC-process, compared to the initial substrate, *Original biowaste*, depicted by a red dot in upwards right. Moreover, this representation of input and output values allows to visualize the degree and the intensity of carbonization; in fact the experiments carried out with higher temperatures have lower values of both H/C and O/C ratios, namely higher temperatures permit to reach higher carbon content in the HTC-coal produced. In particular, the dot relative to the last test with $T_4 = 170°C$ is placed a bit distant compared to the other dots, because, in this experiment, the inner temperature never exceed 180°C (the hydrothermal carbonization usually operates with temperature between 180-220°C because the first reaction, hydrolysis, starts just around 180°C). However, this dot is not so far from the other values, so it could be possible to have similar values with lower temperature only by adjusting the residence time that is with longer residence time, which allows achieving a complete reaction and thus a higher reaction severity. Finally, if we consider the lowest obtained values (H/C of 1.208 and O/C of 0.231) of the first test with inner temperature of 200°C are not so far away from the natural lignite range, namely, H/C of around 0.8-1.3 and O/C of around 0.20-0.38. Therefore, these values suggest that a further carbonization of organic substrate (food waste) with temperature around 200°C could be increase the carbon efficiency but also to reach atomic ratios of H/C and O/C very close to the typical values of natural lignite.

In addition, the amounts of wet HTC-coal, obtained from each tests with food waste on varying the inner temperature, are decreased with the drop of temperature reached inside the reactor. More especially, from the maximum amount of 1.6 kg for the first test with $T_1 = 200°C$ to the minimum amount of 1.1 kg for the last one with $T_4 = 170°C$. There is however a very little difference of 0.1 kg between the second and third tests, $T_2 = 190°C$ and $T_3 = 180°C$, but it is probably due to the manual emptying procedure.

With reference to the process water, the pH is acid with value equal to 3.6 for almost the four experiments, while the values regarding the EC (electro conductivity) range from 2003 μS/cm for *Test 3* with $T_3 = 180°C$ to 5077 μS/cm for *Test 1* with $T_1 = 200°C$.

Finally, the values of TOC (Total Organic Carbon) for the process water are increased in each tests with the drop of inner temperature, ranging from 9934 mg/L for the first test with $T_1 = 200°C$ to 15860 mg/L for the last one with $T_4 = 170°C$. This increase of TOC with low temperature is due to the fact that temperature, decisive process parameter, influence also the carbon distribution in three phases (solid – liquid – gas): higher temperatures increase reaction severity and carbon content of the HTC-coal produced, i.e. the carbon efficiency (CE).

In particular, the trend of these values of TOC, for all the four tests, is depicted in the following ***Figure 60***.

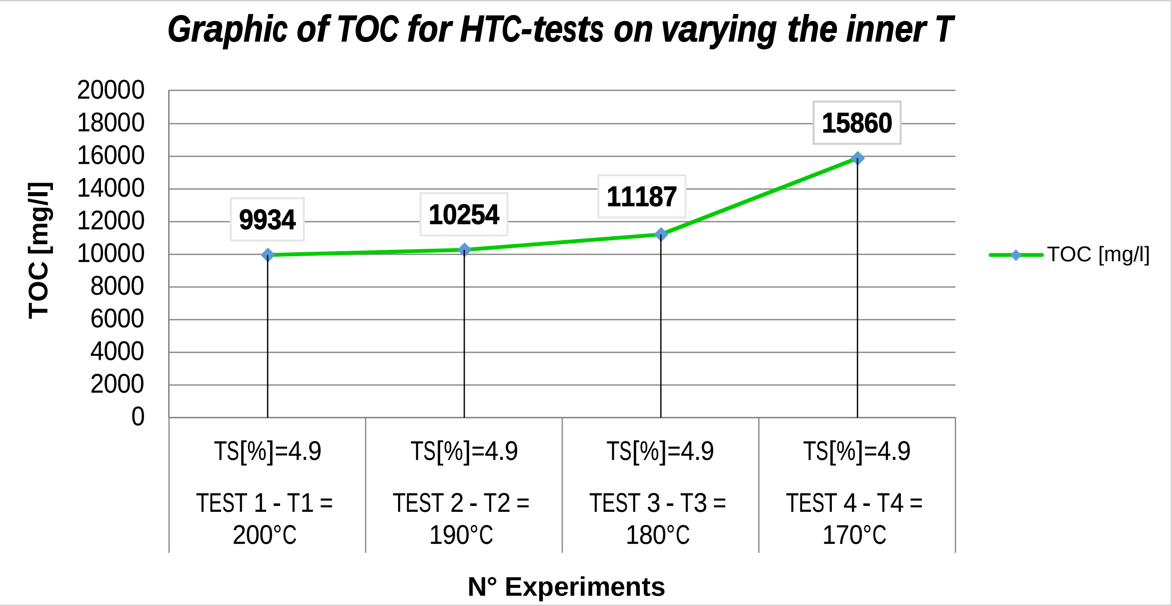

Figure 60: *Graph of TOC for all the tests carried out with biowaste on varying the inner temperature*

It is important to remember that these values of TOC conducted at Eawag (*Shimadzu TOC-L, 720°C catalytic combustion)* are too high to calculate the carbon mass balance because this method did not plan the pre-treatment of centrifugation of process water, before to analyze it.

From these measurements of outputs, it was possible to calculate other parameters (data processing), which further characterized the HTC-reaction. These results are thus summarized in the following ***Table 51*** *(see the relative formulae in the previous Table 34).*

Parameters	**Test 1 – T1 = 200°C** (TS=4.9%)	**Test 2 – T1 = 190°C** (TS=4.9%)	**Test 3 – T1 = 180°C** (TS=4.9%)	**Test 4 – T1 = 170°C** (TS=4.9%)
Solid yield [% dry basis]	41.44	44.81	41.66	35.65
Reaction severity [-]	0.28	0.22	0.18	-
Carbon efficiency (CE) [%]	60.8	66.2	60.7	50.2
Carbonization time (above 180°C) [h]	7.3	6.4	5.3	0
Total reaction time [h]	13.4	11.3	9.9	8.2

Energy content of HTC-coal [kWh]	2.8	3.0	2.7	2.3
Energy consumed [kWh]	13.4	12	11.4	8.8

Table 51: *Results of analysis from measurements of the outputs of tests on varying the inner temperature*

As the ***Table 40*** shows, the values of solid yield for all the experiments are close to each other, ranging from 35.65% for *Test 4 with T_4 = 170°C* to 44.81% for *Test 2 with T_2 = 190°C*. These values are comparable with the value obtained in Biowaste 2 with TS equal to 4.9%, as these four experiments. As regards the carbon efficiency (CE), the results are almost equal for the first three experiments, around 60%, while for the last test with the lowest temperature of 170°C is lower, 50.2%.

Although the first test is carried out with high temperature, both solid yield (41.44%) and carbon efficiency (60.8%) are lower than the second test (44.81% and 66.2% respectively) with inner temperature of 190°C, probably due to the noticeable variations during the HTC-reaction for the purpose of reaching temperature around 200°C inside the reactor.

The reaction severity, defined by temperature and residence time, is decreased with the drop of temperature and the decrease of time with temperature above 180°C, ranging from 0.28 for *T_1 = 200°C* to 0.18 for test with *T_3 = 180°C* (it does not make sense to calculate the reaction severity for the last experiment because it carried out with temperature below 180°C and this formula require the carbonization time that is the time with temperature above this range). Similarly, the energy consumed is gradually decreased from 13.4 kWh for the first test to 8.8 kWh for the last one, this means that lower temperature and lower total residence time required lower energy supply.

The HTC-coal produced has a total energy content around 2.7 kWh, ranging from **2.3 kWh** for the last experiment with the lowest temperature to **3.0 kWh** for the second one with temperature of 190°C; finally, this average value is also about one fourth of the energy required for the reaction (on average 11.4 kWh).

5.3 Global results and discussion

All the experiments carried out with biowaste, both tests on increasing the Total Solids (TS) and tests on varying the inner temperature, produce HTC-coals with comparable characteristics to each other, in terms of elemental analysis (i.e. CHON measurements) and higher calorific values *(see in the next page the* ***Table 52*** *in which all the results obtained are summarized)*. In fact, as regard the carbon content, obtained in all the performed tests, ranges from **65.0%** to **68.5%** (with 66.8% on average) compared to the initial C content of biowaste equal to 46.2% while the higher heating value varies from **28.3 MJ/kg** to **30 MJ/kg** (with 29.1 MJ/kg on average) in comparison with the initial upper heating value equal to 19.3 MJ/kg. Therefore, after HTC-process, the values of carbon content and higher heating value are increased of 20.6% and 46.2%, respectively. In particular, the two lower values of carbon content (65.0%) have been gotten in *Biowaste 6 with TS = 15.2%* for the first series and in *Test 4 with T4 = 170°C* for the second series of experiments. This is due to the trend of the inner temperature during the HTC-reaction; more precisely, when the internal temperature did not stabilized to a determined value for a long times (minimum 4 hours) because of the continuous various of temperature that is an incessant little changes in temperature (i.e. increase and decrease), as in *Biowaste 6*, or also when the inner temperature did not reach high temperature (below 180°C), as in the last test carried out with *T4 = 170°C.* This means that it is very important not only to reach higher temperature during the whole HTC-reaction but also to keep the inner temperature stable for a long times. In fact, although the internal temperature in *Biowaste 6 with TS = 15.2%* reached values above 190°C (maximum temperature of 193°C) and total time with temperature above 180°C of 3.4 hours, the carbon content is low, equal to 65.0%, as in *Test 4 with T4 = 170°C.*

In general, all the HTC-coals produced, through this prototype reactor, have values of carbon content comparable to those of natural lignite (brown coal), with range around 60-70%, but they have a higher calorific value in comparison to this particular type of coal, 29.1 MJ/kg instead of 24 MJ/kg (around 6000 Kcal/kg). In addition to this, the values of HHV of all the coals produced are more similar to those of bituminous coal, also known as black coal, with values of higher heating value ranging from 26 MJ/kg to 30 MJ/kg, although it presents a low carbon content (ranging from 65.0% to 68.5%) compared to this particular coal rank (ranging from 80-90%).

		Original biowaste	**Biowaste1 TS=2.5%** (200°C)	**Biowaste2 TS=4.9%** (200°C)	**Biowaste3 TS=7.4%** (200°C)	**Biowaste4 TS=9.4%** (200°C)	**Biowast5 TS=12.8%** (200°C)	**Biowast6 TS=15.2%** (200°C)	**Test 1 T1=200°C** (TS=4.9%)	**Test 2 T1=190°C** (TS=4.9%)	**Test 3 T1=180°C** (TS=4.9%)	**Test 4 T1=170°C** (TS=4.9%)
IN	Feedstock [kg]	-	1.8	3.6	5.3	6.8	8.3	9.8	3.6	3.6	3.6	3.6
	Water [L]	-	14.6	13.7	12	11	8.2	7	13.7	13.7	13.7	13.7
OUT	HTC-coal (wet) [kg]	-	0.4	1.6	2.8	3.8	4.5	5.9	1.6	1.3	1.4	1.1
	Process water [L]	-	16.2	15.3	14	12.8	11.2	9.7	14.4	14.9	14.8	15.6
SOLIDS	TS output [%]	**-**	33.8	20.6	21.3	19.8	22.9	23.4	21.6	27.6	23.4	26.7
	HHV [MJ/kg_{db}]	**19.3**	30.0	29.3	29.0	28.3	28.9	29.2	29.5	29.6	29.0	28.9
	C [$\%_{db}$]	**46.2**	68.5	67.2	66.8	66.2	66.8	65	67.8	68.3	67.4	65.0
	H [$\%_{db}$]	**6.5**	6.8	6.6	6.6	6.8	6.7	6.8	6.8	6.9	6.9	7.5
	O [$\%_{db}$]	**43.7**	23.2	24.7	24.4	24.7	24.4	26	20.8	23.4	25.3	28.3
	N [$\%_{db}$]	**2.2**	2.6	2.8	3.1	3	3	3	3.2	3.1	3.2	3.2
	H/C [Mol Ratio]	**1.689**	1.198	1.176	1.181	1.232	1.210	1.260	1.208	1.215	1.222	1.390
	O/C [Mol Ratio]	**0.709**	0.254	0.276	0.273	0.280	0.274	0.300	0.231	0.257	0.281	0.326
LIQUIDS	pH [-]	-	3.5	3.5	3.5	3.5	3.5	3.4	3.6	3.8	3.6	3.6
	EC [µS/cm]	-	2615	4439	6233	7840	9446	10577	5077	4983	2003	4953
	TOC [mg/L]	-	5037	8381	9818	13542	18784	17430	9934	10254	11187	15860

Table 52: *Total results of the measurements for all the tests carried out with biowaste (db = dry basis)*

More precisely, the higher heating value is an important parameter to consider if the solid product of hydrothermal carbonization, hydrochar, is specially used as a combustible because this measurement represents the amount of heat produced and released during combustion, so it allows determining how efficient and effective the HTC-coal is.

Therefore, these high values of HHV of all hydrochars, obtained from food waste, confirm that the solid product can be used as an energy carrier, especially in developing countries, substituting in these poor areas traditional fuels, like fossil coal or firewood, contributing at the same time to avoid deforestation and to improve energy conditions.

In the next ***Table 53*** the higher heating value (HHV in MJ/kg) of HTC-coals obtained during these ten experiments are compared to those of other usual solid fuels, as wood and charcoal. In particular, it also compared with the classification (ranks) of coal from peat to anthracite and also with the values obtained using raw rice in the preliminary tests, discussed at the beginning of *chapter 5*.

SOLID FUEL	***HHV [MJ/kg]***
HTC-coal from Food waste	***28.3 - 30***
HTC-coal from Raw rice	*27*
Dry Wood	*14.4 - 17.4*
Charcoal	*27 - 33*
Peat	*13.8 - 20.5*
Lignite (brown coal)	*24*
Sub-bituminous coal (black lignite)	*26*
Bituminous coal (black coal)	*26 - 33*
Anthracite	*35*

Table 53: *Comparison between HTC-coal and other solid fuels in terms of higher heating value*

(Values from http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html)

Moreover, in all the experiments carried out in this research, the amount of dry HTC-coal is smaller than the amount of dry biowaste, namely the solid dry mass is reduced during the carbonization. This is a consequence of the chemical dehydration reaction of the biomass during the HTC-process; therefore, more water (process water) than at onset is found at the end.

As regards the energy consumed during the whole HTC-reactions with biowaste is on average equal to **11.4 kWh**, ranging from the minimum value of 8.8 kWh for *Test 4 with T4 = 170°C* (due to the low temperature reached during the process and low total reaction time) to the maximum value of 13.4 kWh, measured for two tests *Biowaste 1 with TS = 2.5%* and for *Test 1 with T1 = 200°C* (due to the high temperatures reached during the reactions, 207°C and 211°C, respectively). The energy consumed for the first test of series on increasing the TS, with heat applied approximately 10 hours and temperature around 200°C, is almost remained similar for all the six experiments while for the second series of tests on varying the inner temperature, the energy consumed is decreased with the drop of temperature and with low length of the HTC-process (i.e. total residence time).

Finally, regarding the average power consumption of the heating mantle is around **1100 W** for all the experiments carried out with food waste; its trend is not substantially changed with both increase of TS and decrease of temperature.

All the results concerning the energy consumption are summarized in the following ***Table 54*** and ***Table 55***.

	Biowaste1 TS=2.5%	**Biowaste2** TS=4.9%	**Biowaste3** TS=7.4%	**Biowaste4** TS=9.4%	**Biowaste5** TS=12.8%	**Biowaste6** TS=15.2%
Energy consumed [kWh]	13.4	11.8	11	11.6	10.5	10
Average Power Consumption [W]	1231	1167	1075	1104	998	916

Table 54: *Global results of energy consumption for all the six tests increasing the TS*

	Test 1 with T1=200°C (TS=4.9%)	**Test 2 with T1=190°C** (TS=4.9%)	**Test 3 with T1=180°C** (TS=4.9%)	**Test 4 with T1=170°C** (TS=4.9%)
Energy consumed [kWh]	13.4	12	11.4	8.8
Average Power Consumption [W]	1116	1132	1140	1064

Table 55: *Global results of energy consumption for all the four tests on varying the inner temperature*

CONCLUSIONS

Hydrothermal carbonization (HTC) is an interesting thermochemical conversion process, capable of converting biomass with high moisture content (values of 75–90%) in a few hours into a solid product, called hydrochar or HTC-coal, namely into a coal-like material, through the action of water under moderately high temperatures (180-220°C) and pressures (20-35 bar) in a closed pressure vessel.

The solid product, that is the main output with these conditions after HTC-reaction, is a carbon-rich substance and it possesses numerous noteworthy applications, thanks to its properties such as high carbon content, high heating value and accordingly high energy density, compared to the original feedstock, that make this technology attractive for use. In fact, HTC-coal can be used as a renewable combustible, a soil amendment (increasing soil fertility, enhancing water-holding capacity, and so on), a functionalized carbonaceous material (especially for water purification purposes, e.g. adsorption of pollutants), a carbon sequestration technology (mitigating thus climate change but only if the HTC-coal is not used as an energy carrier) and, finally, for a wide range of other electrochemical and catalytic functions.

This technology can be furthermore applied on various sources of feedstock without the need for an energy-intensive drying process (pre-treatment) before or during the HTC-reaction, unlike the usual thermochemical processes (e.g. dry pyrolysis, gasification, etc.). This is another great advantage of this method, allowing thus to open up the field of potential input materials to a variety of non-traditional sources, such as wet material manures, human waste, sewage sludge, municipal solid waste, as well as aquaculture and algae residues.

Therefore, HTC is seen as a promising and innovative technology able to convert wet biomass into a coal-like material, energetically comparable to natural coal. In addition to this, the HTC-process is also seen as a potential methodology, capable of treating problematic biomass like biowaste (i.e. waste organically decomposable, for example food waste), sewage sludge, faecal sludge or industrial waste, converting all them in an output product sterile and hygienic, thanks to the high process temperatures than can destroy pathogens and potentially organic contaminants. In this way, the hydrothermal carbonization could bring improvements of hygienic conditions, especially in developing countries, where an inadequate collection, treatment and uncontrolled disposal of those kinds of waste lead to serious health and environmentally problems. On this subject, the HTC-process can allow to transform any kind of biodegradable waste into value, namely into a stable, solid and transportable solid fuel that can be seen as a promising energy source for the future.

For all these reasons, wide field of applications, great number of advantages and possible benefits of hydrochar, a simple HTC prototype reactor for research purposes was designed and constructed at *Eawag/Sandec* (Switzerland) to assess the suitability of this technology for treatment especially of biowaste and/or faecal sludge in developing countries.

In particular, the aim of this study was to test, for the first time, the constructed HTC-reactor with food waste from the canteen and then to analyze and compare the end-products obtained, determining the potentiality of that substrate (organic fraction) for hydrothermal carbonization. More specifically, this research was focus on study of the HTC-coal used mainly as an energy carrier in developing countries, substituting traditional fuels (i.e. fossil coal, wood and charcoal) contributing at the same time to avoid the major environmental problem of deforestation. In this way, through several experiments with different solid loads and different inner temperatures, it was possible, in this study, to (1) understand the optimal operational parameters, in terms of carbonization temperature and residence time and (2) the changes of hydrochar with the decrease of temperature (valuation of physical, chemical and thermal properties of the HTC-coal), but especially (3) the maximum amount of biowaste per batch to be treated in this HTC-prototype to have thus a final positive energy balance.

In all these experiments carried out with food waste, both high values of upper heating value and carbon content, on average **29.1 MJ/kg** and **66.8%** respectively, were found in all the HTC-coals after the hydrothermal carbonization in comparison to the original feedstock, corresponding to 19.3 MJ/kg and 46.2%. Therefore, in general, the values of carbon content and also the values of atomic ratios H/C and O/C were shown to be similar to those of natural lignite (brown coal) but the high values of calorific value are more comparable to those of bituminous coal (black coal).

However, in tests *Biowaste 6 with TS=15.2%* and in *Test 4 with* $T_4=170°C$ the carbon content was the same and it was also the lowest (65.0%) in comparison with the other results because of the low temperatures reached, below 200°C, inside the HTC-reactor. In fact in the first one, the inner temperature rose up 193°C while in the second one the temperature was always around 170°C. In addition to this, in these two experiments, the values for H/C and O/C in HTC-coal were shown to be slightly higher (1.26 and 0.30 for the first one; 1.39

and 0.33 for the second one) than the other ones and also than in natural lignite, especially for H/C ratio, since the natural lignite range is for H/C around 0.8-1.3 and O/C around 0.2-0.38. These results suggest that a further carbonization of food waste for these two tests is indispensable in order to reach a higher carbon content and a decrease of the atomic ratios, comparable with the other experiments carried out with temperature around 200°C.

Moreover, through the six experiments with different solid loads, it was possible to discover that the maximum amount of biowaste that can be treated, in this specific HTC-prototype reactor of 21 L, is **9.8 kg** with total solids equal to **15.2%**, exactly in test called *Biowaste 6* in this report. This amount of organic waste lets also to have a positive energy balance, which is a larger energy content of HTC-coal, **11.3 kWh** compared to the energy consumed of 10 kWh (precisely 9.97 kWh) during the whole HTC-reaction (10.8h). However, in this test, the amounts of initial food waste (9.8 kg) and water (7 L) did not allow to reach the internal temperature of 200°C because of the rapid growth of pressure above 29 bar. More precisely, the inner temperature stabilized only around 170°C with pressure of 28.9 bar for the last 2 hours, due the necessary drop of external temperature of heating mantle in order to keep the inner pressure below 30 bar, seeing that the maximal pressure allowable for the prototype is exactly 30 bar (we did not want that the overpressure valve opened during all the HTC-reactions, because this valve is used only as a safety device and not as a pressure regulation device; therefore, it should be avoided to reach the maximal pressure of it). Although the total time above 180°C was about 3.4 hours in test *Biowaste 6*, the elemental analysis regarding the percentage of carbon (C) was lower, only 65%, if compared to the other experiments performed with the increase of total solids, 67% on average. In particular, this value, as already mentioned, is the same of that obtained in the last test, precisely in *Test 4 with* T_4*=170°C,* in the second series of experiments carried out with the decrease of internal temperature. So, it would be useful to test again the HTC-reactor with an amount of food waste between 8.3 kg *(Biowaste 5)* and 9.8 kg *(Biowaste 6)* to assess if the internal temperature reaches 200°C with a lower pressure but with the same positive energy balance.

It follows that it is important not only to reach high inner temperatures but also to keep it stable for the whole HTC-reaction without noticeable variations, in order to increase as much as possible the carbon content of HTC-coal and, accordingly, the higher heating value.

In general, it is difficult to make direct comparisons between experimental results from different studies and those obtained in this work, since temperature, pressure, reaction time, reactor design, feedstock and solids concentration significantly influence carbonization process. Nevertheless, all the values, attained during this research, regarding the proximate and ultimate analysis of initial food waste and produced hydrochars, especially for higher heating value and elementary analysis (C, H, O and N), are similar to those obtained and reported in a study of *Berge et al. (2011)*. More precisely, the average of upper heating value, 29.1 MJ/kg, obtained in these ten experiments carried out with food waste, is exactly the same of that reported by *Berge et al.* (*2011)* and also the elemental analysis is comparable with that study, especially for the carbon content, 67.6% compared to our 66.8% on average, obtained during this experimental work.

Then, in order to make the HTC process attractive in developing countries, further investigations are needed to understand, firstly, if the elemental analysis with another type of organic fraction (since the biowaste's composition goes on changing from season to season and year to year especially in developing countries) is similar to those obtained in this experimental research and, secondly, if the values of upper heating value are always higher than those of brown coal, with the purpose to use the final HTC-coal as alternative combustible to the firewood.

The optimal operational parameters for this HTC prototype reactor, in terms of carbonization temperature and residence time, with the purpose of increasing the carbon content in the hydrochar, are a stable inner temperature around **200°C** for a total residence time of about **10 hours**; in this way, the carbonization time, i.e. total time with temperature above 180°C, is about 6 hours, like the experiments carried out with food waste in this study. It is not worth to reach lower temperatures inside the reactor, because, firstly, lower carbonization temperatures take in general lower carbon content and as a result lower higher heating value; secondly, the energy consumed, measured continuously in these ten experiments, was always on average around 11.4 kWh, without noticeable decrease of energy with the relative decrease of internal temperatures.

Moreover, the results regarding the higher heating value (HHV) are very promising, especially if the HTC-coal is used in developing countries as an energy carrier, substituting, thus, traditional fuels with this bio-coal, and guaranteeing, at the same time, the daily energy needs of most people that live in these nations. In addition to this, the HTC-process can bring other improvements in soil fertility and productivity if the hydrochar is used as a soil amendment but also better conditions of life-style of the people in these poor areas, thanks to a better management of biowaste or faecal sludge, through the hydrothermal carbonization.

However, even though this HTC prototype reactor was designed and built for application in developing countries in a simple system with a relative low cost and complexity in comparison to other HTC experimental reactors of a similar volume, it requires high temperatures and high pressures to work, which implies some rigorous requirements with respect to the materials (stainless steel), construction procedure (welding) and additional instruments (e.g. overpressure valve, drain valve, temperature and pressure sensors). In fact, all materials, design and construction procedure must have made by qualified personal; moreover, at the end of its building, the HTC prototype unit needs to be supervised and certified by an entitled authority in order to assure the safety of the reactor in conformity to the directives.

All these necessary requirements probably are not available in all developing countries; therefore, to date, this novel thermochemical conversion process, although can bring improvements through the use of hydrochar, cannot be defined completely as an appropriate technology because of lack of specialized personal, difficulty of retrieval of materials, final total cost that it is still high and, finally, the necessary electric power to heat the heating mantle around the reactor is might an issue in developing countries.

Furthermore, even though the hydrothermal carbonization is described as an exothermic process, the HTC-conversion, during all the performed experiments carried out with food waste, was continuously heated through the electric heating mantle, i.e. external energy was always required to sustain the process. This is probably due to the fact the reaction conditions (about 200°C and 10h) used in these tests were lower than those (240°C with solid load of 20%) used in the study by *Funke et al. (2011)* with the purpose to determine the heat released during hydrothermal carbonization. In fact, in theory, the reaction becomes exothermal for more severe reaction conditions, namely higher temperature and longer residence time. Therefore, during our ten tests at that conditions, the amount of energy released was probably too small and, so, insufficient to self-sustain the whole conversion process: it is probably the main cause of the increase of inner temperature when the external temperature of the heating mantle is decreased or kept stable at determinate range of temperature during the HTC-reaction *(*see for example the test called *Biowaste 3 with TS=7.4%).*

Another problematic of this thermochemical conversion, which complicates its use in developing countries, as well as the requirement of energy supply, is the large amount of process water after HTC-reaction. This liquid phase has generally, depending on feedstock sources, a high load of organic compounds, i.e. high levels of COD and TOC, and for this reason, it requires post-treatment before to be discharged. Different studies state that the process water can be processed with biological (aerobic or anaerobic) treatment to lower the TOC significantly; in fact, according to *Berge et al. (2011)* the BOD/COD ratio of the process water is usually >0.3, confirming that it is amenable to subsequent biological treatment. Although, to date, the post-treatment remains an issue in low-income countries, different team-researchers are looking into the potential of using the HTC-water energetically. In fact, a possible solution to minimize the energy consumption, as well as to keep the consumption of fresh water low, is to re-use the hot process water in the next batch, leading to enrichment and agglomeration of dry organic matter (DOM) and increase of solid yields. However, this recirculation of hot liquid phase is possible only in a multi-batch system (which is a more expensive technology than a single batch) where different HTC-reactors are connected to each other and can be operated in parallel.

To sum up, the main problematic aspects of this innovative thermal conversion process in developing countries are its construction, the energy requirements, the post-treatment of the process water and the need of water, given that the feedstock must necessarily be totally submerged in liquid water during the whole process under high temperatures and autogenous pressures for several hours. Therefore, before to implement this HTC methodology for a long-term in low-income countries, further researches must be carried out in order to solve those issues and obtain lower energy requirements, greater potential energy recovery and minimal environmental impacts.

The constructed HTC-reactor will then be further tested to find options for optimizing the system in terms of energy requirements with the use of photovoltaic panels, to avoid dependency on electricity from the grid. In addition to this, the HTC-reactor, based on the study regarding the energetic optimization, will probably be tested, in the near future, in a developing country (Tanzania) to study on-site construction and operational issue.

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It is following reported a series of bibliographical references relating to the texts expressly mention in this thesis and also other research materials, useful for an in-depth analysis, even though not directly related to a specific quotes.

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APPENDIX

A) RESULTS FROM EXPERIMENTS WITH BIOWASTE:

A1) *Elementary analysis (C, H, O and N), Total Solids and Higher Heating Value of Original Biowaste;*

A2) *Characteristics and amounts, before and after HTC, of all the 6 tests with the increase of Total Solids;*

A3) *Characteristics and amounts, before and after HTC, of all the 4 tests with the same TS=4.9% on varying on the inner temperature;*

A4) *Example of the final frame of the Energy consumption, recorded during the test Biowaste4 with TS=9.4% (this program is in German).*

B) MANUAL FOR USING HTC - REACTOR

A) RESULTS FROM EXPERIMENTS WITH BIOWASTE:

A1) *Elementary analysis (C, H, O and N), Total Solids and Higher Heating Value of Original Biowaste:*

	ORIGINAL BIOWASTE (12-04-13)	
	Sample 1	***Sample 2***
Tare [g]	44.3244	48.2594
Gross Weight [g]	69.674	72.7052
Net Weight [g]	50.0945	53.7431
TS [%]	22.76	22.43
TS Average [%]	22.60	
Higher Heating Value [J/g]	19543	
	19131	
Heating Value Average [J/g]	19337	
Ctot [%]	46.300	
	46.150	
Ctot Average [%]	46.225	
H [%]	6.480	
	6.530	
H Average [%]	6.505	
O [%]	44.560	
	43.160	
	43.460	
O Average [%]	43.727	
N [%]	2.105	
	2.203	
N Average [%]	2.154	

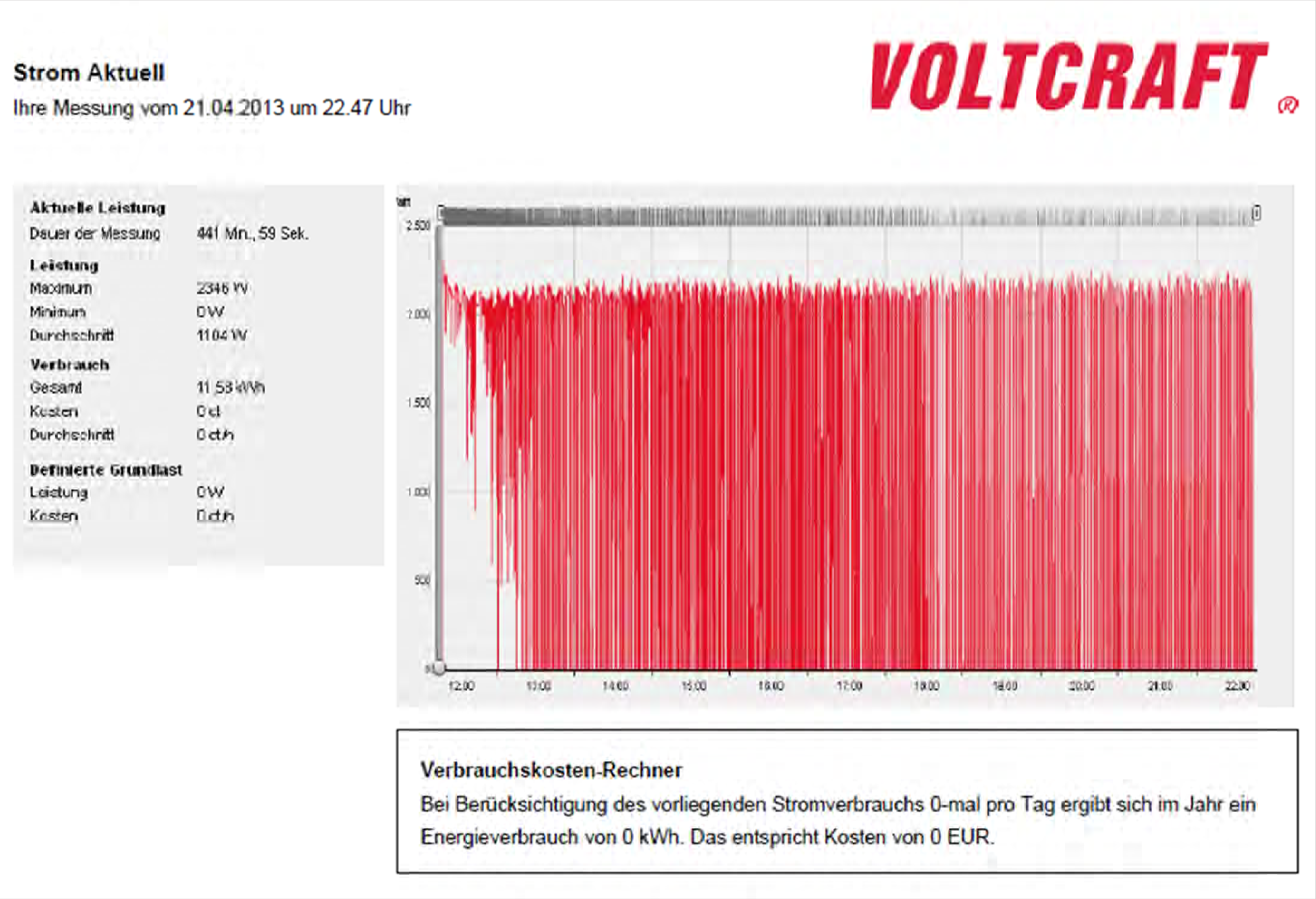
A2) *Characteristics and amounts, before and after HTC, of all the tests carried out with the increase of Total Solids:*

	Biowaste1 TS[%]=2.5	**Biowaste2 TS[%]=4.9**	**Biowaste3 TS[%]=7.4**	**Biowaste4 TS[%]=9.4**	**Biowaste5 TS[%]=12.8**	**Biowaste6 TS[%]=15.2**
Dauer [h]	10.87	10.08	10.18	10.44	10.46	10.84
T_HM [°C]	240	250	250	250	250	250
P_max [bar]	25	25	25	25	30	30
Final P [bar]	2.78	4.46	5.5	7.64	9.01	10.23
Final T [°C]	37	34	33	37	38	47
Amount before HTC						
Biomasse before HTC [kg]	1.8	3.6	5.3	6.8	8.3	9.8
Water before HTC [L]	14.6	13.7	12	11	8.2	7
Tank level before HTC [cm]	13.5	13.8	14	17	17	17
Amount after HTC						
Tank level after HTC [cm]	NA	13.4	NA	NA	NA	9
Coal after HTC [kg]	0.369	1.574	2.817	3.815	4.542	5.939

A3) *Characteristics and amounts, before and after HTC, of all the test with the same TS=4.9% on varying on the inner temperature:*

	TEST 1 – T1 = 200°C TS[%]=4.9	**TEST 2 – T2 = 190°C TS[%]=4.9**	**TEST 3 – T3 =180°C TS[%]=4.9**	**TEST 4 – T4 =170°C TS[%]=4.9**
Dauer [h]	13.43	11.35	9.93	8.21
T_HM [°C]	250	250	250	250
P_max [bar]	30	30	30	30
Final P [bar]	4.72	4.53	4.36	3.25
Final T [°C]	38	35	29	30
Amount before HTC				
Biomasse before HTC [kg]	3.6	3.6	3.6	3.6
Water before HTC [L]	13.7	13.7	13.7	13.7
Tank level before HTC [cm]	13.8	13.8	13.8	13.8
Amount after HTC				
Tank level after HTC [cm]	NA	NA	14	15
Coal after HTC [kg]	1.562	1.369	1.447	1.087

A4) *Example of the final frame of the Energy consumption, recorded during the test Biowaste4 with TS=9.4% (this program is in German):*



Strom Aktuell

Ihre Messung vom 21.04.2013 um 22.47 Uhr

Aktuelle Leistung	
Dauer der Messung	441 Min., 59 Sek.
Leistung	
Maximum	2346 W
Minimum	0 W
Durchschnitt	1104 W
Verbrauch	
Gesamt	11.53 kWh
Kosten	0 ct
Durchschnitt	0 ct/h
Definierte Grundlast	
Leistung	0 W
Kosten	0 ct/h

Verbrauchskosten-Rechner

Bei Berücksichtigung des vorliegenden Stromverbrauchs 0-mal pro Tag ergibt sich im Jahr ein Energieverbrauch von 0 kWh. Das entspricht Kosten von 0 EUR.

B) MANUAL FOR USING HTC - REACTOR

MANUAL FOR USING HTC – REACTOR

CE 1253

Calorifer AG
CH - 8353 Elgg

Datum der Druckprüfung (5CH3)	26.02.2013	
Hersteller	Calorifer AG CH-8353 Elgg	
Baujahr / Fabr. No.	2013	12104
	Mantel-Raum	Rohr-Raum
Max. zul. Druck PS	30 barg	-- barg
Prüfdruck PT	52.5 barg	-- barg
Min. / Max. zul. Temperatur TS	5/280 °C	-- °C
Inhalt	21.8 L	-- L
Fluid-Gruppe	1	--

INSTRUCTIONS:

The main steps for using the reactor can be divided into:

1) Collection and preparation of biomass;

2) Preparation of reactor before starting the reaction;

3) Closing the lid of reactor;

4) Switching-on all the programs and starting the reaction;

5) Control of the parameters (mainly T and P) every hour;

6) Switching-off the reactor and saving the results of all the parameters;

7) Opening the reactor the day after;

8) Cleaning the reactor at the end, after separation of coal from process water.

1) Collection and preparation of biomass:

1. Collection of biomass choice in large bins;
2. Example of organic waste collected before mixing;
3. Use two other bins to put the biomass collected in (Tank 60L);
4. Transfer all the biomass in these two bins and fill the bins with it;
5. Put inside small buckets (Tank 10L) about 2-3 Kg of biomass to blend it (this procedure must be done for all the amount of biomass collected);
6. Use a professional blender to obtain an homogeneous mixture, possibly without the addition of water;
7. Example of biomass after the blending;
8. Mix all the amount of biomass collected with blender and fill the small buckets with the homogeneous mixture;
9. After blending, put the mixture into a big bin and mix again with a simple stick to mix everything together;
10. Put the homogeneous mixture into small buckets and place them in the freezer.


1


2


3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5


6


7


8


9


10

2) Preparation of reactor before starting the reaction:

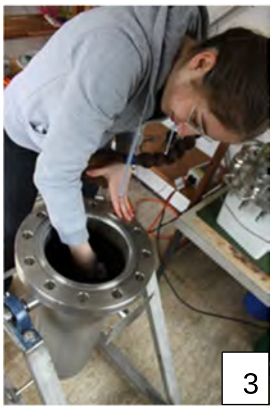
1. Defrost the biomass one/two days before doing the experiment;
2. Weight the exact amount of biomass with a simple digital balance;
3. Clean and dry the reactor with a paper towel before adding water or biomass;
4. Collect the water needed for the reaction with a little tank (Tank 10L);
5. Measure with a graduated cylinder one liter of water at a time (Measuring cup 1L);
6. Add the liter of water measured into the reactor before putting in the biomass (do this for at least four/five times);
7. Add now the biomass weighted at the beginning into the reactor, using a ladle and mix it;
8. Add more one/two liters more of water into the bucket to clean it well and to use all the amount of biomass;
9. Spill this water into the reactor and add also the remaining amount of water required for the reaction (**PAY ATTENTION:** when filling the reactor, before HTC, it should be observed not to fill the reactor above three quarter of the reactor's volume, which means **maximum 17L**);
10. Mix now all the mixture, using, for example, a steel rod;
11. Measure with meter the distance from the mixture to the reactor's edge (**PAY ATTENTION:** it's necessary to leave a free space between **13-18 cm** because the

water density decreases significantly at high temperatures resulting in a higher volume which can exceed the reactor's volume. It's also important to remember that the length of temperature sensor is **25 cm**, so it must be immersed in the mixture for at least 7-8 cm);

12. Dry, at the end, the reactor's edge with a paper towel.


1


2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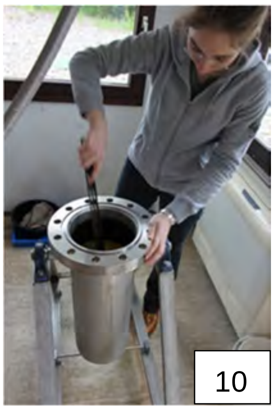
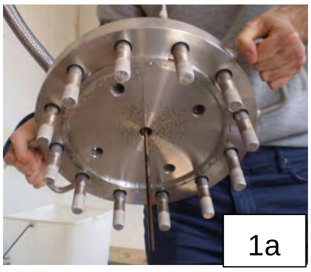

10


11


12

3) Closing the lid of reactor:

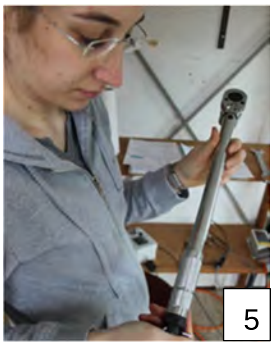
1. Raise and place the lid on the reactor *(Fig. 1a–1b)*; (**PAY ATTENTION:** it's necessary to check, after every reaction, the state of the **graphite sealing disc** (dimension 26 x 21 x 1.5). If it's damaged it need to be replaced. Furthermore, you need to be careful at the length of **temperature sensor** when closing the lid);
2. At first, tighten all the 12 screws by hand;
3. Tools used to close the lid (simple wrenches and torque wrench);
4. Tighten the screws using the two simple wrenches;
5. Close now the screws with a torque wrench *(Fig. 5)*: the first round with intermediate strength **42 Nm** *(Fig. 5a)* and then with the maximum strength **84 Nm** *(Fig. 5b-5c)*; (**PAY ATTENTION:** the tightening and opening of the screws shouldn't occur in the chronological order but should follow a **cross pattern**, like this: **1-7-4-10-2-8-5-11-3-9-6-12**);
6. Make sure that the drain valve is closed before starting the reaction;
7. Position and tighten as much as possible the heating mantle around the reactor *(Fig. 7a-7b)*; (**PAY ATTENTION:** the imposed temperature on the heating mantle shouldn't exceed **300°C**. Other characteristics of heating mantle: diameter = 219mm, length = 500mm, maximal power = 2500W);


1a


1b


2


3


4


5


5a


5b


5c - 6


7a

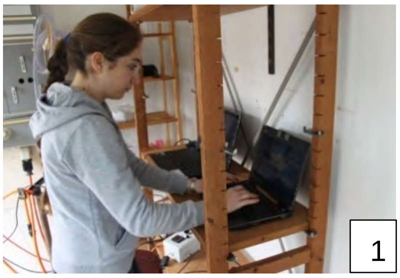

7b

4) Switching-on all the programs and starting the reaction:

1. Use two computers and turn them on (**PAY ATTENTION:** the programs don't work if only one computer is used, so it's necessary to use the **Temperature program** on one PC and the other two programs (**Pressure and Energy consumption programs**) on another one);
2. Connect the USB cables of temperature and pressure on the two PC *(Fig. 2a)* and insert also the red USB-Key on which the energy program is installed *(Fig. 2b)*;
3. Steps for switching-on the **Temperature program** *(SWS – ACS 13A)*:
    - 3.a. At first, turn on the **inner temperature sensor** (turn the knop on *EIN*, on the display the recorded temperature inside the reactor before starting the reaction will appear);
    - 3.b. Switch-on now the temperature program:
        - ✓ the first window that opens asks *"Has serial communication option been added?"* Respond: *Yes*;
        - ✓ on the screen **Main display** click *Online* (on the display the recorded temperature will appear);
        - ✓ on the screen **Trace display** click *Start* (recording cycle 20s - at the bottom it shows the name of the file that will be saved);
4. Steps for switching-on the **Pressure program** *(CCS 30)*:
    - 4.a. At first, turn on the digital manometer (inner pressure sensor), clicking on *Select* (on the display the recorded pressure inside the reactor before starting the reaction will appear);
    - 4.b. Switch-on now the pressure program:
        - ✓ in the first window that opens, it's necessary to click before on **Search** (only a technical write will appear) then click on **Configure** (in a new window, at the bottom, the write *Status: Connected* will appear) and finally click on **New Measurement** (a new window will open where you need to click on

Start – recording cycle 20s - the red line represent the trend of the pressure during the reaction);

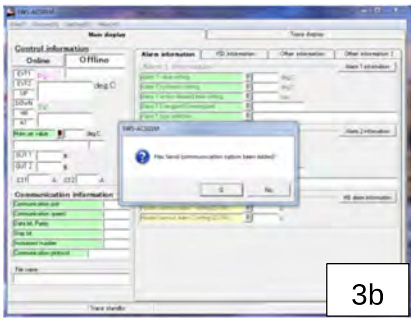
5. Steps for switching-on the **Energy consumption program** *(VSM-101 Voltcraft)*:
    - 5.a. At first, attach the energy meter’s plug in the socket (on this display the values in KWh consumed will appear and also on the display of the external temperature sensor the notice *AUS* that it means *OFF*);
    - 5.b. Switch-on now the energy program:
        - ✓ at first, some windows at the top left of the screen will appear, here you must always click on *OK*;
        - ✓ now the main window will open: you need to click on the symbol of the socket and then you must click on *STARTE MESSUNG* that it means *START MEASUREMENT*;
6. Switch-on now the **external temperature sensor**:
    - 6.a. For starting the reaction, you need to press simultaneously the buttons P and ▽. Then you must impose the temperature of the heating mantle, pressing the button S and increasing the temperature with the button Δ.
    - 6.b. Finally, you must fill in the form of the experiment, which shows all the information (start time, end time, temperature and so on).

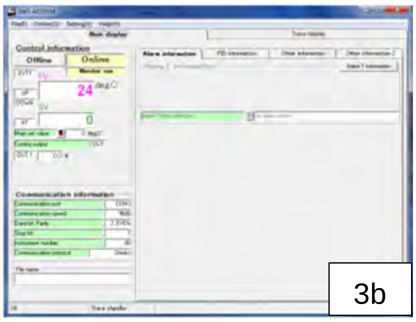

1


2a


2b


3a


3b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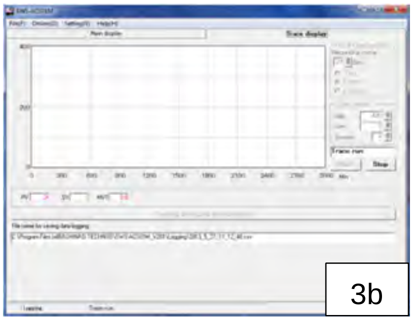
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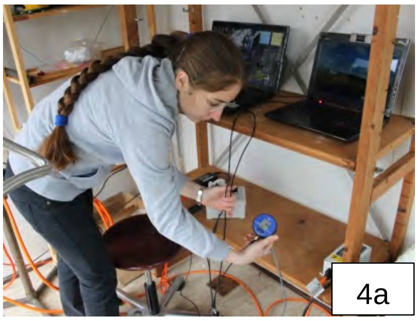
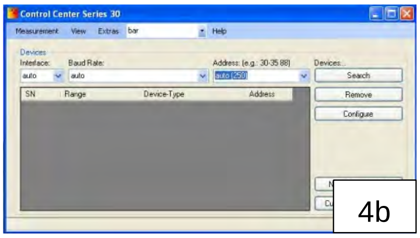
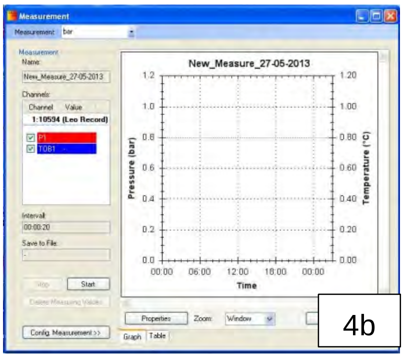
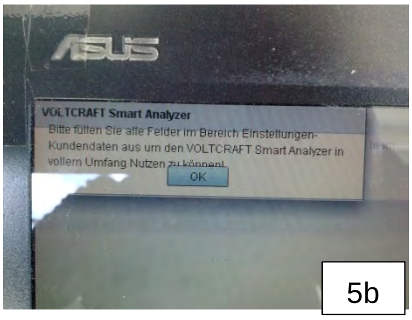

4a


4b

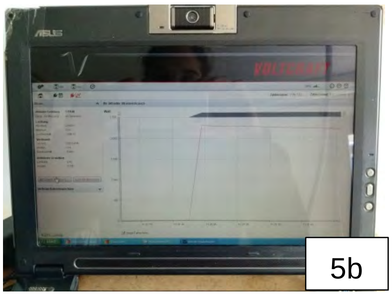

4b

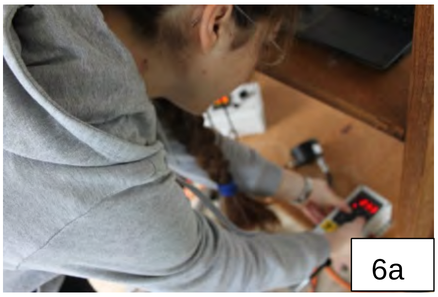

5a

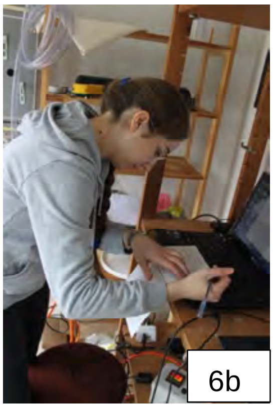

5b

VOLTCRAFT Smart Analyzer

Bitte füllen Sie alle Felder im Bereich Einstellungen-Kundendaten aus um den VOLTCRAFT Smart Analyzer in vollem Umfang Nutzen zu können!


5b


6a


6b

5) Control of the parameters (mainly T and P) every hour:

1. It’s necessary to control the parameters every hour *(Fig. 1a: watch the three programs on two computers)* to adjust, in the event that pressure *(Fig. 1b)* or temperature *(Fig. 1c)* increase very fast, the temperature of the heating mantle with the external temperature sensor (**PAY ATTENTION 1:** depending on the nature of the substrate, the resulting pressure during HTC can increase very fast. When using a **new substrate** for HTC, the reactor shouldn’t be filled with a too high amount of feedstock, **TS not above 5%**. This allows for a better control of the pressure increase. **PAY ATTENTION 2:** the **overpressure valve** should be used as a safety device and not as a pressure regulation device. Therefore, it should be avoided to reach the maximal pressure of the overpressure valve: **30 bar**. **PAY ATTENTION 3:** in no way the **drain valve** should be opened during the reaction! This is used only to drain the residual pressure when the reactor has cooled down).


1a

1b

1c

6) Switching-off the reactor and saving the results of all the parameters:

1. After the total reaction time, that is, time during which heat is supplied to the reactor, you need to switch-off the reaction, with **external temperature sensor,** pressing simultaneously the buttons P and ▽ : the writing *AUS* that means *OFF* will appear on the display *(Fig.1a)*. You need also to write the end time and data on the sheet for each test and also in the other paper where there is the complete list of experiments *(Fig.1b-1c)*;
2. Then it's necessary to save the recorded parameters of temperature, pressure and energy consumption before switching-off the two computers:

2.a. Steps for switching-off the **Temperature program** (SWS – ACS 13A):

- ✓ on the screen **Trace display** click *Stop* (the file is automatically saved in the file name which it's reported at the bottom);
- ✓ on the screen **Main display** click Offline (it will appear on the display the final recorded temperature inside the reactor);
- ✓ close now the temperature program, clicking on the red cross in the upper right, it will open a new window that says *"Do you want to close the program?"* Respond: *Yes* (**PAY ATTENTION:** before closing the program, check that the file is properly saved in the folder);

2.b. Steps for switching-off the **Pressure program** (CCS 30):

- ✓ on the window **Measurement** click before on *Stop*, then you need to click, on the blue box, Measurement , to save these values in file excel (comma-separated file CSV) but it's necessary to create a new folder to put it in.

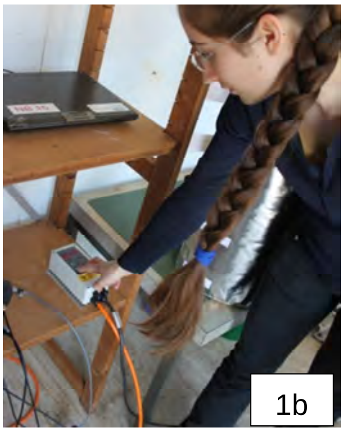
  Finally, you can close the pressure program, clicking on the red cross in the upper right (**PAY ATTENTION:** before closing the program, check that the files are properly saved in the folder);

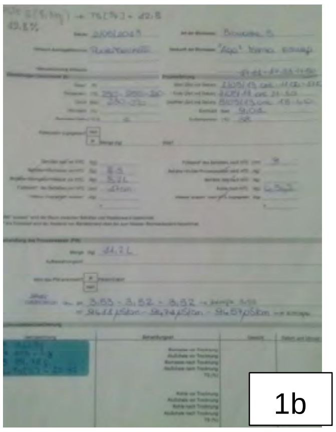
2.c. Steps for switching-on the **Energy consumption program** (VSM-101 Voltcraft):

- ✓ on the main window, where also the red graphic of energy is shown, you need to click on *STOPPE MESSUNG*, that it means *STOP MEASUREMENT*. Then you need to save the recorded values in pdf and in file excel (comma-separated file CSV) in the same folder where you saved the file of pressure, clicking the two bottons of pdf and CSV in the upper of this window. Finally, you can close the energy consumption program, clicking on the red cross in the upper right (**PAY ATTENTION:** before closing the program, check that the files are properly saved in the folder);

3. Now, it's possible to switch-off the all-digital instruments:
   - ✓ **Inner temperature sensor:** turn off the knop on *AUS* that it means *OFF (Fig. 3a)*;
   - ✓ **Inner pressure sensor:** click before on *SELECT* and then on *ENTER (Fig. 3b)*;
   - ✓ **Energy meter:** unplug the energy meter's plug in the socket *(Fig. 3c)*;

   after this, you can switch-off the two computers;
4. At the end, you need to remove the heating mantle around the reactor, in this way it will cool more quickly during the night *(Fig. 4a)* (**PAY ATTENTION:** don't touch the internal temperature sensor, that is, the inner white part of the heating mantle because it's very dangerous for the high temperature; then, place it on the table over the isolated electric mantle *(Fig. 4b)*).


1b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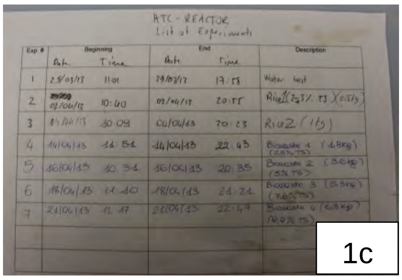
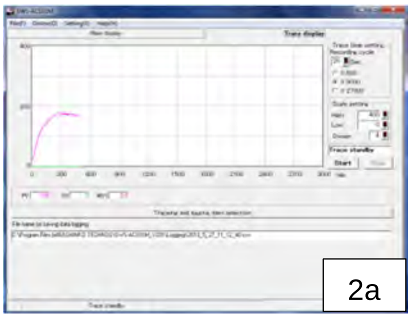

HTC - REACTOR
List of Experiments

Exp #	Beginning		End		Description
	Date	Time	Date	Time	
1	25/03/13	11:01	29/03/13	17:58	Water test
2	02/04/13	10:40	02/04/13	20:55	Rice 1 (2-3% TS) (0.5 kg)
3	04/04/13	10:09	04/04/13	20:23	Rice 2 (1 kg)
4	14/04/13	11:51	14/04/13	22:43	Biowaste 1 (1,8kg) (2,5% TS)
5	16/04/13	10:31	16/04/13	20:35	Biowaste 2 (3,6kg) (5% TS)
6	18/04/13	11:10	18/04/13	21:21	Biowaste 3 (5,3kg) (7,6% TS)
7	21/04/13	12:17	21/04/13	22:47	Biowaste 4 (6,9kg) (9,4% TS)

1c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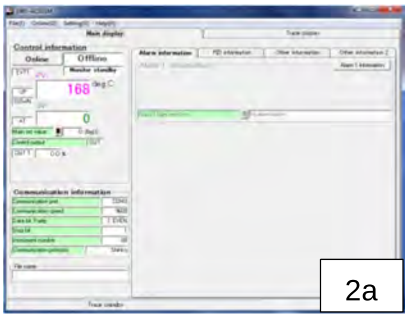
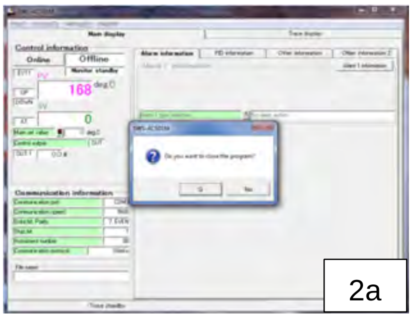
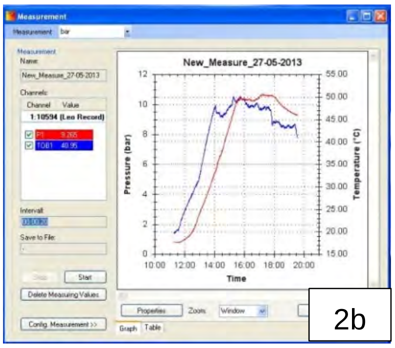
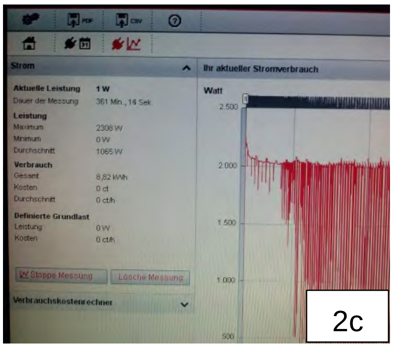

2a

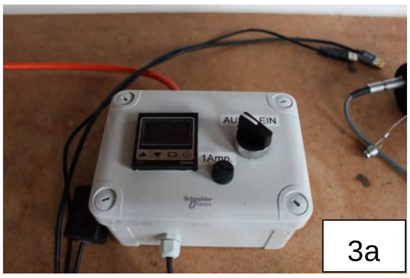

2a



2b



2c



3a

3b


3c


4a

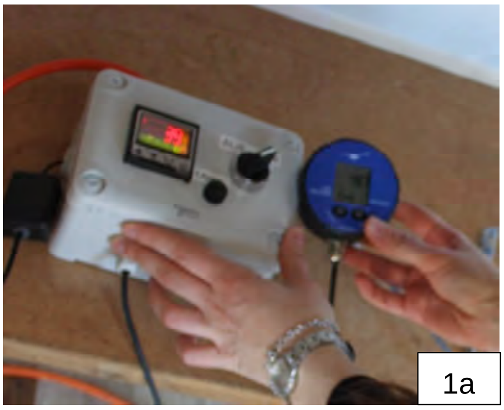

4b

7) Opening the reactor the day after:

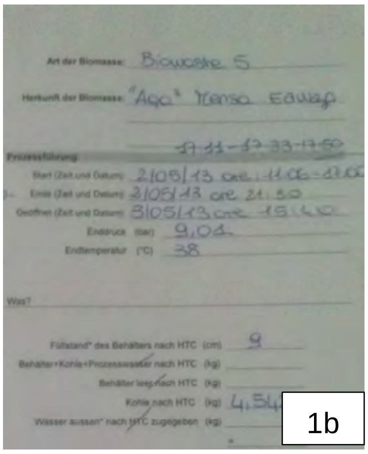
1. Switch-on before the inner temperature sensor (turn on the knop on *EIN*) and the inner pressure sensor (press the *SELECT* button) *(Fig.1a)*, then fill the sheet of the experiment with the end temperature [°C] and end pressure [bar] *(Fig.1b)*;
2. Place now the transparent tube into the drain valve *(Fig.2a)* and position the other end outside of the container *(Fig.2b)*. (**PAY ATTENTION 1:** stay away from the end of the tube and don't breathe the gas output*)*. After this, open slowly the drain valve *(Fig.2c)* to release the residual pressure once the reaction is over, until the pressure reaches pressures **below 1 bar** *(Fig.2d)*. Finally, remember to close the drain valve *(Fig.2e)* then you need to remove the tube and to place it on the shelf *(Fig.2f)*. (**PAY ATTENTION 2:** check always that the drain valve is closed before starting a new reaction HTC);
3. Steps for opening the reactor:
    - 3.a. use the torque wrench at 42 Nm to open the screws following the cross pattern (example: 1-7-4-10-2-8-5-11-3-9-6-12);
    - 3.b. unscrew and manually remove the rings of the screws. Place them on a shelf or in a safe place to avoid losing them;
    - 3.c. wear protection mask, glasses and gloves before lifting up the lid (**PAY ATTENTION:** compounds like phenols which vaporise are harmful to the eyes, the skin and the respiratory tract*)*;
    - 3.d. lift up now the lid of the reactor, paying attention to the length of temperature sensor;
    - 3.e. clean the temperature sensor with a paper towel, to lean against on one side the lid;
    - 3.f. place the lid on top of a bucket;
4. Remove the rod block at the bottom of the reactor *(Fig.4a)*, then tilt slowly the reactor on one hand and block it using the rod block *(Fig. 4b-4c)*;

5. Place now all the containers for emptying procedure: blue container, white bucket and black perforated container;
6. Put above the black perforated container a thick and tightly woven cotton cloth to separate the solid from the liquid;
7. Start emptying the reactor using a ladle *(Fig. 7a)* and continue like this, until you have a bit of coal inside the cloth *(Fig. 7b)*;
8. Press then the coal using the cloth *(Fig. 8a)* and put it into another clean bucket *(Fig. 8b)*, helping to clean the cloth with the ladle *(Fig. 8c)* (**PAY ATTENTION:** weigh before the empty bucket (tare) to later on know the exact amount of coal in [Kg]).

   Continue with the same procedure until the reactor is completely emptied;
9. After this, you need to measure the total liters of process water *(Fig. 9a)*, using a measuring cup (1L) *(Fig. 9b)* and fill the sheet of the experiment with this value *(Fig. 9c)*;
10. Mix now all the process water with a metal rod *(Fig. 10a)* and then take two samples of this water to make after the analysis (pH, EC and TOC) *(Fig. 10b)*;
11. Weigh the coal obtained on the balance and write this value on the sheet of the experiment;
12. Take a sample of coal for the measurement, at first, of TS (Total Solid) *(Fig. 12a)* and then use the dry sample to make the measurements of calorific value and elementary analysis (C,H,N,O) *(Fig. 12b)*. Put the rest inside containers for drying all the coal produced in the oven at 105°C for 24 hours *(Fig. 12c)*.



1a



Art der Biomasse: Biowaste 5

Herkunft der Biomasse: "Aqa" Kenso Eawag

17:11 – 17:33 – 17:50

Prozessführung

Start (Zeit und Datum) 2/05/13 ore: 11:06 – 13:00

Ende (Zeit und Datum) 2/05/13 ore 21:50

Geöffnet (Zeit und Datum) 3/05/13 ore 15:40

Enddruck (bar) 9,01

Endtemperatur (°C) 38

Was?

Füllstand* des Behälters nach HTC (cm) 9

Behälter+Kohle+Prozesswasser nach HTC (kg)

Behälter leer nach HTC (kg)

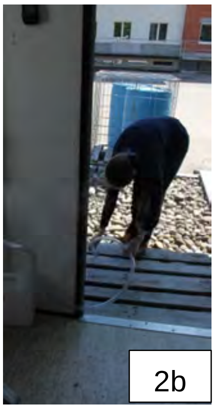
Kohle nach HTC (kg) 4,54

Wasser aussen* nach HTC zugegeben (kg)

*

1b


2a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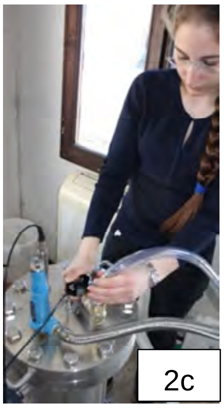
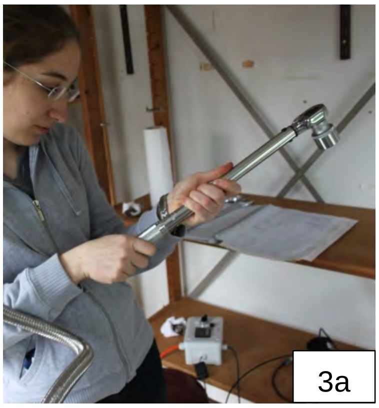

2c


2d


2e


2f


3a


3b


3b


3c


3d

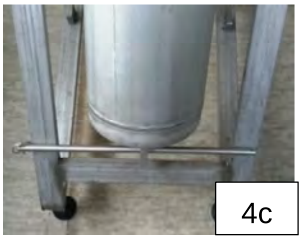

3e


3f


3f


4a


4b


4c


5


6


7a


7b


8a


8b


8c


9a


9b


9c


10a

10b


11


12a


12b


12c

8) Cleaning the reactor at the end, after separation of coal from process water:

1. Take the little tank (10L) with water *(Fig.1a)* and pour a bit of it into the reactor *(Fig. 1b)*;
2. Use all the tools *(Fig. 2a)* that are used to remove the coal and to clean the reactor. Then you need to empty the dirty water, using a bucket *(Fig. 2b)*;
3. After this, you need to dry with a paper towel the inner part of the reactor and the upper part where there is the graphite sealing disc;
4. Wash well the woven cotton cloth with just water and if the cloth is not clean you need to put it into a bucket full of water for one day *(Fig. 4a)*. Finally, you have to tighten it and spread it to dry *(Fig. 4b)*.


1a


1b


2a


2b


3


4a


4b