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Hydrothermal carbonization of biowaste – a step towards efficient carbon sequestration and sustainable energy production

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Abstract

Hydrothermal carbonization is a process that under rather mild temperatures and pressures turns carbohydrates into coal like materials in a few hours or days. In this study, the environmental benefits of hydrothermally carbonized biowaste for energy production, carbon sequestration and soil improvement were evaluated.

Keywords

Hydrothermal carbonization, biowaste, energy, soil improvement, carbon sink, horse manure, seaweed, fiberbank

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Sammanfattning

Hydrotermisk karbonisering (HTC) är en exoterm process som på kort tid och under relativt milda betingelser omvandlar kolhydrater till kolliknande material och vatten. Den har många potentiella användningsområden, bl.a. storskalig omvandling av biomassa till tekniska produkter, råvara till kemisk industri och fordonsbränsle, samt bränsle för elektricitet och värmeproduktion. Produkten skulle dessutom kunna användas som jordförbättringsmedel. Eftersom allt kol som fanns i ursprungsmaterialet bevaras genom HTC-processen och binds i slutprodukten fungerar processen även som en kolsänka. Om slutprodukterna används som jordförbättringsmedel bidrar HTC därför till att minska koncentrationen av koldioxid i atmosfären.

Detta examensarbete hade två syften; det första var att undersöka de miljömässiga vinsterna med storskalig HTC av biomassa för energiproduktion och för användning som jordförbättringsmedel. Det andra syftet var att identifiera några olika typer av svensk biomassa som skulle kunna vara lämpliga för HTC. Hästgödsel, tång och fiberbankar valdes ut som exempel på svenskt biologiskt avfall och prover av dessa transporterades ned till Max-Planck institutet i Potsdam för HTC och analys av slutprodukten.

Slutsatserna är att storskalig HTC av hästgödsel, till skillnad från tång, med fördel skulle kunna användas för uthållig energiproduktion och som jordförbättringsmedel. HTC av tång ger en produkt med lägre värmevärde samt höga halter av tungmetaller. Försöken med fiberbankar misslyckades; cellulosafibrerna hade legat så länge på sjöbottnen att de hade petrifierats.

Storskalig användning av HTC skulle vara ett effektivt sätt att omvandla jordbruksavfall och andra typer av biologiska material till värdefulla slutprodukter. Metoden skulle inte bara vara ett sätt att framställa miljövänlig energi och jordförbättringsmedel; den skulle dessutom kunna lösa hästnäringens stora problem med gödselhantering. Den föreslagna metoden omvandlar snabbt och effektivt hästgödsel till humus utan negativa miljöeffekter såsom läckage av näringsämnen eller utsläpp av växthusgaser.

Civilingenjörsprogrammet Molekylär bioteknik

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1. Introduction

1.1 World in crisis

Our global economy is outgrowing the capacity of the earth to support it, moving our early twenty-first century civilization even closer to decline and possible collapse. We know from studies of earlier civilizations that the lead indicators of economic decline were environmental, not economic [1]. As Jared Diamond notes in *Collapse: How Societies Choose to Fail or Succeed* [2], some societies were able to change course and avoid economical decline. Others were not. The archaeological sites of some early civilizations, such as the Sumerians, the Mayans and the Easter Islanders, that were not able to make the needed adjustments in time, tell their own stories.

But our situation today, compared to the threats against earlier societies, is far more challenging [1]. We have entered an era when human decisions, not natural processes, dominate the global environment [3]. Demand has exceeded the sustainable yield of natural systems at the local level countless times in the past. Now, for the first time, it is doing so at the global level [1].

In 1998, The World Wide Fund for Nature (WWF) published its first Living Planets Report to show the state of the natural world and the impact of human activity upon it. The *Living Planet Report 2006* indicates that humanity's Ecological Footprint, mankind's impact upon the planet, more than tripled between 1961 and 2003. We now exceed the world's ability to regenerate by about 25 % [4].

Fossil fuels have offered astounding opportunities during the 20th century, but now mankind has to face the challenges arising from fossil fuel exploitation [5]. The proven reserves of oil are progressively decreasing [1]. Pollutions are threatening human health, ecosystems and even buildings, and the exploitation of coal, oil and natural gas is damaging ecosystems [5, 6, 7]. Huge military costs, related to securing energy supplies, are further burdening our society [5]. Finally, emissions of greenhouse gases (GHGs) from fossil fuel combustion enhance the natural greenhouse effect and may cause increased mean sea level, changed vegetation zones and retreated permafrost zones as the global temperature increases [6, 7].

According to WWF's *Living Planet Report 2006,* the global footprint of carbon dioxide from fossil fuels combustion increased nine fold from 1961 to 2003. Climate-changing emissions now make up 48 per cent of humanity's global footprint [4].

1.1.1 Global greenhouse gas emissions and their impact on climate

The most important GHGs affected by human activity, are (water vapour excluded): carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (laughing gas, N_2O). Recalculated into CO_2-equivalents (CO_2e) they make up 77%, 14% and 8% of global GHG emissions, respectively. The last percent is attributed to different halocarbons, such as hydro fluorocarbons (HFCs), sulphur hexafluoride (SF_6) and per fluorocarbons (PFCs) [8, 9].

The increased levels of atmospheric carbon dioxide predominately originate from the oxidation of organic carbon from fossil-fuel combustion and deforestation. Methane is a GHG with both natural (e.g., wetlands) and human-influenced sources (predominantly agriculture). Around 60% of the current methane emissions are anthropogenic. Nitrous oxide emissions can also be of both natural and anthropogenic origin. Agricultural processes are mainly to

blame for the upward trend in atmospheric nitrous oxide concentration [8, 9]. The world's GHG emissions by sector are illustrated in Figure 1.

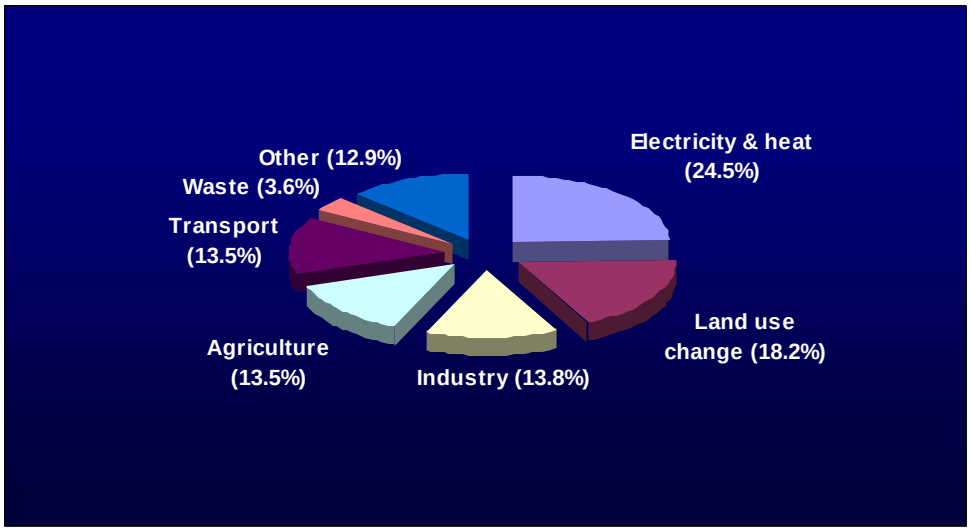

Figure 1. The world's greenhouse gas emissions by sector (%) in 2000 (modified from ref. 8)

Recognizing the risks of potential human-induced global warming, the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) established the Intergovernmental Panel on Climate Change (IPCC) in 1988 [10].

On February 2nd 2007, IPCC adopted the *Summary for Policymakers* of the first volume of *Climate Change 2007* [11]. In the *Summary for Policymakers*, IPCC concludes that global atmospheric concentrations of carbon dioxide, methane and nitrous oxide have increased markedly as a result of human activities since 1750. The carbon dioxide concentration has increased from a pre-industrial value of 280 ppm to 379 ppm in 2005. The methane concentration has increased from 715 ppb to 1774 ppb and nitrogen dioxide from 270 ppb to 319 ppb in 2005 [12].

The warming of the climate system is unequivocal, IPCC writes. This is evident from increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global mean sea level. IPCC states that most of the observed increase in global average temperatures since the mid-20th century is *very likely* (more than 90% confidence) due to the increase of anthropogenic GHG emissions. IPCC predicts a global temperature increase of up to 6.4 °C and a sea level rise with up to 59 cm at the end of the 21st century, compared to 1980-1999. It is also *very likely* that hot extremes, heat waves, and heavy precipitation events will become more frequent. The meridional overturning circulation (MOC) of the Atlantic Ocean is *very likely* to slow down during the 21st century. Mainly due to slow response of the oceans, a further warming of about 0.1 °C per decade would be expected, even if the concentrations of all GHGs and aerosols would be kept constant at year 2000 levels [12].

1.1.2 Future global energy demand

The global energy demand is predicted to increase significantly over the next decades. The International Energy Agency (IEA) published its yearly *World Energy Outlook* in November 2006. In a reference scenario, global primary energy demand will increase by 53% between now and 2030. Over 70% of this increase will come from developing countries, led

by China and India, with China overtaking the United States as the world's biggest emitter of carbon dioxide before 2010 [13].

1.1.3 Outlook

According to the *Stern Review on the Economics of Climate Change*, presented in October 2006, our unwillingness to act to the threats of climate change could be equivalent of losing between 5 and 20% of global GDP[i] each year, now and forever. In contrast, the cost of reducing GHG emissions to avoid the worst impacts of climate change can be limited to around 1% of global GDP each year [14].

To reduce the worst impacts of climate change, the atmospheric GHG levels need to be stabilized between 450 and 550 ppm CO_2e. The current level is 430 ppm, and it rises with more than 2 ppm each year. Stabilization – at whatever level – requires that annual emissions are brought down to more than 80% below today's levels [14].

Climate change is the greatest market failure the world has ever seen, Sir Stern writes [14]. Others would maybe describe it as a striking example of what Hardin in 1968 described as *The Tragedy of the Commons* [15]; that each man is locked into a system that compels him, without limit, to increase his share of the commons, since the negative environmental effects will be shared by everyone and are negligible compared to what he, as an individual, will gain.

In the words of Hardin, freedom of the commons – in this context; the freedom to exploit non-renewable resources and pollute the atmosphere – will eventually bring ruin to all.

What we can not know about earlier civilizations is if they understood what caused their economic decline and final collapse. If so, where they just unable to muster political support to take the right measures as to prevent environmental degradation? For our twenty-first global civilization, however, lack of knowledge can not be blamed for our inability to act. Our knowledge about humanity's impact on the world's ecosystems, together with an archaeological record that shows us what happened to earlier civilizations that faced environmental degradation and failed to respond, suggest that we are in a unique position to respond to today's environmental threats.

To reduce global GHG emissions we must find new ways to meet our energy demands. Also, deforestation needs to be halted and agricultural practices need to be changed. If possible, large scale sequestration of carbon dioxide from the atmosphere would be desirable. Hydrothermal carbonization of abundant low-value biomass could be one step in the right direction.

1.2 Aim of study

Hydrothermal carbonization (HTC) can be described as "coal formation in a day", and is a fast and simple way to turn carbohydrates into different carbonaceous materials. HTC is a carbon neutral, exothermic process and should therefore be more environmental friendly than conventional carbon conversion routes. The aim of this study is to evaluate the environmental benefits with large-scale HTC of abundant low-value biomass ("biowaste"), and to discuss the potential use of the product as an energy source, soil improvement and carbon sink. The study consists of two parts; a literature study and an experimental part.

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[i] Gross Domestic Product; the market value of all final goods and services produced within a country in a given period of time.

Literature study:
For combustion purposes, it is important to note that the physical and chemical properties of HTC-products are that of coal materials, but if combusted, their environmental impact is that of the biomass they originates from. For energy exploitation purposes, the carbon structures therefore must be compared with both coal and biomass.

The HTC process as such will also be compared with conventional carbon conversion routes, such as ethanol, biodiesel and biogas production. The reason for this is to compare the environmental impacts from the different processes and to discuss if the HTC process is a more environmental friendly way of producing energy from biomass. Also, it is important summarize the "lessons learned" from these processes to ensure that old mistakes not are repeated. In addition, carbonaceous end products from HTC could potentially be used in Fischer-Tropsch processes to produce gasoline.

HTC-products in early stages resemble humus or peat and can therefore be applied as soil improvement or fertilizer. Since the process fixates carbon from the atmosphere, the advantages would be two-fold; apart from improving poor soils, large-scale HTC would sequester carbon dioxide from the air. The environmental benefits of HTC-products will be compared with South American so called *terra preta* soils. These are structurally and chemically very similar to HTC-products and their nutrient-improving and carbon sequestration capacities have been thoroughly investigated in earlier studies.

Experimental part:
The objective of the second part was to identufy three different types of abundant, low-value biomass ("biowaste") in Sweden with potentials for HTC. They should not previously have been hydrothermally carbonized at the Max-Planck Institute in Potsdam, Germany, and should all represent nuisance to the environment and be expensive or difficult to degrade. Three different types of biowaste were identified; horse manure, seaweed and fiberbanks. The biowaste was sampled in Sweden and brought to Germany for HTC. Luckily, the author was never stopped in the security control at the airport.

The two parts are seen as interconnected with each other and are therefore not separated. The discussion in the experimental part uses arguments from the literature study when the HTC-products from horse manure, seaweed and fiberbanks are discussed.

2. Biomass - the future of energy supply?

Petroleum geologists seem to agree on that approximately 95% of global petroleum reserves already have been discovered and that world petroleum production will peak rather sooner than later [1]. The total recoverable reserves of coal, on the other hand, are estimated to be around 1 trillion tons, and will last for another 180 years at current consumption levels [16]. The relative abundance of coal makes it an attractive energy source in some countries, but coal is the dirtiest and most greenhouse-intensive of all fossil fuels [16], and should therefore not be considered as an alternative to oil. High energy prices, increasing energy imports, concerns about declining petroleum supplies and greater recognition of the environmental consequences have therefore driven interest towards renewable energy sources [17].

Examples of renewable energy sources are wind energy, solar cells, solar thermal panels, solar thermal power plants, geothermal energy, hydropower, wave power and biomass [1].

2.1 Biomass, bioenergy and biofuels

Biomass, also known as *biorenewable 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) [18]. They are by definition sustainable resources, i.e. resources that are renewed at such rate that they will be available for future generations [19]. Peat is sometimes classified as a biorenewable resource; however, it accumulates so slowly that the formation of new peat would take centuries [20].

Bioenergy is defined as the conversion of biomass into heat or electric power [19].

Biofuels are here referred to as transportation fuels produced from biomass and can be used as an alternative to gasoline and diesel [21]. Biofuels can either be in liquid form such as fuel ethanol or biodiesel, or in gaseous form such as biogas or hydrogen [18, 22]. Biofuels will be discussed in section 5.

2.2 Biomass

Biomass will here be classified into biowaste and dedicated energy crops.

A *biowaste* is a material that has been traditionally discarded because it has no apparent value or represents a nuisance or even a pollutant to the local environment. Biowastes include agricultural residues, yard waste, municipal solid waste, waste from food processing industry, sewage and manure [19].

Dedicated energy crops are plants grown specifically for production of biobased products; that is, for purposes other than food or feed. They are planted and harvested periodically; this does not include cutting down an old-growth forest for firewood. Dedicated energy crops can either be *herbaceous energy crops* or *short-rotation energy crops* [19].

Herbaceous energy crops are plants with no or little woody tissue. They can be thick-stemmed grasses such as sugarcane, energy cane and corn, or thin-stemmed grasses such as reed canary grass and switch grass [19].

Short-rotation energy crops are fast growing woody biomass, including hardwoods and softwoods. Softwoods are pine, spruce and cedar. These species have considerable value as construction lumber or pulpwood, and are therefore mostly only available as logging and manufacturing residues. Examples on hardwood species for energy production are poplar, willows (*Salix spp*.) and eucalyptus [19].

2.2.1 Energy-rich components in plants

Dedicated energy crops contain one or more of four important energy-rich components: oils, sugars, starches or lignocelluloses (fibers). Crops rich in the first three have traditionally been grown, but since energy yields are usually greatest for plants that are mostly “root and stem”, there today is a bias towards the production of lignocellulosic biomass [19]

2.2.1.1 Traditional energy crops

Sugar crops that traditionally have been used for fermentation include apples, grapes and other fruits, sugar cane, sugar beets and sweet sorghum[ii]. The sugars can be directly

[ii] A cane-like plant with high sugar content.

fermented by the yeast *Saccharomyces cerevisae*, which contain enzymes that hydrolyze disaccharides to simple sugars and catalyze the fermentation of four hexoses: glucose, mannose, fructose and galactose [19].

Starch crops contain starch polysaccharides that must be hydrolyzed into simpler sugars before fermentation. Starch accumulates as granules in many kinds of plant cells where it serves as a storage carbohydrate. Cereal grains, such as corn, wheat and barley, are the most widely used sources of starch for fermentation [19].

Oil crops contain, triglycerides, also known as fats and oils. These are esters of glycerol and fatty acids. A wide variety of plants produce triglycerides in commercially significant quantities, for example soybean, sunflower and peanut [19].

2.2.1.2 Lignocellulosic crops

Lignocellulose refers to the three-dimensional polymeric composites formed by plants as structural material. It builds up the cell walls of both woody and herbaceous biomass. Lignocellulose consists of variable amounts of cellulose, hemicellulose and lignin [19].

Cellulose, a homopolysaccharide of glucose [19], is the most abundant material in nature. In higher plants the cell walls are composed of cellulose to give structure [23].

Hemicellulose consists of a large number of heteropolysaccharides built from hexoses, pentoses, and deoxyhexoses, together with a small amount of uronic acid. Hemicellulose has lower chemical and thermal stability than cellulose [19].

Lignin is a phenylpropane-based polymer and the largest non-carbohydrate fraction of lignocellulose. Natural lignins are roughly classified according to plant source; softwood, hardwood and grasses. Unlike cellulose, lignin cannot be depolymerized into its original monomers. Lignin and hemicellulose form a sheath that surrounds the cellulosic portion of the biomass. Lignin protects the lignocellulose from insect attacks and anaerobic processes; even aerobic breakdown of lignin is slow and may take many days [19].

Table 1 lists the cellulose, hemicellulose and lignin contents in different types of biomass.

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40-55	24-40	18-25
Softwood stems	45-50	25-35	25-35
Corn cobs	45	35	15
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Grasses	25-40	35-50	10-30
Wheat straw	30	50	15
Switch grass	45	31.4	12
Paper	85-99	0	0-15
Sorted refuse	60	20	20
Primary wastewater solids	8-15	d.u.	24-29

Table 1. The cellulose, hemicellulose and lignin contents in different types of biomass [24]. d.u. = data unavailable.

2.3 Bioenergy

Renewable energy accounted for 14% of the world's primary energy demand in 2002. Biomass was by far the largest renewable energy source, with a total share of 11% [22].

75% of the renewable energy was consumed in the developing countries, principally in the form of traditional biomass (firewood) and hydropower. The traditional use of biomass in developed countries is predicted to decrease and be replaced by fossil fuels as per capita incomes and urbanization increases [22].

In the developed world, biomass is used in combined heat and electricity production [21]. In 2002, biomass-based electricity in the OECD[iii] countries accounted for between 1% and 3% of electricity generation. Worldwide biomass-fuelled electricity production is expected to triple from 2002 to 2030, with the most significant increase in OECD Europe [22]. Combustion data for some common forest and agricultural residues are shown in Table 2.

Biomass	LHV* (MWh/ton)	LHV (MWh/ton)	Moisture (%)	Ash (%)	Sulfur content (%, DW)
Forest residues	5.3	2.6	45	1.5	0.05
Bark chips	5.3	2	55	3	0.05
Wood chips (Salix)	5	2.2	50	1	0.02
Wood brickets or pellets	5.3	4.7	11	1.5	0.04
Fire wood	5.3	3.8	25	1	0.03
Straw	4.8	4	15	7	0.15
Reed Canary grass (summer)	4.8	4	15	7	0.17
Wheat	4.8	4.2	11	2.1	0.13

Table 2. Combustion data for some common energy crops, forest and agricultural residues. LHV = Lower Heating Value. (*) Dry samples. Modified from Ref. 25.

3. Hydrothermal carbonization

Hydrothermal carbonization (HTC) is a process similar to peat or coal formation [26]. However, while the natural process of peat or coal formation takes place on the time scale of some hundred (peat) to millions (black coal) of years, and hence cannot be considered in material or bioenergy exploitation routes, the time scale of the HTC process is that of day(s) [26, 27]. In the process, sugars and carbohydrates are transformed into black soil, peat, brown coal or other carbonaceous materials [28].

3.1 Background

There are countless trials in the literature to imitate coal formation from carbohydrates with faster chemical processes [27]. As early as in 1913, Bergius and Specht described the hydrothermal transformation of cellulose into coal like materials [29]. Already in those days elemental compositions, the in principal spontaneous character of the reaction, as well as its exothermic character were recognized. It was also Bergius who first varied catalysts, pH and temperature in a more systematic fashion and found certain flexibility in the decomposition schemes depending on the catalysts [30]. Even more systematic investigations were performed by Berl and Schmidt in 1932, who varied the source of biomass and treated the different samples in the presence of water at temperatures between 150 and 350 °C. In a series of papers Berl and Schmidt the same year summarized the current knowledge about the emergence of coal [31]. Later, Schuhmacher, Huntjens and van Krevelen further analyzed the influence of pH on the outcome of the reaction and found large differences in the

[iii] Organization for Economic Cooperation and Development

decomposition schemes, mainly based on mean composition [32]. A real breakthrough was the reports on hydrothermal synthesis of carbon spheres under mild conditions (temperatures ≤ 200 °C), using sugar or glucose as precursors [33, 34].

3.2 The HTC process

Carbohydrates, important constituents of both plants and animals, are polyhydroxy aldehydes or ketones or their derivatives. Compounds classified as carbohydrates range from those consisting of a few carbon atoms to gigantic polymeric molecules. Carbohydrates that cannot be broken down into simpler units by hydrolysis reactions are known as monosaccharides. Examples of monosaccharides are glucose and fructose (both $C_6H_{12}O_6$) [23].

In the HTC process, carbohydrates in a slightly acidic, aqueous solution are mildly heated (180-205°C) in closed recipients, forming condensed, coal-like structures [26, 30]. A schematic reaction equation is given in Equation 1. Depending on the extent of the reaction, four to five water units per carbohydrate molecule are eliminated in the final product [30].

$$[C_6H_{12}O_6]_n \rightarrow n[C_6H_4O_2 + 4H_2O]$$

"carbohydrate" → "coal" + water

Equation 1. A schematic reaction equation for the HTC process [30].

The elimination of water in the presence of water seems counterintuitive, but the reaction is both exothermic in character as well as strongly supported by entropy (due to increase of the numbers of molecules and the degrees of freedom) [30].

For complex biomass, the chemical decomposition cascade of HTC is more complex than for pure glucose. Model examinations with glucose and GC-MS[iv] examinations of the intermediary states of biomass indicate that the main reaction channel of HTC is a very quick partial dehydration of the carbohydrate to hydroxymethylfurfural. The hydroxymethylfurfural subsequently undergoes cycloaddition and polymerization reactions, essentially resulting in structures rich in carbonyl, aliphatic and aromatic hydroxy groups (Figure 2). As mentioned above, four to five water units per saccharide unit are eliminated in the process, depending on the extent of the reaction [30].

Due to the fact that the HTC process progresses through liquid intermediates, which later cyclize/polymerize to the final coal like material, the final product consists of nanometer scaled, globular carbon spheres [27]. The spheres have highly hydrophilic surfaces, with a distribution of hydroxyl (OH) and carbonyl (C=O) groups that are formed from non- or just partially dehydrated carbohydrates [27, 7]. In a typical reaction with glucose as starting material, elemental analysis shows that 70 - 92 wt% of the product can be attributed to carbon. The remaining mass is made up of oxygen and hydrogen atoms in the hydrophilic shells [35].

[iv] Gas chromatography – mass spectrometry

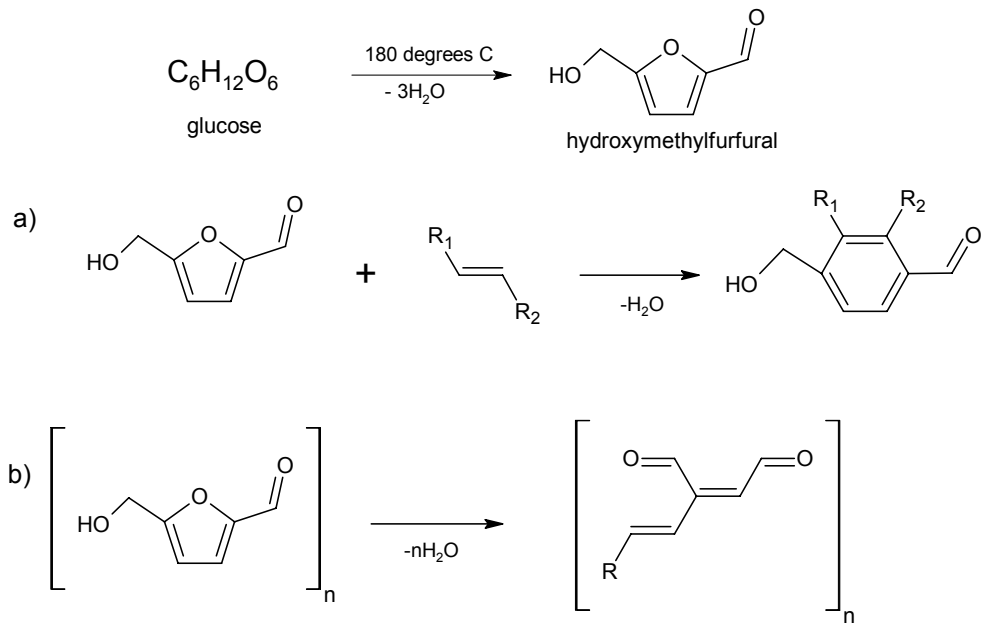

Figure 2. HTC starts with a partial dehydration of the carbohydrate to hydroxymethylfurfural. The hydroxymethylfurfural subsequently undergoes cycloaddition (a) and polymerization (b) reactions [30].

3.3 Advantages with HTC compared to other carbon conversion routes

Once activated, the HTC process is a spontaneous, exothermic process. Because of the high thermodynamic stability of water, it liberates about a third of the combustion energy stored in the carbohydrate. A schematic comparison of HTC with fermentation and anaerobic digestion is shown in Figure 3. The carbon efficiency (CE) of HTC is close to 100% for bare dehydration, i.e. practically all of the starting carbon stays bound in the final carbonaceous material. For this value temperatures below 200 °C and a pH value between 5 and 7 are mandatory [30, 36]. The CEs of fermentation and anaerobic digestion are 66% and 50%, respectively [37].

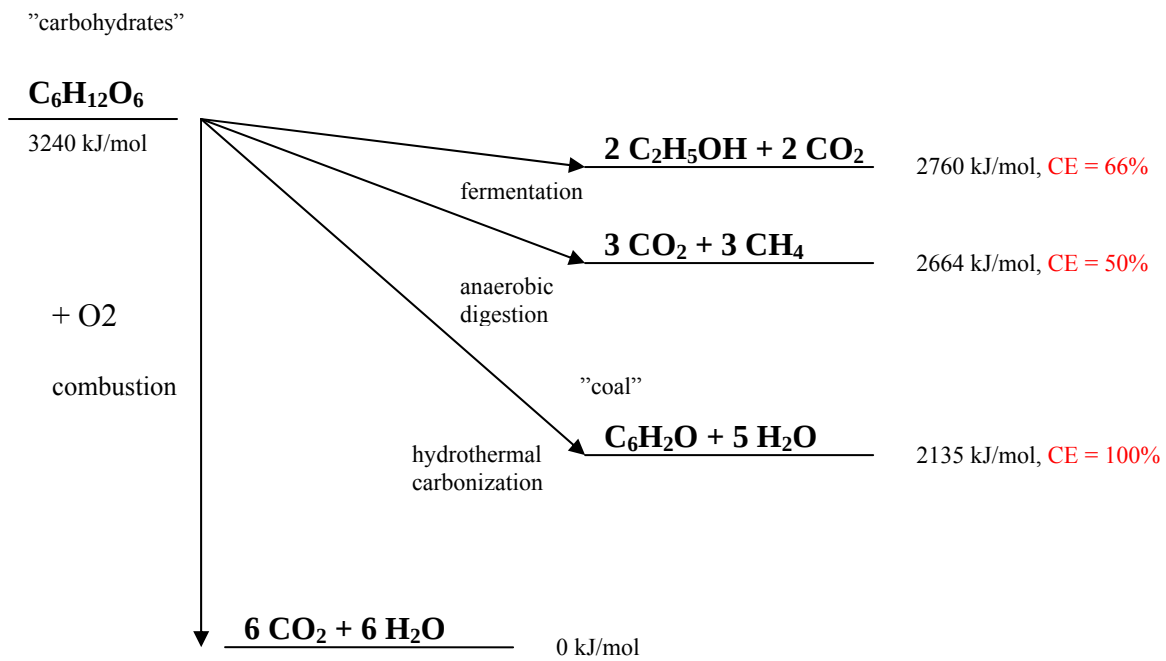

Figure 3. A comparison of different energy exploitation routes for biomass. Modified from Ref. 37.

HTC requires wet starting material. At the end of the process, the final carbon can easily be filtered off the reaction solution. This means that complicated and costly drying schemes and isolation procedures can be avoided [27, 36, 37].

3.4 Complex biomass as starting material

The presence of ternary components in complex biomass can seriously alter the decomposition pathways, as compared with pure, simple carbohydrates such as glucose [27]. All the mechanically soft biomass without extended crystalline cellulose scaffolds in the complex sample is essentially hydrolyzed and carbonized, which results in nm-sized globular carbonaceous nanoparticles [36]. The hard plant tissue, with structural, crystalline cellulose scaffolds, shows a different structural disintegration pathway. The melting point of crystalline cellulose is well above its decomposition temperature, which to a large extent can result in a preserved macro- and microstructure in the final carbonaceous material [36].

The lignin fraction of biomass essentially goes unchanged through the HTC process. By cycloaddition, it can be cross linked to coal, but the essential lignin structure remains stable in the rather mild conditions of HTC [38]. Thus, for the hydrothermal carbonization of biomass, materials with low lignin contents and high cellulosic contents are preferred.

The nanoparticles that are formed from complex biomass are much smaller than for glucose or pure starch. The reason for this might be an improved particle nucleation by nanoscopic side products formed by non-degradable secondary components (salts, polyphenols, tannins, carboxylic acids), as known from classical emulsion polymerization [36]. Specifically, for starting material such as orange peels and oak leaves, improvements of the carbonaceous structures for certain applications have unexpectedly been found, i.e. smaller structural sizes, higher hydrophilocity of the surfaces and higher capillarity [27].

3.5 Potential large scale applications

HTC could be used to sequester carbon from biomass for either material or energy use. Since all carbon in the starting product ideally stays bound to the final structure, large scale HTC of biomass can also be seen as an efficient carbon sink.

One application is the technical synthesis of carbon nanostructures [27, 36, 37]. Recently, it has been shown that the presence of metal ions effectively accelerates the HTC of starch and directs the synthesis towards various metal/carbon nanoarchitectures such as carbon nanocables, nanofibers and spheres [39, 40]. In the presence of iron (Fe^{2+}) ions, both hollow and massive carbon microspheres can be obtained. In contrast, the presence of iron oxide (Fe_2O_3) nanoparticles leads to very fine, rope-like carbon nanostructures [41].

Furthermore, the carbonaceous materials can be used as raw material in the chemical industry, as isolation material in buildings, as sorption coal for drinking water purification as improvement of concrete materials [28]. However, neither these applications, nor carbon nanostructures, will be discussed in detail in this Master thesis.

3.5.1 HTC for energy production

Products from HTC could be used for energy exploitation. This will be discussed in section 4. In section 5, HTC will be compared with conventional processes that convert biomass into energy, such as ethanol, biodiesel and biogas production. Other processes, such as the

Fischer-Tropsch process, can covert coal into transportation fuels. This will be briefly discussed in section 5.

3.5.2 HTC to degrade biowaste

HTC can be used to degrade biowaste from agriculture, for example left-overs from sugar bead and rapeseed production [37]. Orange peels contain flavones and limonenes; substances that will hinder microbial degradation of the biomass [36, 37]. For this reason, from orange juice production, i.e. orange peels, are becoming an acute problem in some areas. HTC has proved to work well for orange peels and results in a product that is suitable as fertilizer [27, 30, 31].

3.5.3 HTC products as soil improvement

The carbonaceous end-products could be used as a fertilizer to improve soil quality. For this application, the carbon-material not only has to be highly porous, it also has to be water-wettable and to contain appropriate functional ion binding groups along its surface [27, 36, 37]. The coal like materials from HTC has been shown to fulfil all these criteria [27, 36]. These aspects will be further discussed in section 6.

3.5.4 HTC for carbon sequestration

More than 80% of the global terrestrial carbon stocks are found in soils [42]. Stable humus produced with HTC will draw carbon dioxide from the atmosphere and keep it in the soil for hundreds to thousand of year [43]. With the growing concerns for global warming caused by increasing anthropogenic emissions of GHGs, mainly from the combustion of fossil fuels and deforestation, it would indeed be desirable to capture atmospheric carbon dioxide and store it as stable carbon materials. The potential of using HTC for carbon sequestration will be further discussed in section 6.

3.6 Precautions

As HTC is an exothermic reaction, it is important not to repeat the reaction procedures without sufficient safety measures. Too high concentrations of too easily carbonizable material can result in spontaneous, rather violent, breakouts of the reaction. Temperatures exceeding 220 °C should also be avoided [36].

4. Coal

Coal is an almost non-volatile, insoluble, non-crystalline, highly complex mixture of organic molecules varying size and structures. It consists of macerals (fossilized plants remains) which are differentiated into three major groups; vitrinite, exinite and inertinite. Vitrinite is the most prevelant group and is believed to be derived from woody plant material (mainly lignin). Exinite is developed from lipids and waxy plant substances. A possible origin for inertinite is char formed by prehistoric pyrolysis, e.g. wood fires [44].

4.1 Coal formation - from plants to peat

When a plant dies and falls into water, anaerobic bacteria will start the decomposition of the plant by removing hydrogen and oxygen through methane, carbon dioxide and water. As the peatification process proceeds, the carbon content increases from about 50% in wood to 55-60% in peat. This very first phase of coalification is called the biochemical phase [44, 45].

The bacterial activity will also produce organic acids and phenols. These compounds accumulate with time in still waters, and finally reach concentrations high enough to halt the

anaerobic decay. With time, more plant debris accumulates and compresses the lower layers of the newly formed peat. This represents the end of the biochemical phase, which typically lasts for a couple of hundred years [44, 45].

4.2 Coal formation - from peat to anthracite

In the geochemical phase, which can extend up to several hundred million years, the peat under the influence of high temperature and pressure, caused by overlying sediments, will undergoe metamorphosis and form coals of increasing rank. The formation of the highest ranked coal, anthracite, requires enormous pressures and high temperatures, which for example can occur upon collision between tectonical plates [45]. Figure 4 shows a simplified representation of coal genesis.

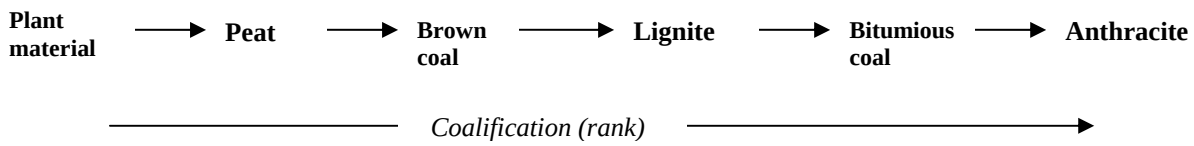

Figure 4. Genesis of coal. Modified from Ref. 46.

4.3 The ranks of coal

The classification of coal is made on the basis of rank. Peat, the first product in coal formation, is considered separate from coal, since it has not undergone metamorphosis in the geochemical phase [45, 47].

Lignite is sometimes referred to as *brown coal*, but some distinction can in fact be made between the two. Brown coal is younger geologically and has very high moisture content. Lignite contains around 70% carbon and has high moisture content. It is relatively soft and ranges in color from brown to black, and often contains easily recognizable plant remains up to the size of branches and stumps. Both brown coal and lignite tend to disintegrate ("slack") when dried in exposure to air [45].

Subbituminous coal is intermediate rank between lignite and *bituminous coal*. It has matured to a point at which the woody structures often seen in brown coal or lignite no longer are seen, and is black in color. The major part of our coal-derived energy comes from bituminous coal. Bituminous coal has lower moisture content and a higher heating value than lignite. It is black and breaks into prismatic blocks. If bituminous coal is heated in the absence of air, it softens. Gases will bubble through the softened mass and as it solidifies, a porous, hard, black solid known as coke is formed. Coke is the fuel used in furnaces to make iron, and its discovery led to widespread availability of cheap iron and was one of the major contributions to the industrial revolution [45].

Anthracite is the highest ranking coal. It is an ideal domestic fuel; it can be handled without dust and burns with a hot, clean flame without smoke or soot. It is low in moisture and sulfur, but it has a slightly lower heating value than bituminous coal. Anthracite does not form coke when heated, but can still fuel iron furnaces thanks to its hardness, strength and slow burning. Anthracite is occasionally called stone coal, and is due to its hardness, luster and commercial value also known as black diamond [45].

4.4 Elementary composition and typical properties of coal

The elementary composition of coal changes with increasing coal rank (Figure 5).

	Coalification (rank) →			
Plant material →	**Peat** →	**Lignite** →	**Bitumious coal** →	**Anthracite**
C %	55-60	70	80-90	92
H %	10	8-5	6-4	3
O %	35	25	10-5	2
C_{ar}/C_{tot}		~0.5	0.6	0.95
H/C		1 →		0.5

Figure 5. Typical elementary composition of peat and coals, showing % of carbon (C), hydrogen (H) and oxygen (O), as well as the proportion of aromatic carbons (C_{ar}/C_{tot}) and the molar H/C-ratio. Modified from Ref. 25, 44, 45, 47.

4.4.1 Minerals

Inorganic constituents can be incorporated in coal in several ways. The most straight forward way is during plant growth. Inorganic ions can also be taken up by ion exchange from the water or from waterborne mineral grains that pass through the coalifying plant material and be incorporated as detrital minerals [45].

4.4.1.1 Sulfur and nitrogen

Of the roughly 80 elements found in coal, the one with the most significant effects on the environment is sulfur. Some of the organic sulfur is a remnant of plant tissue (plant proteins contain 1-1.5% sulfur), but much of the sulfur results from bacterial production. Another principal source of sulfur is the sulfate ion, occurring in low concentrations in fresh water but in high concentrations in saline waters [45]. The sulfur contents of coals tend to depend on the source rather than on the rank [45, 48-50]. During combustion both organic sulfur and pyrite are oxidized to sulfur dioxide (SO_2) and trioxide (SO_3), collectively called SOx gases [45].

Other oxides that are formed upon combustion of coal are nitrogen monoxide (NO) and nitrogen dioxide (NO_2), commonly referred to as NOx gases. However, most of the nitrogen in NOx gases do not originate from the coal, but from atmospheric nitrogen gas which reacts with oxygen during combustion [45].

SOx and NOx are toxic to people, animals and plants. They cause respiratory problems as well as other kind of health problems [45, 51]. The most notorious role of NOx is the contribution to smog formation [45].

Both sulfur dioxide and NOx contribute to acidification of soils and waters [51, 52]. The most serious consequences of acidification of soils are leakage of plant nutrients, increased concentrations of free toxic metals in the soil and bounding of phosphate ions which make them less accessible to plants. Acid lakes will similarly experience increased metal concentrations, in particular aluminum from the surrounding soil [51]. Acid deposition also

accelerates the decay of building materials and paints, including irreparable damage to buildings, statues, and sculptures [53].

The sulfur content in European coal is usually between 0.6 and 1.2%, but coal with higher sulfur contents are mined both in Europe and the U.S. Brown coal from eastern Germany for example, has a sulfur content of 3.5%, whereas Australian and South African bituminous coal has comparatively low sulfur contents – less than 1% [54].

Some typical composition and physical property ranges for peat and various ranks of coal are shown in Table 3.

Class	LHV (MWh/ton)	Volatile matter (%)	Moisture (%)	Sulfur (%)	Nitrogen(%)	Ash (%)
Peat	3.3*	d.u.	40	0.13-0.24	1	2-6%
Brown coal	1.9 - 4	d.u.	45 - >60	d.u.	d.u.	d.u.
Lignite	3.9 – 4.8	24-32	25 - 45	0.6	1.2	3 - 15
Subbituminous coal	4.8 – 6.5	28-45	10 - 25	0.5	1.6-1.9	3 - 10
Bituminous coal	7.7 – 9.4	15-45	2 - 15	0.8-1.3	1.2	4 - 15
Anthracite	7.7-8.7	2-12	3 - 6	0.6	0.9	4 - 15

Table 3. Typical composition and physical property ranges for peat and coal, expressed on a moist, mineral-matter free basis[v]. LHV = Lower Heating Value. (*) 6 MWh/ton, dry matter. d.u. = data unavailable. Modified from Ref. 25, 45, 47.

4.5 Coal combustion

The most straightforward way to use coal is to burn it for heat and electricity production. Most of the heat liberated comes from the conversion of carbon to carbon dioxide and the conversion of hydrogen to water vapour. Hydrogen burning to water vapor produces 3.7 times more energy as carbon burning to carbon dioxide [45].

Coal could be burned as coal-slurries, pellets or powder. It should contain as little moisture as possible; otherwise heat liberated from the combustion will be used to evaporate water. Surprisingly, coal slurries can still burn quite well [45].

4.6 HTC-coal for combustion

When compared to typical properties of natural coal reserves, coal from the HTC process offer great advantages. It does not contain high concentrations of sulfur – the amounts of sulfur equal that of the biomass the coal was produced from. Depending on the biomass used, nitrogen concentrations could vary substantially. However, most of the NOx emissions originate from nitrogen gas in the atmosphere.

Combustion of HTC-coal will further give zero emissions of fossil carbon dioxide. The carbon dioxide that is released upon the combustion of fossil coal deposits was stored in plants million of years ago. Combustion of hydrothermally carbonized biomass will also give emissions of carbon dioxide, but this carbon was recently stored in the plants. As long as dedicated energy crops and biowaste are used, the use of hydrothermally carbonized biomass for energy production can be considered energy neutral (if also transportations and the process itself are energy efficient).

[v] Moist, mineral-matter-free basis is a theoretical analysis calculated from basic analytical data and expressed as if the mineral-matter had been removed and the natural moisture retained.

Furthermore, coal mining causes serious environmental degradation. From this point of view, hydrothermally produced coal from biowaste is a much better alterative, since it does not exploit the ecosystems in search for raw material.

5. Biofuels

The two primary biofuels in use today are ethanol, made from the fermentation of sugar-and starchy rich crops, and biodiesel, made from oil crops [55, 56]. Ethanol accounts for about 90% of global biofuel production, and biodiesel makes up most of the remaining 10% [56]. Pyrolysis and gasification of biomass are other ways to produce biofuels [57].

The various biofuel feedstocks can be grouped into two categories. The *first-generation* feedstock comprises various grain and vegetable crops which are harvested for their sugar, starch or oil content. This feedstock can be converted into liquid fuels using conventional technology [56]

The *second-generation* ethanol feedstock comprises wastes and lignocellulosic dedicated energy crops. These are materials such as wood, tall grasses, crop residues, solid animal waste and solid municipal waste [56, 58]. The conversion process of these materials includes the hydrolysis of the cellulose by cellulase enzymes to fermentable reducing sugars [58]. Many of these technical processes are still under development [56], but several demonstration plants have already started their production. The world leading producer of ethanol from lignocellulosic materials is Iogen Corporation, based in Ottawa, Canada [59]. In Sweden, Etek Etanolteknik AB is producing ethanol form lignocellulosic materials [60, 61, 62].

Second-generation biodiesels are synthetic biofuels derived from biomass, wastes or black liquor[vi]. Examples of fuels are Fischer-Tropsch diesel and dimethyl ether (DME) [63].

Biofuels are often seen as promising alternatives to fossil fuels. A rapidly increasing demand for transportation fuels combined with decreasing petroleum reserves of non-OPEC[vii] states has increased dependency on a limited number of oil providing countries with inherent risks for energy security and sudden price distortions [64, 65]. Biofuels are therefore considered a better alternative for reasons of security and foreign exchange savings, but also for environmental concerns and socioeconomic issues related to the rural sector [66].

In 2005, world biofuel production was equivalent of about 1% of the global transport fuel market. Global ethanol production more than doubled between 2000 and 2005, while production of biodiesel, starting from a much smaller base, expanded nearly fourfold. Biofuel production is poised for even stronger growth as the industry responds to higher fuel prices and supportive government policies [56].

The European Union Biofuels Directive from 2003, demands all member states to aim at having 2% and 5.75% percent of transportation fuels replaced by biofuels in 2005 and 2010, respectively [67, 68]. Only Germany, Austria and Sweden reached the 2005 goal [68].

Sweden has set itself the goal to achieve total oil independence in 2020. The Swedish government aims at replacing a large amount of gasoline and diesel with biofuels, over half of

[vi] A recycled byproduct formed during the pulping of wood in the papermaking industry
[vii] Organization of the Petrolium Exporting Countries

which is hoped to derive from Swedish forestry and agriculture [69]. However, Sweden still has a long way to go. Biofuels accounted for 2.3% of the total use of gasoline and diesel in 2005 [70]. Ethanol is the most important biofuel, but Sweden is far from self-supporting. Imports from Brazil and the EU are of great importance for Swedish biofuel supply [70, 71].

5.1 First-generation ethanol

Ethanol is produced by processing starchy or sugar-rich crops, such as sugar cane, wheat or corn. The sugars are fermented by yeasts to produce ethanol, which is then distilled. In the case of starchy crops, the starch is first converted into sugars using enzymes [55].

The major producers of ethanol are Brazil and the U.S., which together account for about 80% of the world production [1]. Brazil, using sugar cane as the feedstock for ethanol, produced 16.5 billion liters of fuel ethanol in 2005 [56], satisfying 40% of its automotive fuel needs [1]. In the U.S., corn grain is the main feedstock [72]. 16.2 billion liters of fuel ethanol were produced in 2005 [56]equivalent to just under 2% U.S. gasoline use [1]. China ranked third in the fuel ethanol output and the EU as number four [56]. Chinese fuel ethanol is almost exclusively produced from corn, but cassava – a perennial woody shrub with up to 32% starch content – is becoming popular [73, 74]. Cassava has two advantages over other feedstock; it can be cultivated on marginal lands [73], and is not a staple food for the Chinese people [75]. In Europe sugar beets, corn and barley are the dominant crops for ethanol production [1].

Most cars can burn gasoline fuels blended with up to 10% ethanol, some even up to 20%, without any modifications to the engine, and some new cars can burn pure ethanol [55]. In the U.S. and Brazil, 10% and 22% blends are being used, respectively [76]. The European standard is currently 5%, but is expected to be changed to 10% within the next few years [77].

5.2 First-generation biodiesel

Biodiesel is another name for fatty-acid esters. Fatty-acid esters cover vegetable methyl esters, fatty-acid methyl esters (FAME) and fatty-acid ethyl esters (FAEE). In the EU, rapeseed methyl ester (RME) is the most used biodiesel [63].

Biodiesel is produced from a variety of vegetable oils – including soybean, palm, rapeseed, sunflower, peanut and coconut. Discarded frying oils and animal fats can also be used [63].

The oil is treated in a process called transesterification. The oil is extracted either mechanically or by a solvent. It is mixed with an alcohol (methanol or ethanol) and a catalyst and is then reformed into esters [63]. Biodiesel can be used in place of normal diesel without modification of the engine [55, 63].

Germany is the world's leader in biodiesel fuel production, producing more than the rest of the world together. The second largest producers are France and the U.S. [26]. In the EU, rapeseed and sunflower seed are the most common crops for biodiesel production, whereas soybeans are dominating in the U.S. In Asia, palmoil is the dominating raw material [63].

5.3 Environmental and economic aspects of first-generation biofuels

The predicted strong growth of biofuels [56], using the current production technologies based on food crops, would create both economic and ethical problems.

The world's agricultural lands supply more than 99.7% of the world's food (calories), while aquatic ecosystems supply less than 0.3% [80]. Expanding ethanol production will divert

valuable cropland from producing food to the production of feedstock for ethanol factories [81]. The production would compete for the limited agricultural land needed for food and feed production, and raise food prices significantly [1, 17, 19, 55, 56, 58, 78], a major ethical question in a time when one in three people worldwide is affected by malnutrition [78]. The 32 million tons of corn, 12% of the huge U.S. corn crop, transformed into ethanol to replace less than 2% of American gasoline in 2004, would be enough to feed 100 million people at average world grain consumption levels [1]. Even dedicating all US corn to ethanol production would only meet 12% of its gasoline demand [17].

It has been feared that rising food prices, due to the western world's increasing demand for food crop-based biofuels, will lead to urban food riots in lower-income countries that rely on grain imports, such as Indonesia, Egypt, Algeria, Nigeria, and Mexico [83]. In fact, this is already happening – Mexico is in the grip of its worst tortilla crisis in modern history. Tortillas based on corn are the Mexican staple food and provide poor Mexicans with more than 40% of their protein needs. Dramatically increased international corn prices, spurred by demand for the grain-based fuel ethanol, have led to almost four-fold increases of tortilla prices in some parts of the country [84].

Based on current ethanol production technology and recent oil prices, ethanol costs substantially more to produce than it is worth on the market. Without the huge government subsidies each year, most ethanol production would be reduced or cease. Some politicians have also the mistaken belief that ethanol production provides large benefits for farmers, but in fact the farmer profits are minimal [81]. Big corporations, such as Archer Daniels Midland Company [82], are instead criticized for making huge profits on ethanol production [81].

Other concerns about first-generation biofuels are energy balances. Pimentel [75] showed that ethanol production from corn required 29% more energy than could be gained from the final product. Another study showed that corn ethanol has GHG emissions similar to those of gasoline [85]. However, biofuel energy balances are strongly dependent on the type of biomass used for production. Ethanol from Brazilian sugarcane is generally considered one of the best choices, with net GHG benefits and net energy yields several times higher than the energy input. Sugar cane avoids the first phase of the corn process – converting the plant starch into sugars and it also produces more fuel per hectare of crop than corn does [1, 55].

Ethanol production furthermore puts high pressure on the world's water reserves. Sugar cane might be a more greenhouse-friendly feedstock than corn, but it requires more water for growth [55]. Also, the fermentation/distillation process requires large volumes of water. For the production of ethanol from corn, some 15 litres of water are added per 2.69 kg of ground corn, and in the end, around 13 liters of waste water is removed from every liter of ethanol produced. This is not only a waste of water, it is also very energy consuming [81].

The energy yields from biodiesel are also debated. Hill *et al.* [17] compared biodiesel from soybeans with ethanol from corn, and concluded that energy yields, GHG emissions and released air pollutants per net energy gain were lower than for ethanol. The advantages of biodiesel over ethanol are said to come from lower agricultural inputs and more efficient conversion of feedstock to fuel. However, in a study by Pimentel and Patzek [81], it was concluded that biodiesel production using soybean and sunflower required 27% and 118% more fossil energy respectively, than could be gained from the biodiesel.

Also, biofuels contribute significantly to fertilizer and pesticide pollution [1, 17, 55, 75, 86]. Biodiesel, however, contributes to less nitrogen, phosphorus and pesticide pollutions than ethanol, since it can be grown with fewer inputs of fertilizers and pesticides [17, 55].

Biofuel production could soon become the leading threat to animal and plant biodiversity [1, 55, 75, 86]. Sugarcane production is already expanding into the Brazilian Cerrado[viii] and Amazon Basin, and palm plantations are moving further into the Indonesian and Malaysian rainforests [1]. It is estimated that 87 percent of the deforestation in Malaysia from 1985 to 2000 was caused by new palm plantations. In Indonesia, the amount of land devoted to palmoil has increased 118 % in the past eight years [67].

Expanding palm plantations to meet the rising demands for palmoil is often done on the expense of peatland. Of the 27 million hectares of peat land in Southeast Asia, 45% have been deforested and mostly drained and burned. This has released vast amounts of soil carbon into the atmosphere. The current total carbon dioxide emissions from peat lands equal almost 8% of global emissions from fossil fuel burning. Over 90% of these emissions originate from Indonesia, and put the country in 3rd place (after the U.S. and China) in the global carbon dioxide emission ranking [87].

The green fairytale of first-generation biofuels is beginning to look more like an environmental nightmare. As a result, politicians in many countries are rethinking the billions of dollars in subsidies that have supported the spread of these "eco-friendly" fuels [67].

5.4 Biogas

Anaerobic digestion to biogas is the decomposition of organic wastes, including poly-saccharides, proteins and lipids, to gaseous fuel by bacteria in an oxygen-free environment [40]. Typical composition of biogas is 50-70% methane, 25-40% carbon dioxide and small amounts of hydrogen, nitrogen and oxygen gas, as well as hydrogen sulphide. The gas can be used to produce heat and electricity, or as a transportation fuel. In that case, carbon dioxide has to be separated from the gas to yield at least 97% methane [88].

Anaerobic digestion of biogas is a cheap and environmental friendly way to treat organic waste. It gives environmental benefits since it is produced locally on farms and waste is used for the production. It reduces nuisance from odours, flies and rodents as well as the amount of pathogens. Its use for heat, electricity and transportation reduces GHG emissions to the atmosphere compared to other alternatives [89]. However, different types of biowaste give different energy yields. Energy-rich agricultural residues such as sugar beet, fruit and vegetable waste give 4-7 times more methane per unit weight than does manure from cows and pigs [88].

5.5 Outlook for biofuels

Only second-generation biofuels are environmentally sustainable. Ethanol should not be produced from food crops but from plants, bushes or trees grown on land unsuitable for agriculture. This type of biomass neither compete for fertile soils with food production, nor encourage ecosystem destruction [1, 17, 19, 55, 58, 75, 78, 86]. There is also a large potential in the huge amount of low-value or waste lignocellulosic materials that are currently burned or wasted [58].

[viii] The most extensive wood-land savanna in South America, comprising more than 20% of Brazil.

However, energy outputs from ethanol produced from lignocellulosic materials are still less than the fossil energy inputs. Ethanol produced from American switch grass requires 50% more fossil energy than can be gained from the ethanol fuel, and ethanol from wood harvested from sustainable forests requires 57% more fossil energy than the ethanol fuel produced [81].

It is also suggested that it would be uneconomic to use forest products for ethanol production; Swedish forest companies for example, make more money on high-quality products such as paper and timber [90].

5.5.1 Potential benefits of HTC compared to first-generation biofuel production

First-generation biofuel production has been criticized to:

- Divert valuable cropland from producing food to producing biofuels and increase food prices. HTC, however, works well for the same feedstock as used for second-generation ethanol, and will not compete with people for food crops.
- Cost substantially more than its worth on the market. HTC should be a cheaper alternative since abundant low-value biomass can be used. However, the investment costs for a larger HTC facility are to this date uncertain and need to be further investigated.
- Have negative energy-balances and release more GHGs to the atmosphere than fossil fuels. The HTC process does not require energy extensive agricultural or harvesting practices associated with first-generation feedstock. Dewatering and drying processes (Section 11.4.2) should be less energy intensive than distillation of ethanol. The process has higher CE compared to ethanol and biogas production (Figure 3) and ideally, more energy (in the form of heat) is produced during the process than is needed to activate it. However, it is uncertain how much energy a larger HTC facility would require. Energy balances for large scale HTC of biowaste should be a priority for future studies.
- Consume large quantities of water. Since the raw material for large scale HTC processes ideally is biowaste, no water for cultivation is needed. But dry biomass requires water for the process, which might be a problem where water resources are scarce. However, the water can potentially be reused in the process. There might also be useful applications for the wastewater (Section 10.5.1).
- Contribute to fertilizer and pesticide pollution during growth of the feedstock. HTC from biowaste would not contribute to pollutions of this kind.
- Threaten plant and animal biodiversity when peatland, savannas and forests are converted into energy crop plantations. If HTC-products are produced from biowaste, HTC production would not threaten ecosystems.

5.5.2 Second-generation biofuel production compared with HTC

Just like first-generation biofuels, second-generation biofuel production has been criticized to have negative energy balances. As mentioned above, extensive energy-balances for the HTC process should be performed to establish that large-scale HTC from biowaste in fact has a positive energy balance. Furthermore, biofuel production based on forest products has been criticized to be uneconomic. However, HTC processes should mainly use biowaste as raw material.

5.5.3 Coal gasification and liquification – HTC to produce biofuels

There are several reasons why coal is converted into liquid or gaseous fuels. First, liquidified and gasified coal could serve as an alternative to petroleum and natural gas. Second, synthetic

fuels form fewer sulfur and nitrogen oxides during combustion and have fewer ash-related problems. Third, gaseous or liquid fuels are easier to ship and handle than solid fuels [45].

The world's most extensively studied and used process to produce synthetic liquid fuels from coal is the Fischer-Tropsch process (FT-process), which is based on indirect liquefication. The FT-process was developed in Germany in the 1920s and a vital component of the German economy during World War II (WWII). At its peak around 1943, 200 million gallons of fuel were produced each year. However, after WWII, synthetic liquid fuels could not compete economically with natural petroleum [45].

In the process coal is gasified and the resulting syngas (carbon monoxide and hydrogen) is let to react in the presence of various catalysts at fairly high temperatures and pressures. The products, depending on specific conditions can include straight-chain alkanes and alkenes, alcoholes, aldehydes, ketones and fatty acids [45].

It is outside the scope of this Master thesis to discuss whether or not carbon products from HTC would be suitable for processes that convert coal into gaseous or liquid fuels. However, based on the environmental and economic arguments in this section, it is an interesting alternative.

6. Carbon sinks

A carbon sink is any process, activity or mechanism that removes carbon from the atmosphere [91].

6.1 Natural carbon sinks

Atmospheric carbon dioxide is increasing only at about half the rate of fossil fuel emissions; the rest either dissolves in sea water and mixes into the deep ocean, or is taken up by terrestrial ecosystems [91]. Here, only terrestrial ecosystem will be discussed.

6.1.1 Terrestrial carbon processes

The amount of carbon that is converted from carbon dioxide to carbohydrate during photosynthesis is estimated to 120 PgC/yr[ix] [92, 93]. The second large carbon sink, the oceans, absorbs around 90 PgC/yr [94]. For comparison, 7.2 PgC/yr is emitted from fossil fuel combustion and cement production, and 1.6 PgC/yr result from land-use change [12].

Global terrestrial net primary production (NPP), the difference between photosynthesis and autotrophic respiration[x], has been estimated at about 60 PgC/yr [95]. Virtually all of the carbon fixed in NPP is returned to the atmospheric carbon dioxide pool through two processes: heterotrophic respiration[xi] by herbivores and decomposers and combustion in natural or human-set fires [96].

The difference between NPP and heterotrophic respiration determines how much carbon is lost or gained by the ecosystem. This difference is called the net ecosystem production (NEP). The global NEP is estimated to 10 PgC/yr, although this is likely to be an overestimate because of the current biased distribution of flux measuring sites [97].

[ix] 1 PgC/yr = 10^{15} g carbon per year. An emission of 1 PgC corresponds to 3.67 $PgCO_2$.
[x] Respiration by plants.
[xi] The conversion of organic matter to carbon dioxide by organisms other than plants.

When other losses of carbon are accounted for, including harvesting/removals (eventually combusted or decomposed), erosion and export of dissolved or suspended organic carbon by rivers to the oceans [98]; the remainder is the net biome production (NBP). The NBP is the carbon accumulated by the terrestrial biosphere, i.e. the net land uptake on a global scale over periods of a year or more [99].

Total NBP is estimated to have averaged -1.4 ± 0.7 PgC/yr during the 1990s [91]. The terrestrial system is hence acting as a global carbon sink, despite large releases of carbon due to deforestation in some regions.

6.1.2 Soil carbon

More than 80% of the global terrestrial carbon stocks are found in soils [100]. Depending on environmental conditions and the chemical composition of the dead tissue, different soil carbon pools can be distinguished [96]:

- *Detritus*[xii] *and microbial biomass*, with a turnover time of less than ten years.
- *Modified soil organic carbon*, with a turnover time of ten to hundreds of years.
- *Inert soil organic carbon*, composed of molecules more or less resistant to further decomposition.

If carbon sequestration in soils is to be considered an option for mitigation of the anthropogenic greenhouse effect, carbon has to be stored in inert soil pools to prevent fast return of carbon to the atmosphere.

6.2 Anthropogenic carbon sinks

International efforts to mitigate the anthropogenic greenhouse effect aim at reducing avoidable GHG emissions or off-setting unavoidable emissions through sequestration of carbon in the environment [101]. As regards sequestration, many different strategies are discussed in the literature, ranging from wide-spread afforestation[xiii] and reforestation[xiv] in terrestrial ecosystems [100], to pumping of carbon dioxide into deep oceans and geological layers [91]. For terrestrial ecosystems it has been proposed that carbon sequestration can be increased by increasing soil carbon stocks [102-104]. Given that soils contain 4.3 times more carbon than terrestrial vegetation [100], this might seem to be a good proposal. However, efforts aimed to achieve carbon sequestration in soils are often off-set by other GHG emissions [105]. Furthermore, soils generally show low potential to accumulate carbon; for example in conjunction with forest growth [106-109]. Soils hence represent a finite carbon sink at best [101]; they may have low permanency and can be easily depleted upon land use change [110].

6.2.1 Terra preta soils

One of the major problems of sustainable agriculture in the humid tropics is the rapid decomposition of organic matter [111] due to high temperatures, large amounts of precipitation and the lack of stabilizing minerals [112]. In the Brazilian Amazon Basin, upland soils generally have low soil organic matter (SOM) content [113], low pH, low cation exchange capacity [114, 115] and poor nutrient holding capacity [113]. However, in this area, patches of black-earth like soils with enhanced fertility have been found. The origin of these

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[xii] Non-living particulate organic material.
[xiii] The process of converting open land into a forest by planting trees or their seeds.
[xiv] The process of restoring areas of previous woodlands or forest that have been deforested or otherwise removed or destroyed at some point in the past.

nutrient-rich patches, in the otherwise infertile soilscape of the Amazon Basin region, has the focus of intensive debate [112, 113].

The dark soils were most likely created by pre-Columbian Indians 500-2500 years ago, and abandoned after the invasions of Europeans. Despite the prevailing humid tropical conditions and rapid mineralization rates, these dark fertile earths have persisted and have been described in several countries in South America [113]. While the anthropogenic origin of these soils (also called *Amazonian dark earths* or *Terra preta de Indio*) now is widely accepted, the question whether they were intentionally created for soil improvement or whether they are a by-product of habitation is still not clear [113, 116].

The frequent findings of charcoal [117] with highly aromatic humic substances in *terra preta* soils [111] indicate that residues of incomplete combustion (black carbon), mainly from indigenous land management and cooking fires, are a key factor in the persistence of SOM in these soils [112]. Due to the highly aromatic structure of black carbon, it is assumed to be chemically and microbially stable and persists in the environment over centuries or millennia [118]. Thus, when biomass is converted into organic-rich charcoal (hereafter called bio-char), a part of the labile carbon pool in the biomass is converted into a stable SOM pool. Oxidation over time produces carboxylic groups on the edges of the aromatic core, which increases the cation exchange capacity and the reactivity of the black carbon in the soil [112].

6.2.1.1 Terra preta soils as carbon sinks

Large amounts of bio-char in *terra preta* soils make them stable and give them high organic carbon contents - the total carbon content is as high as 250 Mg carbon ha^{-1} m^{-1} compared to typical values of 100 Mg carbon ha^{-1} m^{-1} in nearby soils [112]. Such carbon storage in soils far exceeds the potential carbon sequestration in plant biomass even if bare soil were, theoretically, restocked to primary forest containing about 110 Mg carbon ha^{-1} [113]. *Terra preta* soils therefore have been suggested to act as significant carbon sinks [112].

6.2.2 Bio-char as a carbon sink

Conversion of biomass to bio-char leads to sequestration of about 50% of the initial carbon in the biomass. Far lower amounts are retained after burning (3%) and biological decomposition (<10-20% after 5-10 years). It has been suggested that up to 12% of the total anthropogenic carbon emissions by land use change (0.2 PgC) can be off-set annually in soil, if slash-and-burn techniques would be replaced by slash-and-char. Agricultural and forestry wastes such as forestry residues, mill residues, fields crop residues or urban wastes would add another estimated 0.16 PgC/yr [101].

Apart from drawing carbon dioxide from the atmosphere, bio-char applications to soil are also able to reduce the emissions of other GHGs. A virtual complete suppression of methane emission from soils, as well as reduction of nitrous oxide with up to 80% in grass stands have been shown when bio-char was added to the soil [118]. The reduced emissions may be explained by better aeration (less frequent occurrence of anaerobic conditions) and possibly greater stabilization of carbon. The lower nitrous oxide evolution may also be an effect of the higher carbon/nitrogen-ratio (C/N-ratio), which gives slower nitrogen cycling [101].

In addition, land application of bio-char will lead to enhanced fertility of the soils. Bio-char will act as a soil conditioner enhancing plant growth by supplying and, more importantly retaining nutrients and by providing other services such as improving soil physical and biological properties [120-122].

6.2.3 HTC-products as carbon sinks

In contrast to burning, controlled carbonization such as charcoal production converts large quantities of aboveground biomass into stable carbon pools which are assumed to persist in the environment over centuries [112, 118, 123-125]. For carbon sequestration purposes, HTC of biomass should offer even greater promises than charcoal formation, since the HTC process has close to 100% CE [36], twice that of charring.

The persistence of HTC-products depends on the processing time. Biomass that is hydrothermally carbonized for more than twelve hours will be similar to modified or inert soil organic carbon, i.e. have turnover rates of hundreds of years or more. HTC for less than four hours will give a product similar to detritus [28].

However, as is the case with bio-char, more exact turnover rates of HTC-products need to be determined. It is necessary to establish that HTC-products are not broken down further to release carbon dioxide or other GHGs when added to soil (or otherwise utilized). There has been considerable debate around bio-char and the technical aspects of soil carbon sequestration, such as (i) 'permeancy', i.e. ensuring that carbon sequestered in soil is not released by a subsequent change in practice; and, (ii) measurement and monitoring of carbon sequestration in the soil [101].

Once this has been established, HTC offers a very attractive combination of "carbon-negative" energy (in the form of heat released during the HTC process) and humus production. Consumers of HTC products can participate in active carbon sequestration by using energy produced during the HTC process and applying the product as soil improvement.

HTC-products both structurally and chemically resemble bio-char and should be ideal for soil improvement [126]. They have high carbon contents, are highly porous, are water-wettable and contain appropriate functional ion binding groups along the carbon nanosphere surfaces [27, 36, 37]. Most of the positive aspects regarding soil improvement that have been attributed to bio-char are valid also for HTC-products [35].

7. Biomass with potential for HTC in Sweden

The amount of biowaste has over the last years been steadily increasing in Sweden [127]. Swedish domestic refuse totalled to 2.1 Mtons in 2005. 35 – 40% of this amount, around 800 000 tons, was food waste. Less than 10% (70 000 tons) of the food waste was composted and the rest was combusted with other types of refuse. In addition to the 70 000 tons of food waste, around 250 000 tons of waste from parks and gardens were composted [128, 129].

In 2005, around 455 000 tons of biowaste were biologically treated in Sweden, which is an increase with almost 5 % compared with 2004 [128].

7.1 Horse manure

The total number of horses in Sweden is estimated to be almost 300 000[xv] [130]. A horse of more than 500 kg produces between 8 and 10 tons of manure each year; straw, peat, wood chips, hey and urine included. A smaller horse or a pony produces roughly a fourth of this amount [131]. The total amount of horse manure produced in Sweden is thus estimated to be

[xv] 283 100 horses as of October 2004.

between 2 and 3 million tons a year [132]. To create a closed circle of nutrients and biomass, horse manure should as soon as possible be brought back to the agricultural lands from which the fodder originated [133].

A great majority, 75 %, of all horses in Sweden are kept in densely populated areas [130]. The fodder is often bought from distant farms, and there are often not enough fields to spread the manure in the area. For this reason, it has become complicated and often very expensive for stables to get rid of the manure. Since January 1st 2005, a new legislation in Sweden also forbids the deposition of organic waste [134].

For example, Täby Racecourse and Angarn, two stables located just outside Stockholm, pay 800 SEK (approximately 87 €[xvi]) for each container and additionally 160 SEK (17 €) for each ton of horse manure that is removed. Together the stables host almost 500 horses, and every month, around 400 tons of horse manure is collected. The manure from large stables in urban areas, like Täby Racecourse and several riding schools, does not only creates deposition problems, but also huge costs. In the case of Täby Racecourse, almost 900 000 SEK (97 000 €) is yearly spent on the removal of horse manure [135].

7.1.1 Horse manure as plant fertilizer

Horse manure consists of faeces (primarily undigested fodder), urine, straw, peat or wood chips, left-overs from fodder and water [136]. Fresh horse manure contains significant amounts of nitrogen (N), phosphor (P) and potassium (K), as well as smaller amounts of calcium (Ca), magnesium (Mg), sulphur (S) and mangan (Mn) [131].

The high humus content in the composted horse manure improves the structure and fertility of soils. However, in comparison with other fertilizers, horse manure contains relatively little plant-available nitrogen, and might in the beginning even lower the concentration of the soil's own nitrogen. Phosphor and potassium in horse manure are easily taken up by plants [133].

Farmers know that horse manure can contain bale ropes, horseshoes, plastics and other kinds of wastes [131], and horse manure is therefore not always attractive as fertilizer. The large amounts of bedding materials also lead to low-density products and large volumes to handle [133]. There have furthermore been speculations that lignins and terpenoids from wood chips could be harmful to plants and reduce growth, and therefore some resistance to the usage of horse manure as plant fertilizer. There is no evidence that this would be the case [131].

7.1.2 Composting

Composting is often necessary before the horse manure can be used as fertilizer on agricultural lands, especially if the bedding material is straw or shredded newspaper. If the bedding material is peat, composting is not always necessary and the manure can be spread directly on the fields [131].

7.1.2.1 Positive aspects of composting

Among the advantages with composting are that the weight will be around halved and that larger structures (like straw and hey) will be degraded, which simplifies the spread of the manure. Another benefit is that most seeds, parasites and microbes will be destroyed in the compost as it reaches temperatures of 60 - 70°C [131]. However, some seeds, for example wild oat, can survive these temperatures [133].

[xvi] 1 € = 9.24 SEK, Sveriges Riksbank February 20th 2007, from www.valuta.se

7.1.2.2 Negative aspects of composting

The high amount of bedding material in horse manure gives the manure a high carbon-nitrogen ratio (C/N-ratio). High C/N-ratios makes it difficult to start the composting process, and also prolongs it [133]. Time periods of one to two years are therefore common. To reduce the composting time, the compost regularly needs to be mixed to keep oxygen and water levels high and constant [137].

In Nordic climates, manure must be stored for up to nine months a year [138] since fertilizers only can be spread at a short time interval during the summer. This results in high storage and disposal costs [137]. According to Swedish law, stables with three horses or more must have storage capacity for six to eight months, depending on the number of horses [138].

As much as 50 % of the nitrogen in the manure is lost to the air as ammonium gas during composting [3]. Nutrients such as nitrogen and phosphor often leak out to lakes, rivers and coastal waters where they contribute to eutrophication. Besides leaking out as nitrate (NO_3^-) and ammonium gas, nitrogen leaves the horse manure as nitrous gas or nitrous oxide [133].

In addition to nitrous oxide, significant amounts of other GHG gases are released from composts. The reduction in weight is due to large losses of different compounds, such as carbon in the form of carbon dioxide and methane. Ongoing research at the Swedish Institute of Agricultural and Environmental Engineering aims at estimating the losses of GHG from manure composts [139].

7.1.3 Horse manure in the HTC process

HTC is proposed to be an efficient way to transform horse manure into stable humus with high nutrient content. If manure would be brought to a HTC plant on a daily basis, there would be a minimum of ammonium gas emissions or nutrient leakage. HTC would transform the horse manure into a useful product without loss of carbon dioxide or other GHGs. Costs for stables would be significantly reduced when the manure can be turned into a product after just a few hours, not after years of composting. Furthermore, the relatively high carbonization temperatures would kill all parasites, microbes and seeds in the manure. The only problem that HTC would not solve is that of horse shoes and bale ropes mixed with the manure.

7.2 Macroalgae

Algae are photosynthetic organisms that occur in most habitats. They vary from small, single-celled forms to complex multicellular forms. Macroalgae, or seaweed, are larger algae that live in marine (salt or brackish water) environments [140, 141].

7.2.1 Macroalgae as fertilizers

The use of marine macroalgae as fertilizer in crop production has a long tradition in coastal areas all over the world [142]. In many countries, seaweed and beach-cast are still used in both agriculture and horticulture [143, 144]. Besides supplying nutrients, composted macroalgae improves the soil structure by increasing humus content [145].

However, macroalgae from the Baltic Sea have become less suitable as agricultural fertilizers over the last decades. First, there has been an increase in the growth of filamentous algae due to eutrophication during the last 60 years [146]. In the shallow waters in the archipelagos, brown filamentous macroalgae of the genera *Pilayella* and *Ectocarpus* are today abundant [147, 148], which in the late summer and autumn accumulate as drifting mats [149-151]. The

macroalgal communities today mainly consist of red macroalgal species of the genera *Polysiphonia*, *Ceramium* and *Rhodomela* [152]. The amounts of *Fucus vesiculosus* (bladder wrack; blåstång), *Furcellaria lumbricalis* (kräkel) and *Rhodomela confervoides* (rödris), which traditionally were used as fertilizers in Sweden, are decreasing as the amounts of filamentous algae are increasing [153].

Second, heavy metals easily bind to polysaccharides. It is well documented that they can bind to the polysaccharides in the cell walls of macroalgae where they accumulate [154]. Sea water has commonly a very low heavy metal concentration, but algae can concentrate heavy metals up to high concentrations. Red algae in particular, may concentrate heavy metals by a factor 10^4 from sea water [155].

The relatively high salinity of algae could also make them unsuitable as fertilizers. However, some crops such as white cabbage, beetroots and celery, are relatively salt tolerant and should not be negatively affected [156].

7.2.2 Harvesting macroalgae

Sweden's mainland coast stretches 11 500 km, and together with the coastlines of marine islands (31 700 km) Sweden has 43 200 km of marine coastline [157]. The salinity ranges from 0.5 ‰ in the northern parts of Gulf of Bothnia, to 30 ‰ in Skagerrak and the North Sea on the Swedish west coast [156, 158].

Large quantities of algae are each year being washed up on Swedish shores. On the island of Öland in the Baltic Sea, up to 6900 tons of fresh weight beach-cast are found per km and year [159, 160]. However, the coast of Öland is very shallow and unusual large amounts of seaweed are therefore washed up. An estimate for the total amount of Swedish beach-cast has never been made [159].

Many Swedish municipalities regularly clear their beaches. For example, 1000-2000 tons of seaweed was yearly removed from Äspetstranden in Kristianstad during the 1990s [161].

Removal of seaweed from Swedish beaches will have several positive effects. On a local scale, outdoor and recreational life will be improved, especially during the summer months. When seaweed banks start to decompose they give of an unpleasant smell, with obvious negative effects on beach-linked tourism [156]. Cleaning of beaches also reduces the organic content of the beach sand, which gives a brighter appearance to the shore and increased stability for visitors walking along the beaches. These are qualities that both are economically important for the coastal near tourist industry [160]. Cleaning also reduces the risks for overgrowth of beaches [156].

The amount of nutrients leaking back to the coastal waters will decrease, which has a positive, limiting effect on the eutrophication and algal growths, which commonly cause oxygen deficiency [162-165] and induce toxic hydrogen sulphide production [150]. Large quantities on algae in shallow bays also have negative effects on biological biodiversity [156].

Removal of macroalgae from beaches often results in waste disposal problems on land. As was suggested in Jöborn *et al* [156], it would be of both economic and environmental interest to use the beach-cast as fertilizer, and partly replace the use of commercial fertilizers in coastal areas.

However, Greger *et al*. [166] concluded that although food crops grown on composts made of macroalgae from the Baltic Sea (in particular, the island of Öland) would enhance yields, it cannot be recommended. Concentrations of cadmium (Cd) both in composts from algae and in crops grown in them were greater than the limit values for arable soil and cultivated plants, respectively. Concentrations of copper (Cu), mercury (Hg) and lead (Pb) were not elevated, either in the compost or in the crop plants, but germination frequencies seemed to be lower for seed sown in the algae-composts than in soil. Even though the biomass production in crops cultivated on red algae composts was increased the high levels of cadmium in composts and crops make algae unsuitable as fertilizers. Instead, macroalgal composts could be used in smaller amounts on agricultural soils as a valuable nutrient source for non-food crop cultivation [166].

7.2.3 Macroalgae for HTC

HTC is proposed to be an efficient way for fast degradation of seaweed from Swedish beaches. During the summer months, seaweed is regularly being removed from most Swedish beaches and piled up to decompose. HTC would solve the deposition problem and remove nutrients from the Baltic Sea. It would be desirable to use HTC-products from seaweed as soil improvement, but the risk is that they will contain high levels of heavy metals.

7.3 Fiberbanks

Before the 1960s, Swedish pulp mills lacked equipment to filter their wastewater. As a result significant amounts of cellulose fibers mixed with sewage were released into Swedish lakes and rivers. Large fiberbanks can therefore be found on the bottoms of several lakes and rivers close to old pulp mills [167].

7.3.1 Environmental problems

Most fiberbanks contain significant amounts of mercury. During the 1940-1960s phenyl-mercury (Ph-Hg) was used to impregnate the pulp and to avoid growth of algae and mold onto pipes and machines. Phenyl-mercury followed the sewage out to the waters and was bound to the cellulose fibers on the bottoms of lakes [167, 168].

Swedish fiberbanks also contain dioxins, Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbones (PAHs) [169, 170]. PCB originates from paper with self-copy function that was recycled in the paper mills. The origin of PAH is unknown [170].

The release rates of heavy metals and other pollutants from fiberbanks are strongly dependent on sedimentation, bioturbation (the mixing of the fiberbanks by living organisms), different chemical processes and sorption. The release rate is also dependent on gas diffusion and erosion [44]. Mercury, for example, can be emitted from fiberbanks through gas diffusion, and it has been shown that mercury leaking from fiberbanks is stored in fish tissues [171].

Some different measures are today being used to reduce the release of hazardous compounds from old fiberbanks. Covering and stabilization of the fiberbanks *in situ* are two alternatives, dredging and deposition of the material on land is another option [169].

Dredging removes the sediments from the bottoms of lakes, but temporarily increases the release of pollutants to the surrounding waters. The final deposition of the dredged sediments is also a problem that needs to be solved. The chemistry of the sediments on land might be altered in the presence of oxygen, which might increase mobility of some compounds [169].

7.3.2 Fiberbanks for HTC
HTC is proposed as a way to solve the current deposition problem of cellulose fibers from dredged fiberbanks. If fiberbanks can be hydrothermally carbonized, it is important to find out if the pollutants (mercury, PCB, PAH etc…) will stay bound to the solid phase or be dissolved in the water phase.

8. Sampling

8.1 Horse manure
Horse manure was collected from two stables in the Stockholm-area. Horse faeces mixed with straw and wood chips was collected on November 8th 2006 from Täby Racecourse (Täby Galopp) in Täby. Horse faeces mixed with peat was collected on November 13th 2006 from Östermalm's Ridingschool. The samples were taken from the dung heaps between 8 and 9 am, right after the boxes had been cleaned, and were therefore fresh.

It is almost impossible to get homogenous samples of horse manure from a large dung heap. However, from the author's point of view, the amounts of horse faeces and bedding material that were sampled were representative for the dung heap as a whole. The samples were put in separate plastic boxes and stored at -20° C about an hour after sampling.

8.2 Seaweed
Seaweed was collected on October 28th 2006 from two different locations in the province of Skåne in southern Sweden. The first location was on a rocky beach right outside Ystad city-center. The second location was about 10 km southeast of Ystad; the beach in Kåseberga, just below the famous monuments of Ale Stenar. All seaweed that was taken from the water was freely floating and in close proximity to beaches or rocks. The seaweed was stored in plastic bags and stored at -20 °C after approximately 6 hours.

The species composition was determined with the help of a light microscope. The species below are ordered with the dominating algae first. English (if found) and Swedish common names are also presented [159].

1. *Ceramium virgatum*, a red algea (Grovsläke)
2. *Fucus vesiculosus*, a brown algea (Bladder wrack; Blåstång)
3. *Fucus serratus*, a brown algea (Tothed wrack; Sågtång)
4. *Zostera marina,* a green algae (Ealgrass; Ålgräs)
5. *Stictyosiphon tortilis*, a brown algea (Krulltrassel)

8. 3 Fiberbanks
Samples of a fiberbank were provided by the consultancy firm Grundvattenteknik (GVT) AB in Falun and arrived on November 10th 2006. The samples originated from the waters outside the Skutskär mill in the province of Uppland, approximately 15 km southeast of Gävle. Skutskär mill is a pulp mill, established over one hundred years ago. It is owned by Stora Enso AB and produces 540 000 tons of paper pulp and fluff pulp each year [172].

The brackish waters outside Skutskär are today being dredged for two reasons. One reason is to create a deeper channel; the other is to remove the mercury-contaminated fiberbanks originating from the factory's chlorine alkali production between the years 1940-1977. About 500 000 m^3 of fiberbanks are to be dredged from the sea bottom by GVT AB. The project is estimated to be finished in 2007 or 2008 [173].

9. Experimental procedures

9.1 Hydrothermal carbonization

The different experiments were named according to Table 4.

Experiment	Sample
SW	Seaweed
HS	Horse manure (straw as bedding material)
FB	Fiberbank
HC	Horse manure (wood chips as bedding material)
HP	Horse manure (peat as bedding material)

Table 4. The experiments and their abbreviations.

All experiments, but SW, were run in a 1000 ml stainless steel autoclave with a rotator that homogenized the samples throughout the carbonization process. The seaweed experiment was run in a non-stirred, 60 ml capacity Teflon-lined stainless steel autoclave.

Deionized water was added to the samples in experiments HS, HC and HP, i.e. the experiments with horse manure. In a typical procedure, around 200-300 ml horse manure and bedding material was dispersed in 600 ml deionized water in the 1000 ml autoclave. Seaweed and fiberbanks contain significant amounts of water and hence no extra water was needed. For all experiments, the autoclaves were filled up to around 90% of their capacities.

The HTC process requires, besides from wet starting material, slightly acidic conditions, and therefore citric acid was added to the samples with a pH around 7 or higher.

The 60 ml autoclave containing seaweed was put in a programmable oven at 205°C for 22 hours. The other experiments, which were run in the 1000 ml autoclave, were started at 180°C. After one or two hours the temperature was increased to 205°C and kept there for between 14 and 22 hours. One experiment was left to run over the weekend. The reason for the lower initial temperature was to avoid uncontrolled, exothermic onsets of the reactions. For more details, see Table 5.

Sample	Autoclave size	H_2O	Citric acid	pH before/ after citric acid	Time at 180°C	Time at 205°C	Cooling at room temp	Tot time for HTC, cooling included
SW	60ml	-	-	6/*	-	22h	30min	22h 30 min
HS	1000ml	~600ml	530mg	8/6.5	1h	14h	1h	16h
FB	1000ml	-	250mg	7/6	2h	19h 15min	45min	23h
HC	1000ml	~600ml	220mg	6/5	1h 30min	69h	3h	73h 30min
HP	1000ml	~600ml	-	6/*	1h 10min	18h 20 min	4h 20min	23h 50min

Table 5. Experimental data for the five samples SW, HS, FB, HC, HP. (*) no citric acid added

After cooling in room temperature, the autoclaves were opened and the products were filtered off. The liquid phases were stored in plastic flasks and the solid products dried in vacuum at 60°C over night.

9.2 Analysis

The samples after HTC were sent for elemental analysis to Analytica AB [174]. Both the solid and liquid phases from the HS, HC and HP experiments were analyzed with respect to elemental composition and heating values (solid phases only). Since the FB experiment was considered unsuccessful, neither the solid nor the liquid phases of the fiberbank were analyzed. Only the solid phase of SW was analyzed.

Heating values were analyzed according to SS ISO 1928 and the moisture content according to SS 187 170. The sulfur content was analyzed according to SS 187 177. The phosphor, potassium, lead, cadmium, cupper and mercury contents were analyzed with ICP-MS and ICP-AES, and the chloride content was analyzed with ion chromatography after leaching with water, according to DIN EN ISO 10304-1. The nitrogen, carbon, oxygen and hydrogen contents were analyzed with Leco-600.

The sulphur, phosphor and potassium contents of the liquid phases were analyzed with ICP-AES and the nitrogen content was analyzed with ion chromatography, according to DIN EN ISO 11905-1 (H36). The Total Organic Content (TOC) in the liquid phases was estimated according to DIN EN 1484 H3.

The products were further characterized at the Max-Planck Institute in Potsdam by High Resolution Scanning Electron Microscopy (HRSEM) on a Gemini Scanning Electron Microscope (Carl Zeiss, Oberkochen). Brunauer-Emmet-Teller (BET) nitrogen-adsorption and desorption isotherms were measured at 77 K with a Micrometrics Tristar 3000 System. The isotherms were evaluated using the BET method to give the surface areas. Thermogravimetric Analysis (TGA) was performed on a NETZSCH TG 209 at a heating rate of 20 K per minute under air and nitrogen flow. X-ray Diffraction (XRD) patterns were recorded in reflection mode (Cu Kα radiation) on a Bruker D8 diffractiometer. Energy Dispersive X-ray analysis (EDX) was performed using a Zeiss DSM 962 (Carl Zeiss, Oberkochen).

10. Results

The pressure build-ups during the experiments were 20-30 bars (measured for all experiments but SW). Upon opening, all autoclaves released some gas, predominately methane, as told from the smell. The FB experiment produced less gas than the others.

The liquid phase that was filtered off from the SW experiment was dark in color and foaming, presumably due to lipids. The liquid phases from experiments HS, HC and HP - all with horse manure - were yellow to reddish in color. All three were foaming when filtered, which probably was due to amino acids [175]. The water phase from the FB did not foam.

Apart from FB, the solid phases were dark in color and had distinct coal smells. The solid product from the FB experiment was more greyish in color than the others. For dry weights of the products, see Table 6.

Sample ID	SW	HS	FB	HC	HP
DW product (g)	4.7	30.8	78.1	42.1	21.0

Table 6. Dry weights of products

10.1 High Resolution Scanning Electron Microscopy (HRSEM)

As can be seen in the HRSEM-images in Figures 6, 7 and 8, the cellular, layered architecture of the carbohydrate matrix in the hard biomass is essentially kept throughout the HTC process, presumably also supported by the lignin fraction. The soft biomass, however, is turned into carbonaceous spheres. The drop like appearance indicates that the HTC process progresses via liquid intermediates which polymerize/cyclize to the final carbonaceous material.

Figure 6 shows horse manure mixed with wood chips (HC). The original sample is shown in Figure 6a. Figure 6b shows the sample after HTC (scale bar 10µm). The original texture is well preserved on the macroscale. However, with increased magnification (Figure 6c, d) the disintegration of the original tissue becomes apparent as globular carbonaceous nanoparticles (size approximately 40-100 nm in diameter) are visible.

The theoretical mass loss for pure glucose during HTC is 50 wt%. The mass loss for more complex biomass has been shown to range from 37% up to 63%. The weight loss for soft biomass (for example orange peels and pine needles) is greater than for harder biomass (for example oak leaves and pine cones). Weight losses of this magnitude, and simultaneous preservation of large scale structural features on the macro- and microscale, has consequences on the nanometer scale. Removal of water leads to material shrinkage, which occurs on the nanoscale only [36] and creates a continuous pore system, with pore sizes ranging from around ten to some hundred nm (Figure 6c, d).

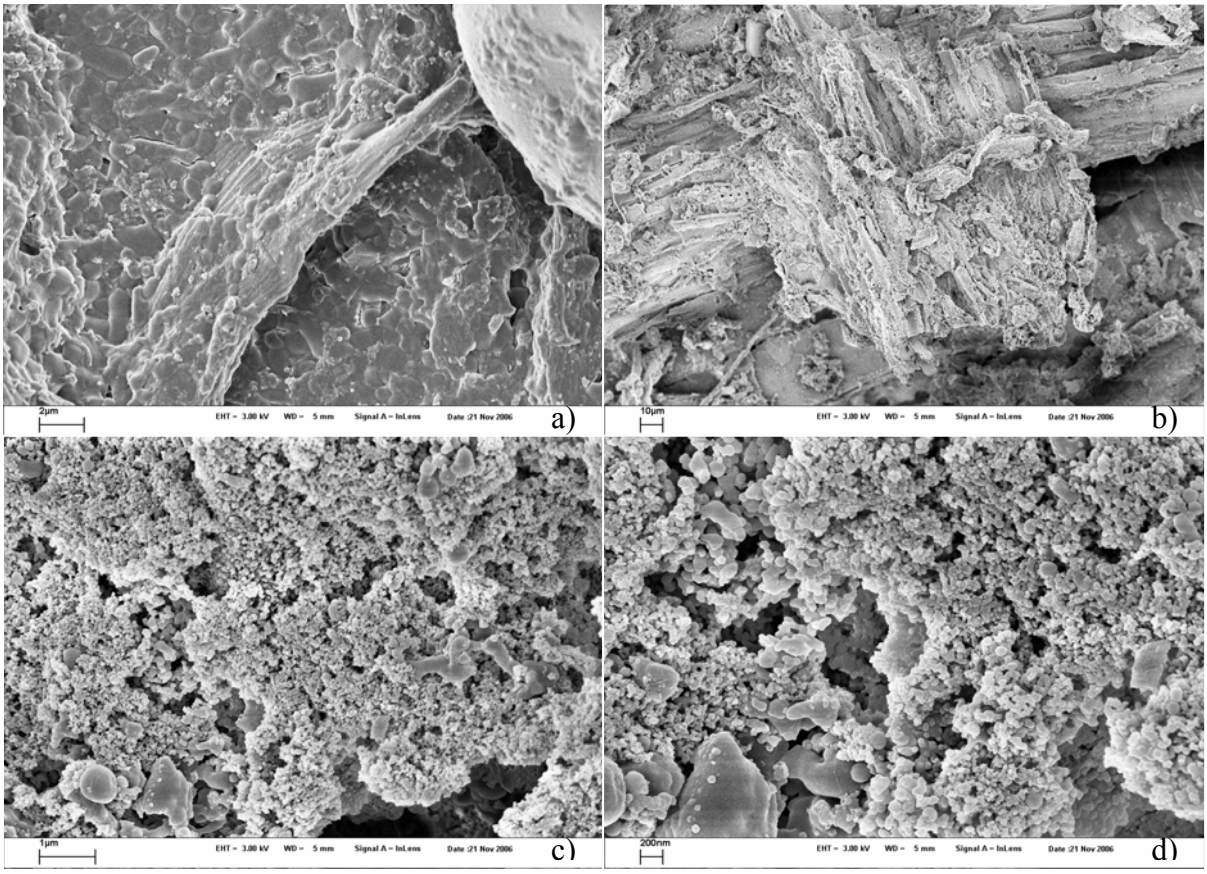

Figure 6. HRSEM of horse manure with wood chips (HC) before (a) and after (b, c, d) HTC. The scale bars are (a) 2µm, (b) 10µm, (c) 1µm and (d) 200nm. In (b), it can be seen that the hard tissue's original texture is preserved on the macroscale throughout HTC. In (c) and (d) the changes on the nanometer scale can be seen; all mechanically soft biomass have become disintegrated into carbonaceous nanoparticles.

Figure 7 shows the seaweed before (Figure 7a) and after (Figure 7b, c) HTC. Other images, with the same or 10µm-resolution (not shown), show that much of the macro-scale structure seems to be preserved through HTC also in the SW experiment. With larger magnification (Figure 7c) the carbonaceous spheres will once again evident.

The fiberbank experiment was considered unsuccessful, supposedly because the cellulose sediments had been petrified during the long time on the sea bottom. Petrifaction is a process in which minerals in the surrounding water enter the cells of dead plants and animals and crystallize. After some time, the organic material has completely been replaced by minerals and the tissue is turned into stone. The assumption was confirmed by the HRSEM-images. Figure 7d) shows the FB experiment after HTC (scale bar 200 nm). The cellulose fiber structures both before (data not shown) and after HTC resembles petrified cellulose material [175]. No carbonaceous nanospheres could be seen. However, during the carbonization process, there was an increase of pressure and temperature in the autoclave which implies some presence of carbonizable carbohydrates.

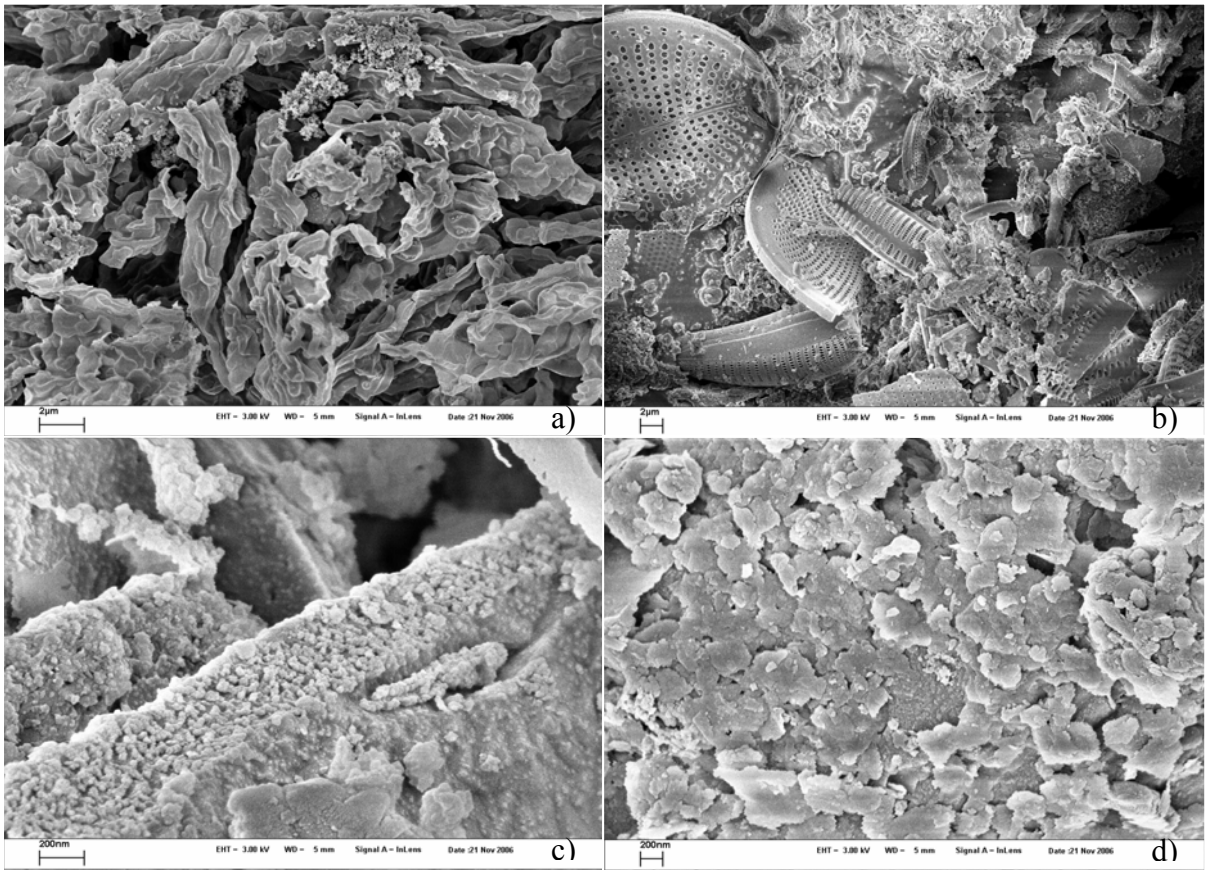

Figure 7. HRSEM of horse manure with seaweed (SW) before (a) and after (b, c) HTC, and fiberbank (FB) after (d) HTC. The scale bars are (a) 2µm, (b) 2µm and (c, d) 200nm. (b) shows the seaweed after HTC. Lots of diatoms and other organisms were present in the sample. (c) shows the carbonaceous nanospheres in the SW sample. The FB sample (d) had been petrified on the sea bottom and could not be carbonized.

Figure 8 shows horse manure with straw and peat. Horse manure before HTC is shown in 8a, b) and after HTC in 8 c-f). For the HS experiment, it can be seen that the structure on the macroscale is preserved through out the HTC process (Figure 8c), but a closer look will reveal the carbonaceous nanospheres (Figure 8d). The HP sample however, is mostly made up of soft biomass, and the samples after HTC reveals no larger structures (Figure 8e, f).

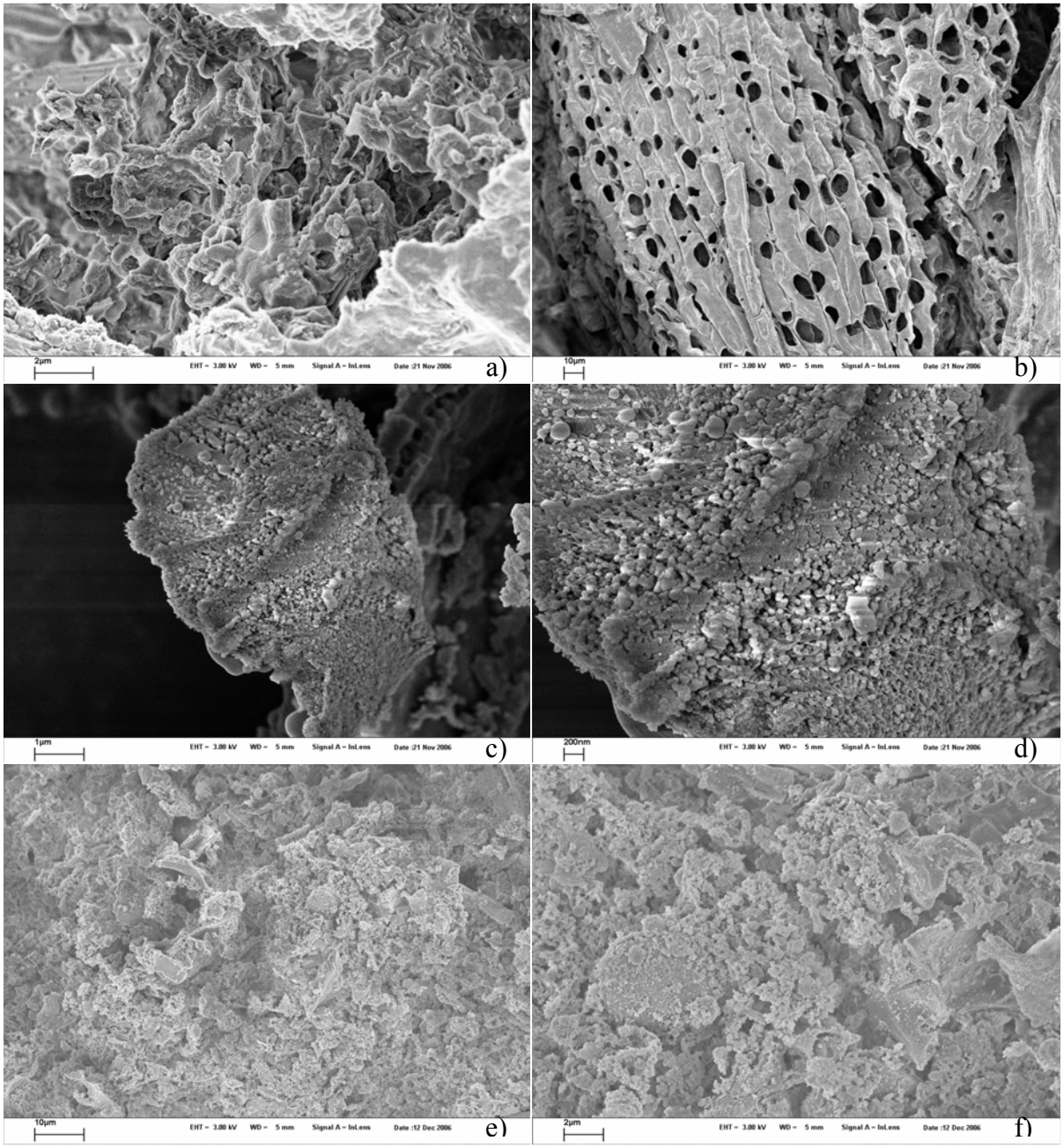

Figure 8. HRSEM of horse manure with straw (HS) before (a) and after (c, d) HTC, and horse manure with peat (HP) before (b) and after (e, f) HTC. (b) shows the structure of the peat moss *Sphagnum fuscum*. The scale bars are (a) 2µm, (b) 10µm, (c) 1µm, (d) 200nm, (e) 10µm and (f) 2µm. In (c) it can be seen that the original, cellular texture of the hard tissue in the sample is preserved on the macro- and microscale throughout HTC. In (d) the changes on the nanometer scale can be seen; all mechanically soft biomass have become disintegrated into carbon nanoparticles. The HP sample was made up of mostly soft biomass, and essentially everything was disintegrated into carbonaceous nanospheres (e, f).

10.2 Brunauer-Emmett-Teller analysis (BET)

The nanometer structure of the pore system was additionally characterized by nitrogen gas sorption measurements, Figure 9. Note the differences in y-value ranges in the graphs. In the FB experiment, the difference between the curves before and after HTC indicates that some carbonization must have taken place. Gas sorption measurements are only sensitive to pore sizes up to 30nm, which means that the macropore structures not are reflected in these measurements.

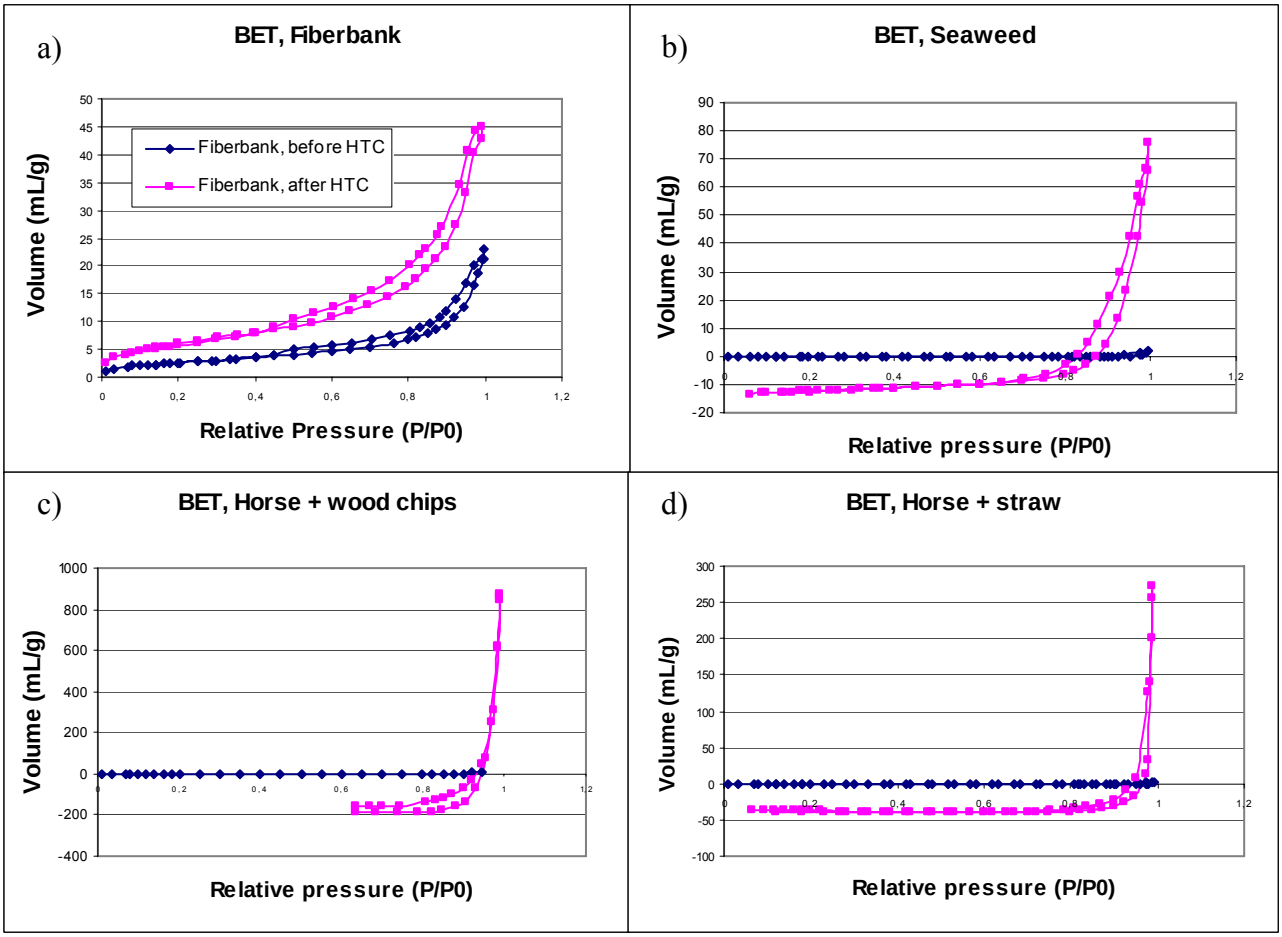

Figure 9. Braunauer-Emmet-Teller analysis. Nitrogen gas sorption measurements of FB (a), SW (b), HC (c) and HS (d). Dark blue dots refer to sample before HTC; purple dots refer to sample after HTC. HP is not presented here but showed similar gas sorption behavior as HC and HS. Note that gas sorption never can be negative. Shown here are the values as returned from the BET analysis. In (b)-(d), the absorption within the lower relative pressure range seems to be negative, which in reality is not the case. All curves should start at 0 mL/g absorption.

The largest nitrogen absorption was found in the HC sample (Figure 9c), which absorbed around 1000 ml nitrogen gas per gram sample at a relative pressure of 1. Hence almost 70% of the HC structure can be attributed to pores. This is in strong contrast to FB an SW in Figure 9 a, b) (compare the values on the two y-axis), which show almost no porosity at all. The high porosities of HC, as well as HS (Figure 9d), improve the water binding capacities of these carbonized materials.

FB shows an onset of a hysteris loop around a relative pressure of 0.5, which indicates very fine pore structure, presumably around 0.5 – 10 nm. The other samples have larger pore sizes (later onsets of hysteris loops).

The surface areas were determined using the BET method. The results are shown in Table 7.

Sample	SW	HS	FB	HC	HP
Surface area (m^2/g)	Before: 0.119 After HTC: 10	Before: 0.6 After HTC: 13.7	Before: 9.05 After HTC: 21.6	Before: XXX After HTC: 27.5	Before: 0.23 After HTC: 18.4

Table 7. Surface areas of the different samples using the BET method. For unknown reason, the measurement of HC before HTC failed.

The BET analysis shows that the porosities were significantly increased after HTC. The surface area increased almost 23 times for HS, and around 80 and 84 times for HP and SW, respectively. FB, starting on a relatively high value, increased 2.4 times.

10.3 Thermogravimetric Analysis (TGA)

In the TGA, the percent weight losses of the samples were recorded under heating at a uniform rate in oxidative (oxygen, O_2) or inert (nitrogen, N_2) gas flows. The temperature was increased from room temperature to almost 1000 °C. The weight loss that occurs when the samples are heated to some 100 °C comes from the evaporation of water. After that, further weight losses come from coking and finally combustion of the carbon (under oxygen flow only). Under oxygen flow, only inorganic compounds (ash) remain after the temperature has reached 700 °C. The results from the TGA under oxygen and nitrogen flow are shown in Figure 10 and 11, respectively.

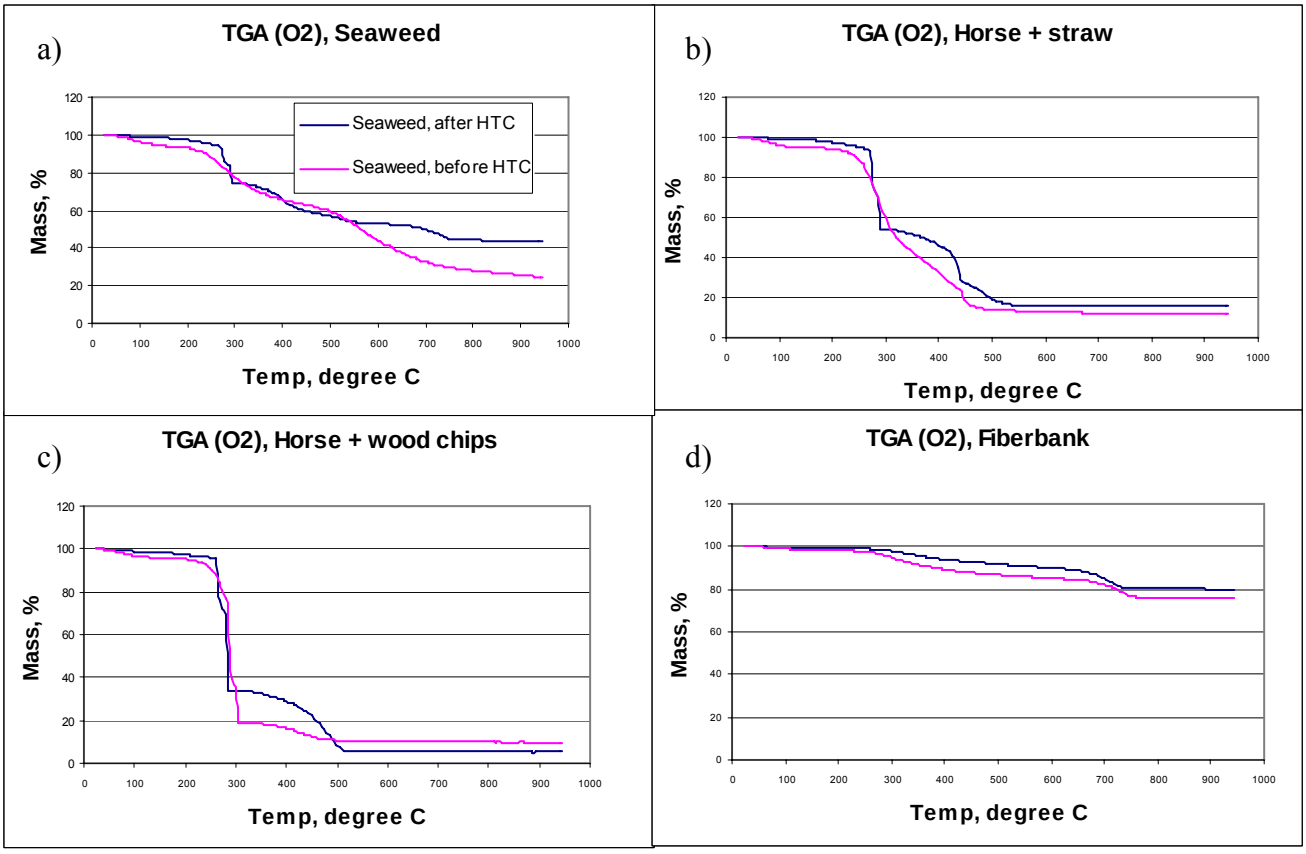

Figure 10. Thermogravimetric analysis under oxygen flow for SW (a), HS (b), HC (c) and FB (d). A dark blue line refers to sample before HTC and a purple line to sample after HTC. HP is not presented, but showed similar behaviour to HS and HC.

The horse manure samples (Figure 10 b, c) contained the smallest amount of inorganic compounds, with HC containing even less inorganic compounds than HS. This can be seen from the graphs; in Figure 10c) the graph ends on a lower value than in Figure 10b). This was expected, since combustion of straw will give more ash than combustion of wood chips (Table 2, Section 2.3). Both HS and HC experience large percental weight losses when the temperature has increased to around 300 °C, which is due to coking of the carbon materials and loss of significant amounts of gases. After that, there is second weight loss ending around 500 °C. This weight loss is due to oxidation (combustion) of the carbon materials. The remaining fraction is ash.

In Figure 10 d), it can be seen that the fiberbank mostly consisted of inorganic compounds. Even after a temperature increase to 700 °C, only 20% of the weight has been lost.

SW (Figure 10a) similarily has high ash content. As already has been pointed out, seaweed samples will contain mussels, seashells, sand and other organic compounds, which add to the large ash fraction.

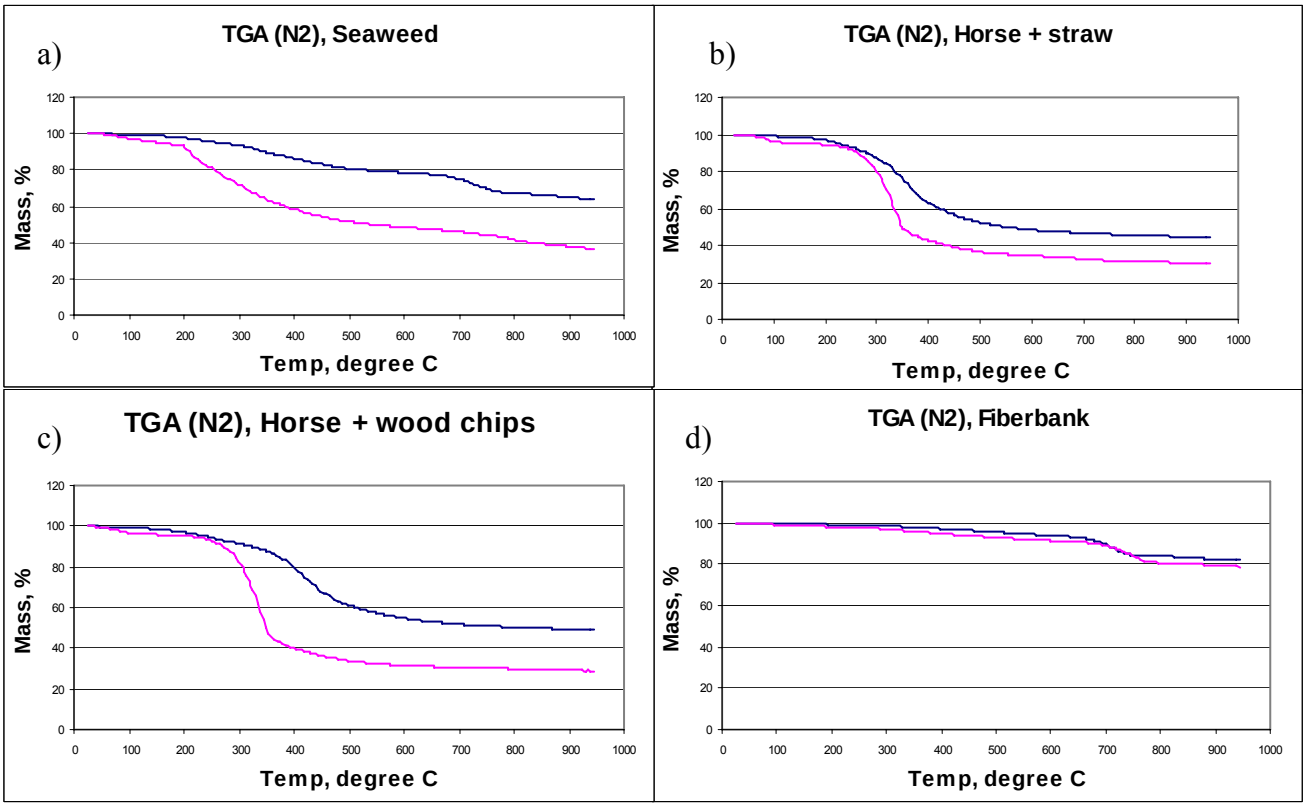

Figure 11. TGA under nitrogen flow for SW (a), HS (b), HC (c) and FB (d), as in Figure 10.

Under nitrogen flow, the final step of oxidation (combustion) does not occur. As was noted in Section 4.3; when coal is heated in the absence of air, coke is formed. The percental weight loss during heating represents the loss of different gases that are produced during the coke formation.

10.4 X-ray Diffraction (XRD)

XRD is one of the most important characterization tools used in solid state chemistry and materials science. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for identification. It can also be used for structure determination of crystalline materials. The samples before HTC were put in 800 ºC under nitrogen flow. The results from the XRD analysis are shown in Figure 12.

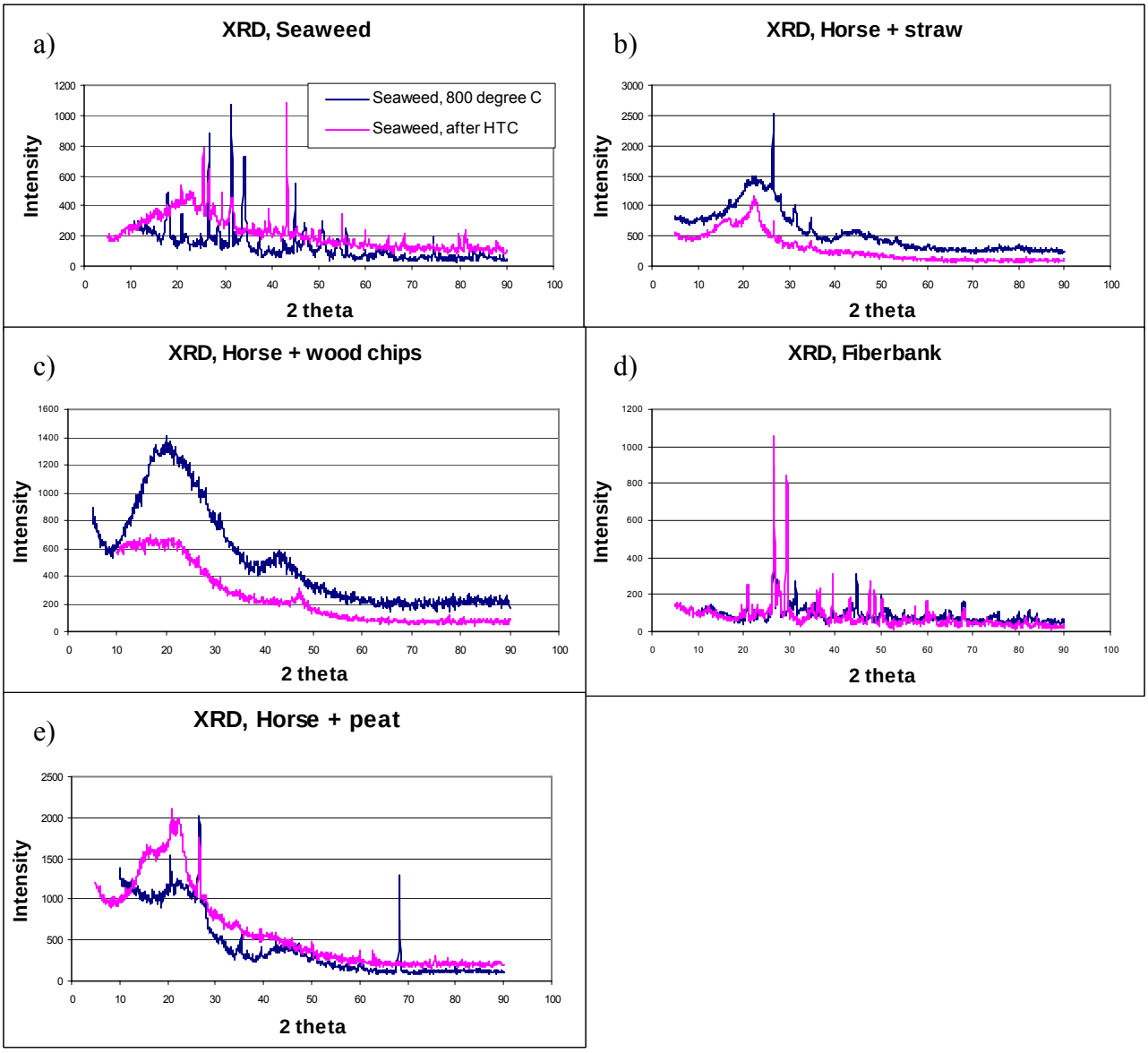

Figure 12. X-Ray Diffraction analysis for SW (a), HS (b), HC (c), FB (d) and HP (e). As in 10a), dark blue lines indicate sample at 800 °C under nitrogen (before HTC), purple lines indicate samples after HTC.

The graph for HC in Figure 12 c) has an appearance that is expected for coal materials, with broad peaks around $2\theta = 20$ and $2\theta = 40$. HC also contains little inorganic compounds. The HS and HP graphs also have two peaks around $2\theta = 20, 40$ (Figure 12 b, e), but contain significantly more inorganic components than HS, which is expected for peat and straw compared to wood chips.

In Figure 12a), the SW sample, the same two peaks can be discerned. However, the sample contains significant amounts of inorganic compounds, which is evident from the many peaks in the graph. In the FB sample (Figure 12d) it is hard to discern any peaks around $2\theta = 20, 40$. Instead, several other peaks reveal the large amount of inorganic compounds in the FB sample.

10.5 Elemental analysis

The results from the elemental analysis can be seen in Tables 8-14. Data for both samples as received and dry samples will be shown. Only dry samples will be discussed below.

10.5.1 Horse manure

Sample	Moisture (%)	Ash* (%)	K (mg/kg)	P (mg/kg)	S (mg/kg)	N-tot (g/kg)	C* (%)	O* (%)	H* (%)
HS	1.5	14.6/14.8	3880	8750	2290	26	55.3/56.1	21.5**/20.5	5.8**/5.7
HC	1.1	4.9/4.9	2280	3970	1820	17	68.6/69.3	18.83**/18.06	5.9**/5.8
HP	1.8	9/9.2	3130	3720	2210	23	62.1/63.2	20.49**/19.26	5.9**/5.8

Table 8. Analysis of horse manure after HTC, solid phases. (*) sample as received/dry sample, (**) water included.

Sample*	Higher heating value (HHV) (MWh/ton; kcal/kg; MJ/kg)	Lower heating value (LHV) (MWh/ton; kcal/kg; MJ/kg)
HS	6.447; 5544; 23.215	6.103; 5248; 21.978
HC	7.893; 6787; 28.421	7.542; 6485; 27.159
HP	7.100; 6105; 25.567	6.750; 5805; 24.307

Table 9. Analysis of horse manure samples after HTC, solid phases. (*) Sample as received.

Sample*	Higher heating value (HHV) (MWh/ton; kcal/kg; MJ/kg)	Lower heating value (LHV) (MWh/ton; kcal/kg; MJ/kg)
HS	6.542; 5626; 23.559	6.204; 5335; 22.340
HC	7.9880; 6862; 28.734	7.633; 6563; 27.485
HP	7.228; 6215; 26.028	6.884; 5920; 24.789

Table 10. Analysis of horse manure samples after HTC, solid phases. (*) Dry sample.

Sample*	K (mg/l)	P (mg/l)	S (mg/l)	N-tot (CFA) (mg/l)	TOC (mg/l)
HS/w	2940	15.1	189	727	12
HC/w	867	51.8	57.1	133	10
HP/w	937	7.96	88.3	317	6.7

Table 11. Analysis of horse manure samples after HTC. (*) Water phases.

The carbon content in peat is around 55 % and increases up to around 70 % for lignite. The hydrothermally carbonized horse manure contained between 56% and 69% carbon (Table 8). The highest carbon content was found in the HC sample, which also had been hydrothermally carbonized for the longest time (three days). The lowest carbon content was found in the HS sample, which had the shortest carbonization time of all samples (16 hours).

The Lower Heating Values (LHVs) of the dry horse manure samples are in the range of 6.5 - 8 MWh/ton (Table 10). The LHVs for subbituminous and bituminous coal are 5.4 - >9 MWh/ton (Table 3, Section 4.4.1.1). The sample that was carbonized for the longest time, HC, had the highest heating value. However, these heating values can not be directly compared to those of fossil coals. Subbituminous and bituminous coal have moisture contents of 10-25% and 2-15%, respectively, where as the coal material from horse manure in this study was dried.

Fresh horse manure (with straw) has a moisture content of around 22%. The ash content is 12% and the heating value (not said if it is LHV or HHV) is 3.2 MWh/ton [176]. Straw contains 15% moisture, and when dried the LHV increases from 4 MWh/ton to 4.8 MWh/ton (Table 2, section 2.3). Compared to straw, dried horse manure (with straw) might therefore

have a heating value around 4-4.5 MWh/ton. Hydrothermally carbonized horse manure hence gives more energy than fresh, dried horse manure upon combustion.

Bituminous coal generally contains between 0.7 - 1.3% sulfur. The hydrothermally carbonized horse manure had sulfur concentrations ranging from 0.18 – 0.23 % (Table 8). Hydrothermally carbonized horse manure contains more sulfur than most short-rotation energy crops but is in the same range as herbaceous energy-crops (Table 2, section 2.3). Hydrothermally carbonized horse manure would emit smaller amounts of SOx gases than fossil coal when combusted.

The ash content for peat is between 2 - 6% and for coals 3 - 15% (Table 3, section 4.4.1.1). The ash content of the hydrothermally carbonized horse manure was 5 - 15%, and hence similar to coal, but larger than for biomass (1 - 7%, Table 2, section 2.3).

Hydrothermally carbonized horse manure should ideally be used as soil improvement to avoid depletion of humus and nutrients from agricultural lands. However, compared to fertilizers sold on the market, horse manure contains relatively little nutrients. Hammenhög's sells fertilizer for gardens in Sweden. Two of their products are "Växupp" NPK 18-4-10, an all-round fertilizer, and "Gräsgödsel" NPK 21-4-7, specially made for lawns (nitrogen, phosphor and potassium contents of 18, 4, 10%, and 21, 4, 7%, respectively) [177]. Hammenhögs fertilizers hence contain approximately 10 times more nutrients than hydrothermally carbonized horse manure, which contains 1.7-2.6% nitrogen, 0.4-0.9% phosphor and 0.2-0.4% potassium (Table 8).

The water phase contains lots of valuable nutrients and should not be discarded. Preferably, it should be use as fertilizer. Fluid plant nutrients ("Blomstra växtnäring") that can be purchased in ordinary food stores in Sweden contain 51g nitrogen, 10g phosphor and 43g potassium per liter, much more than the liquid HTC-phase (Table 11). On the other hand, "Blomstra växtnäring" should be diluted some 100 times before applied to plants. Also, the HTC water could be recycled and used in more than one HTC process, which would increase the concentration of nutrients.

10.5.2 Seaweed

Sample	Moisture (%)	Cd (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	S (%)	Cl (g/kg)	K (g/kg)	P (g/kg)	N-tot (g/kg)
SW	6.5	2.35	18.8	<0.05	9.2	0.21	8.35	14.8	2.84	11

Table 12. Analysis of the seaweed sample after HTC, solid phase.

Sample*	Higher Heating Value (HHV) (MWh/ton; kcal/kg; MJ/kg)	Lower Heating Value (LHV) (MWh/ton; kcal/kg; MJ/kg)
SW	3.371; 2899; 12.140	3.022; 2599; 10.822

Table 13. Analysis of seaweed sample after HTC, solid phases. (*) Sample as received.

Sample**	Higher Heating Value (HHV) (MWh/ton; kcal/kg; MJ/kg)	Lower Heating Value (LHV) (MWh/ton; kcal/kg; MJ/kg)
SW	3.606; 3101; 12.984	3.279; 2820; 11.808

Table 14. Analysis of seaweed sample after HTC, solid phases. (**) Dry sample.

The concentrations of cadmium, copper and mercury in SW (Table 12) were similar to those found in a recent study by Greger *et al.* [166]. The concentrations in beach-cast samples from the Baltic Sea in Greger *et al*. were 1-5 mg cadmium, 7-22 mg copper and <0.002 mg

mercury per kg DW. However, the lead concentration was at least 90 times lower compared to the hydrothermally carbonized seaweed in this study, <0.1 mg lead per kg DW.

Composts of newly washed-ashore brown and red macroalgae from the same study [3] had the following qualities: 3 ‰ sulfur, 1-2.4 g chlorine, 2-6 g potassium, 1-1.5 g phosphor and 21-27 g nitrogen per kg. The concentrations of chlorine, potassium, and phosphor were thus lower in Greger *et al*., but this could reflect the fact that those concentrations were measured from the pure compost. However, Greger *et al*. report a much higher concentration of nitrogen than this study does (Table 12).

Due to the high concentrations of heavy metals, hydrothermally carbonized seaweed should not be used as fertilizers for food crop cultivation. The concentrations of heavy metals are similar to those in earlier studies, and especially cadmium has been shown to be easily transferred to plants grown on seaweed composts [166]. However, in Greger *et al*., the concentrations of lead in both macroalgal composts and plants were under detection limit. In this study the concentration of lead was significantly higher (>90 times higher than in Greger *et al*.), which could lead to elevated lead levels in plants if they are grown on hydrothermally carbonized seaweed.

The LHV for SW was 3.3 MWh/ton (Table 14), about half of the LHVs of the horse manure samples. The LHV for brown coal, the coal of lowest rank, ranges between 1.9 and 4 MWh/ton. The second lowest rank of carbon is lignite with a LHV of 4-5.4 MWh/ton (Table 3, section 4.4.1.1). The LHV for hydrothermally carbonized seaweed is also slightly lower than for common types of (dried) energy crops, which are in the range of 4.8-5.3 MWh/ton (Table 2, section 2.3). Hydrothermally carbonized seaweed could hence be used for combustion, but it would not give as much energy as hydrothermally carbonized horse manure. Seaweed contains small mussels, seashells and other organisms, as well as sand and other inorganic compounds, which is one source of the lowered heating value.

The sulfur content in SW was 0.21%, which is about the same as for hydrothermally carbonized horse manure (0.18 - 0.23%, Table 8). It is higher than for different short-rotation energy crops (Salix, forest residues and wood pellets) but about the same as for herbaceous energy crops (Reed Canary grass and wheat). This is presented in Table 15 (data from another study that what was presented in Table 2, section 2.3). Table 15 also compares heavy metal concentrations in SW and energy crops. Concentrations of copper and lead were all higher in SW than in both short-rotation and herbaceous energy crops, but the mercury concentration was not elevated in SW, compared to the other types of biomass. Cadmium, which was said to be the major problem regarding fertilizers, was even higher in Salix than in SW, but lower for the other types of energy crops. However, the LHV is lower for SW. Upon combustion for heat or electricity production, larger amounts of SW will hence be needed.

Biomass	Ash (%, DW)	LHV* (MWh/ton)	Cd (mg/kg, DW)	Cu (mg/kg, DW)	Hg (mg/kg, DW)	Pb (mg/kg, DW)	S (%, DW)
SW	d.u.	3.28	2.35	18.8	<0.05	9.2	0.21
Salix	1.9	5.04	2.57	1.75	0.17	0.008	0.04
Forest residues	2.7	5.53	0	3	0	2	0.04
Wood pellets	0.6	5.29	0.15	1	0.012	0.4	0.01
Reed Canary grass	2.5	5.22	0.075	2.28	0.025	1.28	0.1
Wheat	1.7	4.64	d.u.	4.47	d.u.	0.43	0.4

Table 15. Comparison of heavy metal and sulfur concentrations between the seaweed sample (SW) and common energy crops. (*) Expressed on a dry, ash-free basis. d.u. = data unavailable. Recalculated from Ref. 178.

11. Discussion

11.1 Horse manure

Hydrothermally carbonized horse manure would be an excellent energy source. However, using it as soil improvement will offer great environmental benefits, since nutrient and in particular humus is returned to soils. HTC of horse manure increases the porosity and surface area. When applied as soil improvement, hydrothermally carbonized horse manure will improve aeration and cation exchange capacity of the soils.

If the horse manure is hydrothermally carbonized shortly after grooming, only very small amounts of ammonium gas will leave the manure. The nitrogen would not be lost to the atmosphere, as is the case when it is composted.

Also of great importance is that the carbon is kept in the product and not released as carbon dioxide or methane to the atmosphere. If all horse manure in Sweden were hydrothermally carbonized, huge quantities of GHGs emissions would be saved each year.

Hydrothermally carbonized horse manure would hence be desirable to use as soil improvent for several different reasons; to increase soil fertility, to return nutrients to the soils and to reduce GHG emissions.

In addition to the environmental benefits associated with HTC of horse manure, there are economic benefits. Today, stables pay for the removal of manure. There is no need to collect the manure into containers since this is done on a daily basis by stable-grooms. The containers can easily be picked up and driven to the HTC facilities.

Combustion of hydrothermally carbonized horse manure for energy production can be seen as carbon neutral, in all cases but one. Peat, a very common bedding material, is not considered to be a renewable resource. The carbon dioxide emitted during combustion must be considered fossil, another reason why horse manure preferably should be used for soil improvement.

11.2 Seaweed

HTC of seaweed would be a fast and efficient way to remove seaweed banks with benefits for both the environment and beach visitors. Hydrothermally carbonized seaweed should not be used as a fertilizer for food crops because of the high levels of heavy metals. It could perhaps

be used as soil improvement in smaller amounts for non-food crop cultivation, for example in park plantations.

Also, seaweed contains large amounts of inorganic compounds. For this reason, seaweed will produce significant amounts of ash when combusted, and it therefore unlikely that it would be attractive for combustion and heat and energy production.

Most municipalities today remove seaweed from major beaches and pile it up in banks which soon start to decompose and give off unpleasant smells. One major problem with the HTC of seaweed on larger scales is that seaweed often contains a lot of sand. However, one Swedish municipality is using a machine to remove the sand from the beach-cast before it is removed from the beach. In this way, the municipality has lowered the transportation costs significantly [161]. For HTC, seaweed should be as sand-free as possible.

11.3 Fiberbanks

Because of the current deposition problems, it would have been attractive if the fiberbanks would have worked well in the HTC process. However, this was not the case. The cellulose fibers had been petrified after decades on the sea bottom and could not be carbonized.

11.4 General discussion

11.4.1 Oxidation

Mild oxidation of coal occurs by the absorption of oxygen from the air. The carbon atoms to which oxygen becomes attached liberate less energy on further oxidation or combustion than do carbon atoms attached only to hydrogen or other carbon atoms. On a macroscopic scale, this effect is observed as a reduction in the heating value. In extreme cases, up to 40% of the heating value can be lost in six months; however with good packing of the coal and minimal air flow, the losses can be held below 1% per year, even after several years [45].

The samples in this study were analyzed about a month after carbonization. In the time between experiments and analysis, the carbon materials were kept in air-tight plastic containers. It is difficult to say if the samples were oxidized to a great extent or not, and if this influenced the heating values and elemental compositions.

11.4.2 Wastewater

Ethanol production has been criticized for consuming more energy than it produces. This is, in part, due to the high energy consumption in the distillation process.

The HTC process requires water. If the samples are not wet enough, water needs to be added. Fresh seaweed does not need addition of extra water, but horse manure does. The products are coal slurries. For every liter of coal slurry-product, 6 - 7 dl of water can be filtered of.

Removal of water from coal is classified into two categories; dewatering and drying. Dewatering is normally used when water has been added during handling or processing; for example water added to form slurries for pipeline transport or water acquired during physical cleaning processes. Centrifugation and vacuum filtration are common dewatering processes. Drying is commonly used to reduce moisture content in coal [45].

Depending on the desired product, there are different scenarios:

1. The desired product is a coal slurry to be used in fuel cells, FT-processes, direct combustion or other processes. If this is the case, the excess water does not pose a problem. Coal slurries are also easier to transport and handle than coal.
2. The desired product is humus, and will be used as fertilizer and soil improvement. For these purposes, dewatering of the coal slurry should be enough. No expensive or complicated drying schemes are hence needed. Without drying of the product, energy will be saved. On the other hand it will be more energy consuming and expensive to transport moist humus to its final location.
3. The desired product is a coal powder which will be combusted for energy extraction. In this case, the product both has to be dewatered and dried.

There are two aspects of the problem; the environmental aspect of wastewater and the cost and energy associated with filtering and drying.

In a large scale plant for HTC of horse manure, waste water could probably be reused. This would increase the concentration of nutrients in the waste water and make it even more suitable for different applications, such as irrigation of agricultural fields during the growing season. However, substantial quantities of water will be produced in a large HTC plant, which during the winter months would pose a problem. During those months, other applications for the nutrient-rich waste water need to be found.

Wastewater from hydrothermal carbonization of seaweed could in theory be brought back to the sea from where the seaweed came from. Environmental aspects of wastewater treatment have to be considered for every type of biomass used.

11.4.3 Energy balances

Extensive energy balances have been done for many kinds of biofuels, for example ethanol and biodiesel (Section 5.3). More than once, they have showed that the conversion of biomass into biofuel consumes more energy than can be obtained from the final product. This Master thesis has not focused on energy balances, and it is yet to be shown that HTC of biomass on larger scales actually is a gain of energy. If the product is to be seen as a carbon sink, it has to be established that the HTC not consumes energy and diminishes the environmental benefits.

For this specific study, the temperature was kept at a constant 205 ºC with the help of a heating oven. In theory, HTC only requires activation energy. In addition, energy is released during the process. It is important that the energy released during the process is not wasted.

For future studies, energy balances for large-scale scenarios of different kind of biomass are of great importance. Different scenarios for wastewater treatment also have to be included.

11.4.4 Carbon turn-over rates

Further research is needed to establish the carbon turn-over rate in different types of biomass that have been hydrothermally carbonized for different periods of time. For this specific study, the carbon in the hydrothermally carbonized horse manure is estimated to stay in the soil for at least 500 years [28].

12. Conclusions

HTC-products used for heat or energy production are more environmental friendly than fossil fuels. The elemental composition depends on the biomass used as starting material, but the

fossil carbon dioxide emissions will always be zero. The HTC process is exothermic and has a very high carbon efficiency (100% in theory), a great advantage compared to conventional processes that convert biomass into energy. Furthermore, almost any type of biomass made of carbohydrates can be used in the process. HTC-products that are used for soil improvement will not only increase soil fertility but also sequester carbon from the atmosphere.

In this study, samples of horse manure, seaweed and fiberbanks were hydrothermally carbonized. Horse manure gave the best result. The products both had high heating values and nutrient contents and can be used for both energy extraction and soil improvement. Also, the raw material can be obtained for free; stables today pay to have their horse manure collected.

Hydrothermally carbonized seaweed had a lower heating value. The products also contain high concentrations of heavy metals and should therefore not be applied to agricultural soils. HTC as a way to degrade beach-cast would be beneficial both for the environment and beach-visitors, but due to the relatively high concentrations of heavy metals and high ash content, it is uncertain if HTC-products from seaweed would be of any economic value.

The cellulose fibers in the fiberbanks were petrified and could therefore not be hydrothermally carbonized.

In future studies, large scale-scenario energy balances should be performed. The whole process (collection of biowaste to product) must be considered. It is uncertain how much energy a larger HTC facility would require, and how efficiently the energy emitted in the process can be used as heat.

Furthermore, the carbon turn-over rates for HTC-products from different types of biomass when applied as soil improvement have to be established. Under the Kyoto protocol, the only form of carbon sequestration so far allowable through the trading program is carbon stored in newly afforested land. It is clearly established that inert forms of soil represent long-term storage of carbon. Maybe also hydrothermally carbonized biomass soon can be recognized as a tradable commodity under the Kyoto protocol.

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