Refining of hydrochars/ hydrothermally carbonized biomass into activated carbons and their applications
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献给爷爷和奶奶
Abstract

Hydrothermally treated biomass could not only be used as a fuel or a fertilizer but it can also be refined into high-value products. Activated carbons are one of those. In the studies of this thesis, four different hydrothermally carbonized (HTC) biomass, including horse manure, grass cuttings, beer waste and biosludge, have been successfully made into activated carbons. The activated carbon materials were in the forms of powdered activated carbons, powdered composites of activated carbon and iron oxide nano-crystals, and activated carbon discs.

The HTC biomass and the activated carbons were characterized and analyzed using several methods. The biomass were carbonized to different extent during the hydrothermal treatment, which depended on the different natures of the biomass. The HTC biomass were activated into powdered activated carbons by both physical activation, using CO$_2$, and by chemical activation, using H$_3$PO$_4$. Full factorial design matrices were applied to design experiments and study the influence of different parameters used during both physical and chemical activation. Activated carbons with embedded iron oxide nanoparticles were synthesized through hydrothermal carbonization followed by CO$_2$ activation. These composites had high surface areas and showed a strong magnetism, and the powders could be separated from liquid phase by applying a magnetic field. Strong and dense activated carbon discs were also prepared from powdered HTC beer waste by pulsed current processing (PCP) and a subsequent CO$_2$ activation procedure.

The potential for carbon dioxide separation from nitrogen, and methylene blue adsorption in aqueous solution, were assessed for the powdered activated carbons produced from HTC biomass. They showed good performance in both applications.

Keyword: Hydrothermally carbonized biomass, activated carbon, full factorial design, activated carbon disc, nanoparticles, iron oxide, CO$_2$ separation, methylene blue, adsorption
中文摘要

水热法处理生物质废料不仅可以用来制备生物质燃料和有机肥料，还可以制备成高附加值的产品。多孔活性炭就是其中之一。在这篇论文里，包括马粪、草、啤酒渣和造纸厂有机污泥在内的四种水热碳化的生物质废弃物，被制备成了不同的活性炭产品。这些产品包括粉末状活性炭、活性炭和纳米氧化铁的粉末复合物、还有圆柱形活性炭。

论文中使用了多种表征方法来研究和分析水热碳化的生物质以及其活性炭产物。不同生物质的水热碳化程度不同，这主要取决于各生物质的自然特性。水热碳化后的生物质通过碳酸活化法和磷酸化学活化法被制成了粉末状活性炭。在物理活化法和化学活化法中，我们使用了完全因子设计法来设计实验，并分析不同参数对活化结果的影响。本论文还通过水热碳化和二氧化活化法制备了包埋纳米氧化铁晶体的活性炭复合材料。该复合材料具有高的比表面积和很强的磁性，使得这种粉末状的复合材料可以很容易从液相中通过磁场被分离出来。在本论文中，粉末状的水热碳化啤酒渣通过放电等离子烧结法和二氧化碳活化法制备成高强度和高密度的圆柱形活性炭。通过论文中研究的方法制备的粉末状活性炭被证明在从氮气和二氧化碳混合气里分离二氧化碳的应用中，还有从水溶液中吸附亚甲基蓝染料的应用中均有很好的性能。
List of publications

This thesis is based on Paper I to Paper IV:

Paper I:
**Iron oxide nanoparticles embedded in activated carbons prepared from hydrothermally treated waste biomass***

*Specific contribution: Lead role in this project; characterization and analysis of HTC biomass; synthesis, characterization and analysis of the iron oxide nanoparticles embedded activated carbons; lead role in writing.*

Paper II:
**Activated carbons for water treatment prepared by phosphoric acid activation of hydrothermally treated beer waste***

*Specific contribution: Lead role in this project; characterization and analysis of HTC beer waste; synthesis, characterization and analysis of the chemically activated carbons; methylene blue adsorption measurements and analysis; lead role in writing.*

Paper III:
**Strong discs of activated carbons from hydrothermally carbonized beer waste***

*Specific contribution: Lead role in this project; characterization and analysis of HTC beer waste; synthesis, characterization and analysis of the activated carbon discs; lead role in writing.*

Paper IV:
**Activated carbons prepared from hydrothermally carbonized waste biomass used as adsorbents for CO₂***
Specific contribution: Lead role in this project; characterization and analysis of HTC biomass; synthesis, characterization and analysis of the activated carbons; CO\textsubscript{2} adsorption measurements and analysis; lead role in writing.

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Publications not included in the thesis:

Paper V: **Cobalt selenium oxohalides: Catalysts for water oxidation**

Specific contribution: N\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O adsorption measurements and analysis.

Patent: **Magnetic activated carbon and methods for preparing and regenerating such materials**

Specific contribution: Characterization and analysis of HTC biomass; synthesis, characterization and analysis of the iron oxide nanoparticles embedded activated carbons.
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1 Introduction

1.1 Hydrothermal conversion

The term “hydrothermal” comes originally from the field of geology. Nature created fossil fuels like coal and crude oil from plants and animals in the hydrothermal reactions, which took millions of years. Humans have mimicked such natural processes by using so-called hydrothermal conversions to transform carbohydrates and biomass into not only biofuel but also value-added chemicals and materials within a few hours.\(^1\)–\(^3\)

Hydrothermal conversion is sustainable, preserves resources and is an environmentally friendly concept for the chemical industry.\(^4\) It is a complex process with physical and chemical transformation of carbon-rich compounds, taking place in water at elevated temperatures and high autogenic pressures.\(^1\) Hydrothermal conversion can be classified into hydrothermal gasification, hydrothermal liquefaction and hydrothermal carbonization by different regions above the vapor pressure curve and the critical point in the phase diagram of water (Figure 1.1).\(^2\)

Hydrothermal gasification usually happens when the temperature is high; typically, a temperature > 215 °C is needed. Burnable gases, such as hydrogen and methane, are the desired products in the process. Kruse\(^5\) divided the hydrothermal gasification into three main types according to the reaction conditions and main gas products:

I. Aqueous phase reforming: when the temperature is around 215 - 265 °C, carbohydrates such as glucose, sorbitol, glycerol, methanol, and glycol, are gasified to mainly hydrogen and carbon dioxide with the help of a heterogeneous metal catalyst (Pt, Ni, Ru, Rh, Pd, Ir).\(^6\)–\(^9\)

II. Catalyzed near-critical gasification: biomass or organic compounds are gasified into methane and carbon dioxide at around 350 – 400 °C.\(^6,10\)
III. Supercritical water gasification: biomass or organic compounds are gasified to mainly hydrogen and carbon dioxide without the addition of catalysts.\textsuperscript{11}

![Figure 1.1 Schematic overview of hydrothermal conversion processes and the main products with their typical temperature and pressure ranges by Kruse.\textsuperscript{5} The vapor–pressure curve of water is shown as well. (From Kruse et. al., Curr. Opin. Chem. Biol. 2013, 17, 515-521. With permission)](image)

Hydrothermal liquefaction is a hydrothermal process for obtaining liquid products, known as bio-oil, from carbohydrates or biomass together with water as a solvent at a relatively low temperature and high pressures.\textsuperscript{12,13} Usually, a temperature of 300 – 350 °C and a pressure of 15 – 20 MPa are used for the hydrothermal liquefaction process.\textsuperscript{2} The “oil” produced from hydrothermal liquefaction is dominated by phenols or molecules with phenolic groups. Catalysts play a critical role in the hydrothermal liquefaction, for example alkali hydroxides, hydrogen carbonates, carbonates, and noble metals.\textsuperscript{1,2} Lignin is one of the most promising precursors for making bio-oil through hydrothermal liquefaction due to its large availability. In the hydrothermal liquefaction of lignin from empty palm fruit bunch, the reactivity with the alkalis was found to be in the order of K$_2$CO$_3$ > KOH > NaOH.\textsuperscript{1}

Hydrothermal carbonization takes place when the temperature is comparably low, usually between 160 °C and 250 °C. In this region, liquefaction and gasification are limited and a carbon-rich solid product dominates.\textsuperscript{2} There are also dissolved organics in the aqueous phase and a minor amount of gas as by-products in the hydrothermal carbonization. However, the prod
uct distribution is mainly determined by the feedstock and process temperature, but also reaction time and the load of solids. Hydrothermal carbonization can convert a variety of feedstock to solid products with a carbon content similar to lignite or peat.\(^\text{14}\) Hydrothermal carbonization can happen without the presence of a catalyst. However, there is a report showed that Fe as catalyst could influence the hydrothermal carbonization process.\(^\text{15}\) Both pure carbohydrate and biomass can be used as feedstock for the hydrothermal carbonization process, but the physical or chemical reactions are more complex for biomass.

1.1.1 Hydrothermal carbonization of pure carbohydrates

Hydrothermal carbonization is a combination of a series of chemical reactions. It is easy to control the reactions, design the products, and study the fundamentals of the process when the feedstock is a pure carbohydrate. Carbohydrates (such as glucose, fructose, xylose, maltose, sucrose, amyllopectin, and starch) and carbohydrate derivatives (hydroxymethylfurfural and furfural) have been treated under hydrothermal conditions to make carbon-rich materials.\(^\text{16-18}\) It was proposed that the hydrothermal carbonization reaction basically takes place in three important steps: (1) the carbohydrates dehydrate to (hydroxymethyl)furfural; (2) the (hydroxymethyl)furfural polymerized into polyfurans; (3) the polyfurans carbonized via further intermolecular dehydration.\(^\text{4}\) Especially powerful was \(^{13}\text{C}\) NMR spectroscopy to reveal these steps.\(^\text{18}\)

The solid products produced from hydrothermal carbonization are spherical particles having morphological similarities and the same chemical and structural composition practically throughout all starting precursors of pure carbohydrates and carbohydrate derivatives, with the size from 100 nm to 5 \(\mu\text{m}\).\(^\text{16}\) It was proposed and reported that, based on the results obtained by elemental chemical analysis and by means of spectroscopic techniques (Fourier transform infrared spectroscopy (FTIR), Raman, and X-ray photoelectron spectroscopy (XPS)), the typical hydrothermally carbonized sphere has a core-shell structure, with a hydrophobic core of a condensed aromatic structure, and a hydrophilic shell with a lot of functional groups.\(^\text{19}\)
1.1.2 Hydrothermal carbonization of biomass

Complex biomass could also be carbonized under the hydrothermal condition. Lignocellulosic biomass is the most abundant renewable resource on Earth. Such biomass is composed of three main components: cellulose, hemicellulose and lignin. Due to the complexity of raw biomass, the hydrothermal carbonization of such precursor becomes complex. The decomposition and degradation of cellulose are much more difficult than for lignin and hemicelluloses. It has been reported that under hydrothermal conditions and with the help of Fe ions, the soluble fraction of the biomass hydrolyzed into simple carbohydrates, and then carbonized into spherical particles. It is the same principle as the hydrothermal carbonization starting from pure carbohydrates. There are also insoluble parts in biomass, which become porous carbonized species and preserve the primary fibrous structure of the plant tissues after hydrothermal carbonization. The carbon microspheres are usually well separated from the carbonized fibrous tissues.

The mechanism of the hydrothermal carbonization of biomass is still not quite clear. Titirici et al. have proposed that the hydrothermal carbonization of cellulose takes place in two different routes. One route is: 1) the cellulose hydrolyzed into glucose; 2) glucose then dehydrated into (hydroxymethyl)furfural; 3) (hydroxymethyl)furfural polymerized or aromatized into a condensed carbon structure. Another route is: cellulose is decarboxylated and condensed into an aromatic structure, following a reaction scheme that can be associated with a more classical pyrolysis process.

After the hydrothermal carbonization process, the atomic C, H and O composition of the biomass change significantly. Under the hydrothermal treatment, the biomass gets “carbonized” as the atomic ratios of O/C and H/C decrease. A van Krevelen diagram is useful to understand how the atomic composition changes during hydrothermal treatment, and how the resulting hydrothermally carbonized biomass relates to naturally occurring: coal, lignite, and peat. Figure 1.2 shows the atomic composition of the hydrothermally carbonized biomass produced with different temperatures, compared with the feedstock. The typical ranges for biomass, peat, lignite, coal, and anthracite are also indicated. The diagram used input from the paper of Hoekman et al.
1.2 Refining of hydrochars/hydrothermally carbonized biomass

There are many applications of the hydrothermally carbonized (HTC) biomass, such as use as fuel and fertilizer,\textsuperscript{23,24} or simply as a carbon sink.\textsuperscript{16} The hydrothermally carbonized biomass/ sugars can be used as a high quality solid fuel, because the heat value of the biomass increases after the hydrothermal carbonization. It has been reported the heat value of the hydrothermally carbonized biomass is even higher than that of lignite.\textsuperscript{24} Furthermore, the hydrothermally carbonized material could also be refined into high value products, for instance, into activated carbons and modified functional materials of various kinds.\textsuperscript{25,26}
1.2.1 Activated carbons

Activated carbons belong to a set of carbon materials with a highly developed internal pore structure, a large surface area (as high as 3000 m$^2$/g), variable surface chemistry characteristics, and a high degree of surface reactivity. Activated carbons are not truly amorphous, but they have microcrystalline structures. This microcrystalline structure differs from that of graphite with respect to interlayer spacing. Graphite’s interlayer spacing is 0.335 nm, while activated carbons have interlayer spacings of 0.34-0.35 nm. The orientation of the stacks of aromatic sheets is different as well. Activated carbon has a less ordered orientation than graphite. The elemental composition of a typical activated carbon has been found to be 88% C, 0.5% H, 0.5% N, 1.0 % S, and 6-7% O, with balancing constituents of ash compounds. The surface chemical characteristics are much dependent on non-carbon elements and their corresponding moieties. Particularly important are the carbon-oxygen surface groups, because they influence the wettability, polarity, and acidity, and other physico-chemical properties.

![Figure 1.3 Pore structure of activated carbon. Micro pore (≤ 2 nm), mesopore (2 - 50 nm), macropore (≥ 50 nm)](image_url)

Various methods used to determine the shapes of the pores have indicated that there are ink-bottle shaped, regular slit shaped, V-shaped, capillaries open at both end, or with one end closed, and many more different shaped pores. However, it has been difficult to obtain accurate information on the actual shape of the pores of activated carbons. It is well accepted that there are different kinds of pores according to the size of the pore: micropore (≤ 2 nm), mesopore (2 - 50 nm), macropore (≥ 50 nm), which could be tuned by carefully choosing the precursor or changing the processing parameters, for example activation time, the ratio of activation agent to precursor,
activation temperature, flow rate of gas, and so on. Figure 1.3 shows the pore structure of a typical activated carbon.

Traditionally, the precursors for producing activated carbons were coal, peat, lignite, and wood. But nowadays, more and more biomass and agricultural waste are treated to make activated carbons, such as almond shell, cherry stones, coffee husks, corn cob, cotton stalk, dates stone, durian shell, herb residues, olive stone, rice bran, rice husk, rice straw, rice hulls, sugarcane bagasse, sawdust, tea waste, walnut shells, waste apricot.

In applications, activated carbons are used in different physical forms, for example, as powdered activated carbon, granular activated carbon, or occasionally in the form of an activated carbon tablet. For a certain application, activated carbon could also be made into composite materials.

Activated carbons can be produced in many different ways, which could be classified into two main types: physical activation and chemical activation. These types are described below.

1.2.1.1 Physically activated carbons

Activated carbons could be produced by physical activation, which is a two-step process. The first step involves carbonization of the precursor at high temperature under an inert atmosphere (usually N₂ for economic consideration). The second step is activation at high temperature in oxidizing atmosphere, such as air, steam and CO₂, without any other reactants added in the precursor.

A traditional carbonization method is pyrolysis, which is a thermal treatment of a carbonaceous raw material at temperatures of 400-800 °C in an inert atmosphere. During this treatment, the precursor decomposes into three fractions: chars, tars and gases. Temperature, heating rate, the nitrogen flow rate and residence time affect the result of pyrolysis. In general, an increasing temperature reduces the yields of chars, but increases the yield of tars and gases. As the preference is that the fraction of char should be maximized, the pyrolysis is usually performed at medium temperature with a slow heating rate. A large part of the non-carbon elements such as oxygen, hydrogen and nitrogen is eliminated during the pyrolysis. They leave as gases or volatile species under the pyrolytic decomposition of the precursor. The residual carbon atoms transform into stacks of aromatic sheets, which are packed in a random manner. Those irregularly arranged aromatic sheets generate interstices, or pores, which are filled with the tarry matter from the
decomposition of the carbonaceous precursors or blocked by the decomposed products during the carbonization step. 

After the pyrolysis step, the intermediate product is activated in an oxidizing atmosphere; here, the pore structure in carbonized char is further developed and released. Air, steam and CO₂ are commonly used activating agents. A significant surface area starts to develop at temperatures > 700 °C, and the optimal temperature is usually within 700–900 °C. Under the oxidizing atmosphere, certain moieties of the char are especially prone to oxidization, so that as combustion proceeds, a preferential “etching” takes place and internal pores are created. The structure of the pores and the pore size distribution are mainly determined by the nature of the precursors and the carbonization and activation process. The activation also removes disorganized carbon, so that the stable carbon structures are exposed to the action of the activating agent to develop microporous structure. In the latter stage of activation, the widening of existing pores and the formation of large pores by burnout the walls between the adjacent pores also takes place. Usually, prolonging the activation time could result in the increase in transitional porosity and macroporosity, and decrease the microporosity.

The carbonization process using pyrolysis could be replaced by a more sustainable carbonization - hydrothermal carbonization, discussed in section 1.1. Compared with the high temperature used in pyrolysis, a relatively low temperature (160-250 °C) is used in hydrothermal carbonization. The carbon content increases, oxygen and hydrogen decrease after the hydrothermal carbonization. Because water is needed in the hydrothermal system, a wet precursor could be used without a drying step. Using hydrothermal carbonization in preparing activated carbons has another advantage: it has high carbon efficiency, because it releases much less gases than pyrolysis, and all the decomposed by-products are in the water phase. The activated carbons prepared from hydrothermally carbonized precursors have equally high surface area as those from pyrolyzed precursors, even though the pyrolysis gives higher carbon content than hydrothermal carbonization.

Apart from the two-step physical activation process, there is also single-step physical activation process, when carbonization and activation take place simultaneously. Steam is the commonly used activating agent in the single-step physical activation.

1.2.1.2 Chemically activated carbons

Chemical activation involves impregnation of the precursor with a chosen chemical in solid or liquid form before going to thermal treatment. In the
chemical activation process, carbonization and activation steps are carried out simultaneously. The most common activating agents are ZnCl₂, H₃PO₄, KOH, K₂CO₃, or NaOH, which work as dehydrating agents and oxidants. The activating agents could reduce the formation of tar, and help to generate pores by partial oxidation. The activation temperature used in chemical activation is between 400 and 800 °C, this range is lower than for physical activation. Chemical activation usually takes 0.5 to 4 hours, after which the chemicals working as activating agents have to be removed by washing with water. The most important parameter in chemical activation is the ratio of chemical agent to precursor, which influences the development of porosity significantly. The optimal ratio typically varies for different activating agents.

The chemical agents help developing the porosity of activated carbons via dehydration and degradation reactions. During the activation, there are interaction between the chemicals and the carbon skeleton.

For chemical activation with H₃PO₄ as the activating agent, Jagtoyen and Derbyshire proposed that the acid firstly attacks the structure of the precursor by hydrolyzing glycosidic linkages in hemicellulose and cellulose and by cleaving aryl ether bonds in lignin. Thereafter, H₃PO₄ forms phosphate linkages, such as phosphate and polyphosphate esters, which serve to connect and crosslink biopolymer fragments. These phosphate and polyphosphate esters cause the dilation of the precursor. The pores form in the washing step as a consequence of the removal of these esters.

Compared with physical activation, chemical activation has several advantages: it results in better development of the porosity, and consequently a higher surface area; it usually gives higher yield; it is carried out in a single step, combining carbonization and activation; it performs at lower temperatures. The main drawbacks are the environmental and economic concerns of using chemical agents, and the additional washing of the chemicals after the activation.

In addition to the conventional thermal treatment for the chemical activation, microwave heating is also an efficient heating method. Carbon materials are generally very good microwave absorbers and are heated by microwaves very effectively. Microwave heating can shorten the thermal treatment time considerably and, hence, reduce energy consumption. In conventional heating, there is a thermal gradient from the hot surface of the char particle to its interior, which leads to a long heat conduction time for the caloric transport. However, in microwave heating, a very large thermal gradient develops from the interior of the char particle to its cool surface and makes the microwave-induced reactions to proceed more quickly and effec-
atively at a low bulk temperature. The property of the resulted activated carbons is quite comparable to those produced by conventional heating.

1.2.1.3 Activated carbon composites

Activated carbon composites can have properties that are enhanced or new as compared with pure activated carbon materials. Activated carbons could be combined with other porous materials to moderate and enhance the functionalities in relation with the porosity. For example, hydrophobic SiO$_2$ aerogel/carbon composite materials made by mixing activated carbons with the sol-gel during the aerogel production, showed good performance in adsorption of 2, 4, 6-trinitrotoluene (TNT) in water phase. An alumina/activated carbon composite had significant capacities to adsorb Alizarin Red-s and Methylene Blue from aqueous solutions and an outstanding catalytic activity and stability for the hydrodesulfurization of dibenzothiophene. Elutritlite is a mineral waste from coal mining and contains mainly aluminosilicate and organic carbon. A zeolite/activated carbon composite could be made from natural elutritlite, which showed high capacity in CO$_2$ adsorption. Graphene/activated carbon and carbon nanotube/activated carbon composites are used as high-performance electrode materials for supercapacitors, in terms of specific capacitance, resistance and volumetric capacitance.

Activated carbons could also be incorporated with metal oxide nanoparticles to get new properties. CuFe$_2$O$_4$/activated carbon composite, developed using a simple chemical co-precipitation procedure, combined the adsorption features of activated carbon with the magnetic property and the excellent catalytic properties of powdered CuFe$_2$O$_4$. Such a composite can be used to adsorb catalytically degrade acid orange II (AO7) in water, and could be easily separated from water after applying a magnetic field. TiO$_2$/activated carbon composites exhibit bifunctionality of adsorption and photocatalysis in synergism, and have been studied for the removal of organic pollutants from water. A RuO$_2$/activated carbon composite is also a good candidate as a positive electrode in an alkaline supercapacitor. ZnO/activated carbon nano-composites work very well as catalysts in the photodegradation of rhodamine B. A MoS$_2$/activated carbon composite is an active and stable acid catalyst for the electrochemical hydrogen evolution reaction by water splitting. Iron oxide/activated carbon composites, prepared either by impregnation in the pore structure of activated carbon or by precipitation on the surface of the carbon, have magnetic properties that allow them to be easily separated from the working system. A Fe$_3$O$_4$/activated carbon composite could effectively separate methyl orange from aqueous solution and be efficiently regenerated by hydrogen peroxide.
1.2.1.4 Activated carbon tablets/discs

Activated carbons need to be appropriately structured to suit their intended applications. Such structuring includes a control of the macroscopic dimensions, mechanical properties, as well as the pore distributions at various length scales. Well-defined powders of activated carbons can be used directly in certain applications to water treatment, granulated activated carbons are suitable for other applications to water treatment, but for applications to gas separation well defined pellets or beads of activated carbons are most useful. Activated carbon tablets or discs with good mechanical strength could reduce the pressure drop and attrition in certain gas adsorption processes and have a long lifetime. Dense activated carbon tablets/discs are also beneficial when it comes to the volume effectiveness in applications such as adsorbed natural gas (ANG) technologies.

There are various approaches to produce activated carbon tablets/discs. Traditionally, binders are needed to prepare activated carbon tablets/discs from activated carbon powders. Typical binders used are humic acid-derived sodium salt, polyvinyl alcohol, novolac phenolic resin, Teflon and adhesive cellulose-based binders. To make activated carbon tablets/discs, the activated carbon powders are mixed with the binder with a certain ratio, before drying and hot compression. The resulted tablets/discs need to go through pyrolysis to carbonize the binder. Binder-free briquetting could also be used to make activated carbon tablets/discs from a powder, but higher pressure and temperature than the binder applied method are usually needed.

Instead of pressing the porous activated carbon powder to make the tablets/discs, the activated carbon tablets/discs could also be prepared by shaping the precursor in to non-porous tablets/discs, which subsequently is carbonized and activated either chemically or physically. Moreover, apart from the conventional hot compression, a more efficient compression approach called as pulsed current processing (PCP) could be applied to prepare the tablets/discs. PCP uses pulsed direct currents to increase the temperature in a fast speed.

1.2.2 Other refined products

In addition to activated carbons, the solid products from hydrothermal carbonization could be refined into other products. Functional materials could be made by modifying the surface of the solid products from hydrothermal
carbonization, thanks to the polar oxygenated surface groups such as carboxylic groups, hydroxyl groups, and ketones. Moreover, there is abundance of furanic compounds in the materials from hydrothermal carbonization, which also offer the opportunity for surface modification.

The sulfonated hydrothermally carbonized material could be synthesized by $\text{H}_2\text{SO}_4$ treatment of spherical product from hydrothermal carbonization of glucose, which could be applied as a solid acid catalyst for esterification of oleic acid for the production of biofuels. Amino-groups could be grafted on the surface of the hydrothermally carbonized material, thanks to the abundant hydroxyl groups on the surface. Etherification of carbonaceous materials has been achieved by addition of 3-chloropropyl amine to hydrothermal carbonized spheres. Hollow spheres from hydrothermal carbonization could also be silylated on the hydroxyl groups on the surface of the hollow spheres by (3-aminopropyl) triethoxysilane (APTES). HTC substances and post-pyrolyzed carbon spheres were modified by maleimide, tetracyanoethylene, and 4,5-dicyano-1,3-dithiol-2-one (DCDTO). The DCDTO-functionalized HTC substances were then hydrolyzed in order to obtain thiol-functionalized materials. It has also been reported that a large number of oxygen-containing functional groups could be additionally created on the surface of HTC substances by a simple thermal treatment at a relatively low temperature (i.e., 300 °C) in air.

1.3 Application of activated carbons

Due to their high surface area, well developed pore structure, and high degree of surface reactivity, activated carbons are used in diverse areas, such as catalysis, purification, decolorization, deodorization, dechlorination, separation, and concentrating in order to permit recovery and to filter. Activated carbons are relatively inexpensive, which allows them to be widely applied in many products and related processes, including foods, pharmaceuticals, chemicals, petroleum, nuclear technology, automobiles. Gas adsorption and water treatment are among the most interesting applications of activated carbons.

1.3.1 Activated carbons for gas adsorption

Activated carbons are excellent and versatile adsorbents in a range of gas adsorption and gas storage processes. They can selectively adsorb gas molecules, which give them the capability of separating certain gases from the others. Purification of air is one of the largest uses of activated carbons.
There are two main types of adsorption systems for air purification. One is the purification of air for immediate use in inhabited spaces, where clean air is a requirement. For example, activated carbons are used to clean indoor air by removing pollutants like formaldehyde and other aldehydes. For this application, the concentrations of pollutant gases are usually below 10 ppm, so that the adsorbent could work for a long time before being replaced. The other type of adsorption system prevents pollution of the air from industrial exhaust streams before release to the atmosphere. For instance, the effluent gases from industry and processing units contain a large number of pollutants, such as NO$_x$, SO$_x$, H$_2$S, vapors of CS$_2$, and styrene, which could be separated from the stream by activated carbons before release. The effluent gases from automobile also contain a lot of NO$_x$ and SO$_x$, which could be effectively removed by activated carbons before release to atmosphere. Carbon molecular sieves, as one kind of activated carbons, are used to make ultrapure nitrogen by separating O$_2$ from air. Certain activated carbons are excellent adsorbents for the pressure swing adsorption (PSA) technology that could be used for carbon capture and storage (CCS). Activated carbons have selectivity for CO$_2$ over N$_2$ in the flue gas. For adsorption of small gas molecules with low concentration, such as CO$_2$, the large amount of micropores in the activated carbon plays an important role. Activated carbons, in the form of carbon molecular sieves, have also been found to be an effective adsorbent for biogas upgrading. A typical biogas from fermentation contains mainly a burnable component, CH$_4$, but also a quite significant amount of CO$_2$. To make a high quality fuel from biogas, activated carbon shows good performance to purify biogas by separating CO$_2$ from CH$_4$. Natural gas, composed mainly of CH$_4$ (85-95%), is a widely used energy source in the world. However, it needs a safe way to be stored in some applications, such as fuel for vehicle. The adsorbed natural gas (ANG) technology using activated carbons for a temporary storage offers a safer and lower pressure storage method than the compressed natural gas (CNG) technology, and no need for refrigeration as in the liquefied natural gas (LNG) technology. Typically, the CNG technology needs a storage pressure of 18-24 MPa, while the ANG technology usually needs a pressure of 3.5-4 MPa. The low pressure storage of ANG could not only improve the safety criteria but also considerably reduce the compressing costs incurred by the traditional CNG storage. For the ANG technology, the activated carbons are preferred to be used in a form of tablets or discs, powders would be less volume effective.
1.3.2 Activated carbons for water treatment

The removal of organic and inorganic pollutants from aqueous phase, including drinking water, industrial waste water, and municipal waste water, is a very important application of activated carbons. It has been reported that around 80% of the world production of activated carbon is used in liquid-phase applications.\(^5\)

The adsorption in aqueous phase using activated carbons results from interactions between the carbon surface and the adsorbates. These detailed physical and chemical natures of these interactions vary with the nature of the adsorbate as well as the surface chemistry of the activated carbon. Pollutants in the water can be classified in various ways and one common way is to classify them into two types: heavy metals and organic pollutants.\(^6\) For heavy metal ions, electrostatic interactions are important. These interactions can be attractive or repulsive, depending on three factors: (i) charge density of the carbon surface; (ii) chemical characteristics of the adsorbate; and (iii) ionic strength of the solution. Positively charged adsorbates are prone to be attracted by negatively charged carbon surface, and it is opposite for the negatively charged adsorbates. Other important interactions are: (i) van der Waals forces; (ii) hydrophobic interactions; and (iii) hydrogen bonding interaction.\(^6\)

Abundant surface functional groups and a highly developed porosity of activated carbons make them versatile adsorbents for applications to aqueous systems. Variable amounts of heteroatoms in the surface groups of the activated carbons, oxygen, hydrogens, nitrogen and sulphur, allow various functionalities. These atoms and molecular structures, which might have origin in the raw material or could be introduced during preparation or post treatments, largely influence the charge, hydrophobicity and electronic density of the surface of activated carbons. The carbon surface chemistry is determined by the presence of heteroatoms\(^7\) and has a great influence on both electrostatic and non-electrostatic interactions with adsorbates. The pore size and overall pore texture of the activated carbons also play an important role in the adsorption from aqueous phase. Micropores are good for the physical adsorption of small molecule or ions, while mesopores or macropores facilitate adsorption of large organic molecules.

The properties of the adsorbate such as molecular size, solubility, pKa, and nature of the substituents (in the case of aromatic adsorbates), influence very much the adsorption processes on the activated carbon adsorbents.\(^8\) When the activated carbon is in contact with an aqueous solution, electric charges are generated on its interface with water, which results from either the dissociation of the surface functional groups of the carbon or the adsorp-
tion of ions from the solution. The surface charge is strongly influenced by the solution pH and the surface characteristics of the activated carbon. There are three different proposed mechanisms for the adsorption of ions in an aqueous solution. The first states that adsorption is determined by electrostatic adsorbate–activated carbon interactions, which mainly depends on the carbon surfaces functionality, especially oxygen-containing surfaces complexes (ion-exchange process). The second one suggests that enhanced adsorption capacity depends mainly on the microporosity. The third mechanism is that the adsorption occur on the basic and acidic sites, as a consequence of the amphoteric carbon surfaces.

1.4 Aims of this study

Hydrothermal treatment of biomass is an effective way of disposing waste biomass. The resulting HTC biomass has special characteristics. The aims of this study are to understand the structure and properties of HTC biomass and to demonstrate that the HTC biomass could be refined into activated carbons.

To understand what we get from biomass waste after the hydrothermal carbonization, the chemical structures of four different HTC biomass (grass cuttings, horse manure, beer waste and biosludge) were studied and characterized through a series of methods. Understanding of the chemical structure of HTC biomass will benefit finding a way to use it. In this thesis, the four different HTC biomass were refined into powdered activated carbons by physical activation using CO$_2$ and chemical activation using H$_3$PO$_4$. The influences of the conditions on making activated carbons were analyzed by full factorial design. A composite of activated carbons and iron oxide was synthesized through hydrothermal carbonization and CO$_2$ activation. The composite was characterized thoroughly by various methods. Strong and dense activated carbon discs were synthesized from HTC biomass by using pulsed current processing and activation by CO$_2$. The properties of the discs of activated carbons were studied.

Another aim of the thesis is to investigate the application of the powdered activated carbons from HTC biomass. We studied the application of the activated carbons in CO$_2$ adsorption and methylene blue adsorption from water.
Two main methods are applied to make activated carbons: physical and chemical activation. As described in Chapter 1, physical activation is a two-step process: the precursors are firstly treated by pyrolysis or hydrothermal carbonization to increase the carbon content; secondly they are activated at a high temperature by oxidizing gases, such as CO$_2$, steam, or air. In chemical activation the precursors are mixed with activation agents such as H$_3$PO$_4$, KOH, ZnCl$_2$ and KCO$_3$, before a high temperature treatment. The activation agents and resulting compounds are washed away after high temperature treatment. In this thesis, I present findings from both physical activation of hydrothermally carbonized biomass by CO$_2$ and chemical activation with H$_3$PO$_4$.

The raw materials studied in the papers of this thesis were mainly waste biomass, including horse manure, beer production waste, grass cuttings and biosludge. Those wastes usually have low value; some of them cause environmental problems. Before activation, they were carbonized by hydrothermal carbonization.

### 2.1 Hydrothermally carbonized biomass

Four different biomass wastes were treated by hydrothermal carbonization. As described in the papers of this thesis, the biomass was divided into pieces of a centimeter size and placed in an autoclave reactor. Water, organic acid and small amount of FeSO$_4$ as a catalyst were added. Temperature was increased to 180-230 °C, and the pressure equilibrated to 10-20 bar. After a few hours, the slurry of HTC biomass and water was pumped to a large vessel and equilibrated for 5-6 h at a somewhat elevated temperature, after which it was cooled and filtered. After drying the HTC biomass were characterized by $^{13}$C NMR spectroscopy, X-ray photoelectron spectroscopy (XPS) and SEM. Moisture, ash, surface areas, and element analyses of HTC biomass were performed using standardized methods, and presented in Table 1. HTC biosludge had much more ash than did other HTC biomass, due to the heterogeneous nature of biosludge from paper mills and related chemicals used. The moisture content was ~4-7 wt.% for HTC biomass, and this level is consistent with the somewhat hydrophilic nature of HTC biomass related
to polar functionalities. The biomass were not quite well carbonized compared with pyrolysis, and the HTC biomass have very low surface areas.

**Table 2.1** Moisture, ash, BET surface areas, and element composition of hydrothermally carbonized (HTC) biomass. Reproduced using the data from Paper I and Paper II

<table>
<thead>
<tr>
<th>HTC of:</th>
<th>Grass cuttings</th>
<th>Beer waste I</th>
<th>Beer waste II</th>
<th>Biosludge</th>
<th>Horse manure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>6.5</td>
<td>3.9</td>
<td>5.1</td>
<td>4.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Ashes (dry basis)</td>
<td>4.8</td>
<td>5.1</td>
<td>3.8</td>
<td>9.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Ultimate (wt. %, dry basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>61.9</td>
<td>59.5</td>
<td>55.5</td>
<td>53.3</td>
<td>53.2</td>
</tr>
<tr>
<td>H</td>
<td>5.3</td>
<td>6.6</td>
<td>5.6</td>
<td>6.1</td>
<td>5.9</td>
</tr>
<tr>
<td>N</td>
<td>2.62</td>
<td>5.16</td>
<td>3.1</td>
<td>0.79</td>
<td>1.34</td>
</tr>
<tr>
<td>S</td>
<td>0.28</td>
<td>0.49</td>
<td>---</td>
<td>0.40</td>
<td>0.38</td>
</tr>
<tr>
<td>O&lt;sup&gt;a&lt;/sup&gt;</td>
<td>25.1</td>
<td>23.2</td>
<td>34.1</td>
<td>29.9</td>
<td>32.0</td>
</tr>
<tr>
<td>O/C (atomic ratio)</td>
<td>0.30</td>
<td>0.29</td>
<td>0.46</td>
<td>0.42</td>
<td>0.45</td>
</tr>
<tr>
<td>H/C (atomic ratio)</td>
<td>1.02</td>
<td>1.32</td>
<td>1.21</td>
<td>1.36</td>
<td>1.33</td>
</tr>
<tr>
<td>S&lt;sub&gt;BET&lt;/sub&gt; (m&lt;sup&gt;2&lt;/sup&gt;/g)</td>
<td>6</td>
<td>25</td>
<td>6</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated by difference; <sup>b</sup>the first batch was used for physical activation; <sup>c</sup>the second batch was used for chemical activation

The XPS method provides quantitative chemical information for the outermost 2-10 nm of surfaces. As shown in Paper I, the O/C atomic ratios on the surface were different from the average values for each of the samples. HTC horse manure and biosludge had lower O/C atomic ratio on the surface than the average number, which means they were carbonized better on the surface during hydrothermal carbonization. While HTC beer waste I had the opposite tendency, which also means it did not carbonize well on the surface compared to the other parts. In Table 2 of Paper I, different chemical states of carbon were quantified by XPS and sorted into four types according to the different functional groups: unoxidized carbon (C1-carbon: C-C, C-H, C=C groups, such as found in hydrocarbon chains/aromatic groups), one bond to oxygen (C2-carbon: C-O, C-O-C functional groups), more oxidized carbon C3-carbons and C4-carbons (e.g. ester and carboxylic acid functional groups). For the four samples, most of the total carbon (60-73%) were present as non-oxidized carbon (C1-carbon), with HTC horse manure having the highest value for C1.
Solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy is an effective tool to characterize carbonaceous materials. In Paper I and III, solid state $^{13}$C NMR spectra were recorded to investigate the molecular structures of the HTC biomass. These spectra showed close resemblance to those recorded on HTC glucose by Baccile et al.\textsuperscript{18} and those recorded on HTC sucrose and HTC maltose by Titirici et al.\textsuperscript{17} and a fair resemblance to those recorded on HTC swine manure by Cao et al.\textsuperscript{101} A direct polarization solid state $^{13}$C NMR spectrum for HTC grass cuttings is shown in Figure 2.1a. The HTC grass cuttings was black, and the atomic composition and its $^{13}$C NMR spectrum indicated that it was similar to lignite in its chemical composition and structure.\textsuperscript{102} A $^{13}$C NMR chemical shift of $\sim$175 ppm indicated acid groups, $\sim$210 ppm ketones, $\sim$105 and $\sim$150 ppm $sp^2$ hybridized carbons with and without oxygen, $\sim$130 ppm aromatic groups and $\sim$30 ppm $sp^3$ hybridized aliphatic carbons.\textsuperscript{18}

In the solid state $^{13}$C NMR spectrum for HTC horse manure (Figure 2.1b), peaks at 65, 72, 75, 84, 89 and 105 ppm was attributed to the unreacted cellulose, using the assignment of Titirici et al.\textsuperscript{103} The solid state $^{13}$C NMR spectrum from HTC horse manure in Figure 2.1b showed that this solid had more similarities to peat than to lignite.\textsuperscript{104} These similarities were consistent with the brown color and the elemental composition of the solid.\textsuperscript{105} In these less condensed solids, acid and ketone groups were missing. Instead, there were indications of remaining groups of O-CH\textsubscript{x} type by their characteristic chemical shifts of $\sim$ 60-80 ppm. The fraction of $sp^2$ hybridized carbons was smaller than that for HTC grass cuttings, indicating a lower degree of carbonization for these brown solids. The solid state $^{13}$C NMR spectrum recorded on HTC horse manure after extraction (Soxhlet) in acetone was also measured. The spectrum (Figure S4 in Paper I) of the extracted solid had no significant signals in its aliphatic region, but was otherwise very similar to the spectrum of the non-extracted HTC horse manure in Figure 2.1b. The extracted fraction contained compounds with significant amounts of methylene groups, possibly related to lipids, or their degradation products. The degree of extraction was higher in acetone than in pentane and, hence, we speculate that the liquid fraction also contained some polar groups. The $^{13}$C NMR spectra of HTC biosludge and beer waste were shown in Figure S1 and S3 in Paper I.
Figure 2.1 $^{13}$C nuclear magnetic resonance spectra for hydrothermally carbonized (HTC) biomass. (a) HTC grass cuttings; (b) HTC horse manure. Reproduced using data from Paper I.
The morphologies of the HTC biomass are quite different from each other, depending on the precursor waste. The SEM micrographs in Figure 2.2 visualize that the underlying shapes of the biomass largely remain unaffected by the hydrothermal treatment. Figure 2.2a shows the condensed structure of grass cuttings, the carbon spheres are mixed in the layer structure. In Figure 2.2b, the spheroidal particles are probably from the yeast cells applied in the beer production, they kept the shape during the hydrothermal process. The complex structure of biosludge in Figure 2.2c originated from the different lignocellulosic fibrous material, and mixed with the chemicals added in the paper and pulp industry. The fibrous structures of the horse manure in Figure 2.2d remained after the hydrothermal treatment.

2.2 Physically activated carbons

In Paper I and IV, the physical activation was conducted on the powdered hydrothermally carbonized biomass using CO$_2$. In a typical preparation, a batch of ~5 g of HTC biomass was activated in a flow of CO$_2$. The tempera-
ture was ramped from room temperature to the set temperature, at a rate of 10 °C/ min, and activated for a designated time. Afterwards, the activated HTC biomass was cooled to room temperature. CO₂ was flowed through the reactor bed during all steps. Activation temperature, activation time, and flow rate of CO₂, are optimized with a set of experiments. Figure 2.3 shows the schematics and a photo of the homemade reactor used for all the activation experiments.

Figure 2.3 Schematics and a photo of the reactor used for activating hydrothermally carbonized (HTC) biomass. From Paper I
Figure 2.4  a) N₂-adsorption isotherms and b) pore size distribution of commercial activated carbon and activated carbons prepared from four hydrothermally carbonized (HTC) biomass at 800°C with CO₂ at a flow rate of 17 dm³/h and an activation time of 2 h. “■”HTC horse manure; “▲”HTC grass cuttings; “●”HTC beer waste I; “▼”HTC biosludge; “◆” a commercial activated carbon. Reproduced using data from Paper I

N₂ adsorption at its temperature of boiling point (i.e. 77.4 K) is a standard method to characterize porous materials. Activated carbons usually contain pores in a wide range of sizes. However, some activated carbons could be prepared to have pores in a narrow range, for example carbon molecule sieve is highly microporous. In Paper I and IV, we have prepared activated carbons from HTC biomass by CO₂ activation, showing different porous char-
acteristics. In Figure 2.4a, isotherms for activated HTC grass cuttings and HTC beer waste are typical for microporous materials (type I according to the classification of IUPAC). Isotherms for activated HTC horse manure, HTC biosludge and a commercial activated carbon are quite different. These isotherms show hysteresis for adsorption and desorption, which are typical for capillary condensation and mesoporosity. In Figure 2.4b, the associated pore size distributions are estimated from the adsorption branch with a density functional theory (DFT) description. With less carbonized HTC precursors such as HTC horse manure it was easy to get large pores; while better carbonized HTC precursors such as HTC grass cuttings were activated into highly microporous carbons.

The properties of the activated carbons depend on both the chemical nature of the HTC biomass and the process conditions applied. In table 2.3, data from Paper I are presented for activated carbons activated at fixed process conditions. Activated HTC grass cuttings and horse manure had specific surface areas similar to a commercial activated carbon. Activated carbons from HTC beer waste and biosludge had lower specific surface areas. The yields were higher for activated carbons of HTC beer waste I and grass cuttings than for HTC horse manure and biosludge. The higher yields were correlated to a higher degree of carbonization for these two carbons.

**Table 2.2** Yield, ash content, and textural properties of activated carbons from hydrothermally carbonized (HTC) biomass. From Paper I

<table>
<thead>
<tr>
<th>HTC biomass</th>
<th>Yield (wt.%)</th>
<th>Residue (wt.%)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S_{BET}</td>
<td>S_{ext}</td>
<td>S_{mic}</td>
<td>V_{t}</td>
</tr>
<tr>
<td>Horse manure</td>
<td>13.1</td>
<td>37.4</td>
<td>749</td>
<td>405</td>
</tr>
<tr>
<td>Grass cuttings</td>
<td>31.0</td>
<td>12.0</td>
<td>841</td>
<td>99</td>
</tr>
<tr>
<td>Beer waste</td>
<td>24.1</td>
<td>16.3</td>
<td>570</td>
<td>64</td>
</tr>
<tr>
<td>Biosludge</td>
<td>14.9</td>
<td>55.9</td>
<td>326</td>
<td>136</td>
</tr>
<tr>
<td>Commercial</td>
<td>---</td>
<td>9.3</td>
<td>745</td>
<td>218</td>
</tr>
</tbody>
</table>

*Activated at 800 °C with CO₂ at a flow rate of 17 dm³/h and an activation time of 2 h. Textual properties were determined by N₂ adsorption.

The influence of activation temperature is significant. As can be seen in Figure 2.5, when the activation time is below 800 °C, the HTC biomass mainly developed micropores. However, when the temperature reached 800 °C, there were more large pores developed. Moreover, increasing flow rate of CO₂ and prolong the activation time could widen the micropores to mesopores, as proved by the pore size distribution in Figure 2.5b.
Figure 2.5 a) N$_2$-adsorption isotherms and b) pore size distribution of activated carbons prepared from hydrothermally carbonized horse manure. Activated carbons prepared at different temperatures and activation times as indicated in the figure. ■ 600°C-2h-17dm$^3$/h; ◆ 700°C-2h-17dm$^3$/h; ◇ 800°C-0h-17dm$^3$/h; △ 800°C-0h-48dm$^3$/h; ▼ 800°C-1h-17dm$^3$/h; ● 800°C-2h-17dm$^3$/h; ▲ 800°C-2h-48dm$^3$/h. From Paper I

To analyse the influence of flow rate of CO$_2$, activation time and O/C ratio in the activation of HTC biomass on the weight loss, specific surface areas (BET), micropore areas, micropore volumes, and total pore volume, full factorial design was implied in Paper I. A screening experiment was used to determine the experimental variables and interactions that have significant influence on the result. The number of experiments needed depends on the factors that are investigated, for example, if the combinations of $k$ factors are investigated at two levels, a factorial design will consist of $2^k$ experiments. In Paper I, three factors were investigated with 2 levels, with the sign of “-” (minus) for low level and “+” (minus) for high level, as
shown in Table 2.3. Figure 2.6 shows the eight experiments in our full factorial design.

Table 2.3 Conditions for physical activation

<table>
<thead>
<tr>
<th>Factors</th>
<th>Values</th>
<th>Low level (-)</th>
<th>High level (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: O/C ratio</td>
<td></td>
<td>0.29</td>
<td>0.45</td>
</tr>
<tr>
<td>B: CO₂ flow rate (dm³/h)</td>
<td></td>
<td>17</td>
<td>48</td>
</tr>
<tr>
<td>C: activation time (hour)</td>
<td></td>
<td>0</td>
<td>8</td>
</tr>
</tbody>
</table>

* Activation for 0 hour means the reactor started cooling down immediately when the temperature reached 800 °C

Figure 2.6 The experiments in a full factorial design with three variables. A: O/C ratio, B: flow rate of CO₂ (dm³/h), C: activation time (hour); “-” low level, “+” high level

The experiments were evaluated in order to fit a polynomial model in the Paper I, which is a third order interaction model:

\[ Y_n = a_0 + a_1A + a_2B + a_3C + a_{12}AB + a_{13}AC + a_{23}BC + a_{123}ABC + e \]  

(1)

\( Y_n \) is the responses: weight loss, specific surface areas (BET), micropore areas, micropore volumes, and total pore volume. A, B and C are factors (see
Table 2.3); $a_0, a_1, a_2,$ and $a_3$ are main effects; $a_{12}, a_{13}, a_{23}$ and $a_{123}$ are interaction effects.

The main effects and interaction effects were calculated from the experiment results. Figure 2.7 show the effects on the total pore volume ($V_{\text{tot}}$). O/C ratio ($A$) played the most significant positive effect on the total pore volume, flow rate of CO$_2$ ($B$) had negative effect, and the activation time ($C$) had a positive effect. The combination of different factors played mostly negative effects. Detailed analyses for the different effects are shown in Paper I.

**Figure 2.7** Impact of the three factors on the total pore volume got from full factorial design. O/C ratio is coded as “A”, flow rate of CO$_2$ is “B” and activation time is “C”. From Paper I
Figure 2.8 Scanning electron microscopy images. a) Activated carbon from hydrothermally carbonized (HTC) horse manure, note how the underlying shapes in the biomass have survived both the hydrothermal treatment and activation in CO$_2$; b) Activated carbon from HTC grass cuttings shows micropores on the carbon sphere; c) Activated HTC beer waste shows carbon spheres; d) Activated HTC biosludge shows mesopores. Reproduced using data from Paper I

In Paper I and IV, we used SEM to study the effect of the activation on the morphology. The SEM micrograph in Figure 2.8 shows the morphology of the four activated carbons prepared from HTC biomass. Figure 2.8a visualizes that the outer shapes of HTC horse manure largely remained after hydrothermal carbonization and subsequent activation in a flow of CO$_2$ at an elevated temperature. The preserved shapes of the underlying objects (cells etc) could allow for complex forms of activated carbons to be produced by an appropriate choice of biomass. Such preserved shapes could speculatively circumvent a need to use post-synthetic structuring of the activated carbons. In the SEM micrograph of Figure 2.8b for an activated carbon from HTC grass cuttings, there are significant amounts of pores visible on the carbon sphere, most of which are with small sizes. In Figure 2.8c, the HTC beer
waste I was kept the carbon spheroidal shape after the activation. Figure 2.8d shows the mesopores of the activated carbon prepared from HTC biosludge.

2.3 Iron oxide embedded activated carbons

Composites of activated carbon and magnetic particles have porous structure, and could also be easily separated from liquid medium by applying a magnetic field. In Paper I, iron oxide and activated carbon composites were synthesized using the same procedure as used for making the powdered physically activated carbons. The FeSO$_4$ added in the hydrothermal carbonization worked as a catalyst, but also got crystallized under the hydrothermal condition. As can be seen in Table 2.4, from Paper I, the amount of iron introduced in the HTC biomass was 0.8-1.9 %.

Table 2.4 The content of Fe in hydrothermally carbonized (HTC) biowastes and activated HTC biowastes determined by atomic absorption spectrophotometry. From Paper I

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fe (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTC of:</td>
<td></td>
</tr>
<tr>
<td>Horse manure</td>
<td>1.85</td>
</tr>
<tr>
<td>Grass cuttings</td>
<td>0.79</td>
</tr>
<tr>
<td>Beer waste I</td>
<td>0.80</td>
</tr>
<tr>
<td>Biosludge</td>
<td>1.51</td>
</tr>
<tr>
<td>Activated HTC of:</td>
<td></td>
</tr>
<tr>
<td>Horse manure</td>
<td>7.54</td>
</tr>
<tr>
<td>Grass cuttings</td>
<td>2.30</td>
</tr>
<tr>
<td>Beer waste I</td>
<td>4.11</td>
</tr>
<tr>
<td>Biosludge</td>
<td>8.13</td>
</tr>
</tbody>
</table>

In Paper I, The iron oxide introduced HTC biomass were further activated into activated carbons in physical activation using CO$_2$. The iron component got concentrated when the volatiles lost and the carbon reduced by reacting with CO$_2$. The amount of iron increased to as high as ~8 wt.%, as shown in Table 2.4. The iron was in the form of Fe$_3$O$_4$ crystalline structure in the composite, as determined by powdered X-ray diffraction (XRD) in Paper I.
In Paper I, we showed that the composite of iron oxide and activated carbon from HTC horse manure had a surface area of 750 m$^2$/g and a pore volume of 0.82 m$^3$/g, which was very comparable to a commercial activated carbon. Transmission Electron Microscopy (TEM) images in Paper I (shown here in Figure 2.9a) showed that the micropores of the carbon structure appeared to be randomly distributed. Also in the same paper, TEM images (here Figure 2.9b) showed the size of iron oxide crystals was in the range of 20-40 nm, and those nano crystals were in octahedral shape. The size of the iron oxide crystals was larger than the pore size of the composite. To further determine how the nano crystals were located in the composite, electro-tomography was conducted in Paper I. The result proved that the nanoparticles were very well embedded within the matrix of carbon. The movie of the electro-tomography is presented in the supplementary of Paper I. A schematic illustration of the composite is presented in Figure 2.10, which shows how the iron oxide nano crystals are embedded in the carbon matrix. The embedded iron oxide nanoparticles could prevent them from being lost during use in liquid phase. Comparing with magnetic composites made by precipitating iron oxide nanoparticles in the pores of already activated carbons, the composite materials studied in Paper I could avoid pore blockage as well. The iron oxide nanoparticles are embedded within the amorphous wall of activated carbon, thanks to the incorporation of the iron already during hydrothermal treatment.
In Paper I, we showed that the powdered composite of iron oxide nanoparticles and activated HTC horse manure could be easily separated from liquid by a small magnet. Certain magnetic properties of the composite were quantitatively characterized by a magnetization curve presented in Figure 2.11. The composite showed a coercive field of about 40 Oe, and a remnant magnetization of 1 emu/g, at a temperature of 300K. The embedded Fe$_3$O$_4$ nanoparticles displayed both superparamagnetic and ferrimagnetic characteristics, due to the particle size of Fe$_3$O$_4$.\textsuperscript{70,106,107} The superparamagnetic properties originate from the small iron oxides particles (<30 nm) and the ferrimagnetic properties from larger iron oxides particles >30 nm. The superparamagnetic limit of Fe$_3$O$_4$ has been reported to be ~30 nm.\textsuperscript{106} The demagnetizing portion of the data presented in Figure 2.11 was modelled with the Langevin equation\textsuperscript{108} using a regression analysis, from which a particle volume was obtained. From the particle volume, an average diameter of ~30 nm was calculated by assuming a spherical form. This size agreed well with the particle sizes of 20-40 nm observed by TEM. The saturation magnetization with respect to the weight of the Fe$_3$O$_4$ phase was calculated to be 90 emu/g, at 300 K, which is close to the value reported for bulk Fe$_3$O$_4$ (93 emu/g, 290 K).\textsuperscript{109} When the magnetic field was removed, the main part of the activated composite particles lost their magnetism due to their superparamagnetism, but some particles retained their magnetism due to their larger size.
Figure 2.11 Magnetization curve of the magnetic activated carbon prepared from hydrothermally carbonized horse manure activated at a temperature of 800 °C with CO\textsubscript{2} at a flow rate of 17 dm\textsuperscript{3}/h and an activation time of 2 h. The inset shows the low field region of the hysteresis. From Paper I

2.4 Chemically activated carbons

Chemical activation with H\textsubscript{3}PO\textsubscript{4} as the activation agent was used in Paper II and IV. As was described in Paper II and IV, the chemical activation process was started by adding and mixing two gram of HTC beer waste II with 8 ml of H\textsubscript{3}PO\textsubscript{4} solution (with concentrations of 40 - 85 wt\%) and kept overnight. These mixtures were dried at a temperature of 100 °C for two hours before further activation using the same home-made vertical steel reactor as was used for the physical activation (c.f. Figure 2.3). The temperature was increased with 10 °C/ min to the set point of 600-700 °C. At this temperature, the precursor was activated for one to three hours in a flow of N\textsubscript{2}. Afterwards, the activated HTC biomass was cooled to room temperature and washed thoroughly in hot water until the pH conditions of the eluate stabilized at a pH = 7.

In Paper II, thermogravimetric analyses (TGA) were performed to identify the useful range of temperatures for the activation. The shape of the TGA curves for HTC beer waste and the HTC beer waste/ H\textsubscript{3}PO\textsubscript{4} mixture differed significantly, as shown in Figure 2.12. The impregnation of H\textsubscript{3}PO\textsubscript{4} shifted the degradation of HTC beer waste to high temperatures. The main mass loss for the HTC beer waste occurred at temperatures of 200-500 °C. However, for the mixture of HTC beer waste and H\textsubscript{3}PO\textsubscript{4} the mass was lost in two steps. A moderate mass loss occurred at temperatures < 500 °C, and the main mass
loss occurred in a narrow temperature range of 600-700 °C. \( \text{H}_3\text{PO}_4 \) appeared to play the role as a catalyst and promote bond cleavage reactions and the formation of crosslinks via processes such as cyclization and condensation. Jagtoyen and Derbyshire reported that \( \text{H}_3\text{PO}_4 \) combine with organic groups and form phosphate and polyphosphate bridges that can connect and cross-link with biopolymer fragments. The narrow temperature range of 600-700 °C was used for \( \text{H}_3\text{PO}_4 \) activation in this thesis.

![Figure 2.12 Thermogravimetric curves for hydrothermally carbonized (HTC) beer waste II and for HTC beer waste II that was impregnated with 85% \( \text{H}_3\text{PO}_4 \). The curves were recorded in an atmosphere of N\(_2\). From Paper II](image)

Table 2.5 Moisture, ash, bulk density, particle size, and textural properties of the precursor (hydrothermally carbonized (HTC) beer waste) and the activated carbon prepared by \( \text{H}_3\text{PO}_4 \) activation (From Paper II)

<table>
<thead>
<tr>
<th>Beer waste II</th>
<th>Moisture (wt.%)</th>
<th>Ash (wt.%)</th>
<th>Density (g/cm(^3))</th>
<th>Mean particle size (µm)</th>
<th>Median particle size (µm)</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Iodine no. (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTC</td>
<td>5.1</td>
<td>3.81</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>6</td>
<td>---</td>
</tr>
<tr>
<td>Activated HTC</td>
<td>---</td>
<td>---</td>
<td>1.798 ± 0.001</td>
<td>192</td>
<td>132</td>
<td>1070</td>
<td>472</td>
</tr>
</tbody>
</table>

In Paper II, a series of activation was performed following a full factorial design, producing activated carbons with a surface area as high as ~1070
m²/g and an iodine number of 472 mg/g, as can be seen in Table 2.5. The density of the activated carbon is 1.798 g/cm³ as determined by helium pycnometry, and the mean particle size and median particle size from light scattering/diffraction measurement are 192 µm and 132 µm, respectively.

**Figure 2.13** a) N₂-adsorption and desorption isotherms and b) pore size distribution of activated carbon prepared from hydrothermally carbonized beer waste II at 600 °C with H₃PO₄/carbon ratio of 5 at a flow rate of 48 dm³/h and an activation time of 1 h. Pore size distribution was calculated by both adsorption branch and desorption branch of the isotherms using BJH model. From Paper II

The N₂-adsorption and desorption isotherms from the activated HTC beer waste in Paper II are presented in Figure 2.13a. They are very typical for the activated carbons prepared from HTC beer waste by chemical activation with H₃PO₄. The adsorption and desorption isotherms are of the type IV when using the IUPAC’s categorization pattern. The hysteresis loop shows a H4 type according to the IUPAC’s classification,¹⁰ and the loop is at relative
pressure $0.44 < p/p_0 < 0.8$ indicates the presence of a significant fraction of pore openings that are smaller than the size set by cavitation of liquid nitrogen (pores $< 4 \text{ nm}$). The $N_2$ adsorption and desorption isotherms of the activated carbons prepared from HTC beer waste by chemical activation with $H_3PO_4$ in Paper II are quite different from those of the physically activated HTC biomass by $CO_2$ in Paper I. The pore size distribution in Figure 2.13b was calculated by the BJH method for the mesopores domain.$^{111}$ A peak was presented at the pore size around 4 nm when calculated from desorption branch. However, when calculated from the adsorption branch, the pore size distribution does not exhibit this peak as expected. This difference is caused by the cavitation of liquid nitrogen during the desorption, and the mesopores had ink bottle shapes with openings that were $< 4 \text{ nm}$.$^{112}$

**Figure 2.14** Scanning electron micrographs of hydrothermally carbonized (HTC) beer waste II (a) and a corresponding activated carbon prepared from the HTC beer waste II at 600 °C with $H_3PO_4$/carbon ratio of 5 at a flow rate of 48 dm$^3$/h and an activation time of 1 h (b). Reproduced using images from Paper II

In Paper II, we also used SEM to image the changes in morphology during activation with $H_3PO_4$. The SEM images in Figure 2.14 feature the precursor and a corresponding activated carbon. The aggregated spheroidal particles in Figure 2.14a are quite typical for HTC biomass. In Paper I and IV, it was shown that physical activation in $CO_2$ did not change the morphology. However, chemical activation of the HTC beer waste II by $H_3PO_4$ created visible morphological differences. These differences are visible in Figure 2.14a-b. The activated carbon in Figure 2.14b had small underlying particles, and a lot of pores and slits that appear to have been created from the etching by $H_3PO_4$. These features were not visible in the SEM image of the HTC beer waste II precursor in Figure 2.14a.

As was discussed in section 1.2.1, the abundant surface functional groups of activated carbons make them quite versatile. In Paper II, the density of
acids groups on one of the activated carbons was determined by Boehm titration. On activated carbons, the acid groups are typically classified into three groups: carboxyls and carboxylic acids, lactones and lactols, and phenols, with the strength of acidic groups as follow: carboxyl $>\text{lactone} > \text{phenol}$. NaOH is assumed to neutralizes carboxylic, lactonic, and phenolic groups; Na$_2$CO$_3$, carboxylic and lactonic; NaHCO$_3$, only carboxylic group. With these assumptions, the number of different acid sites can be determined by titration with these bases. Table 2.6 shows that the activated carbon contained 1.5 meq/g acid groups, most of which are relatively strong acid groups (lactonic and carboxylic). Compared with physical activation, the chemical activation with H$_3$PO$_4$ appear to introduce more acid groups.

Table 2.6 Surface functional groups of the activated carbon prepared from hydrothermally carbonized beer waste II. From Paper II

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>nCSF (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic</td>
<td>0</td>
</tr>
<tr>
<td>Lactonic</td>
<td>0.7</td>
</tr>
<tr>
<td>Carboxylic</td>
<td>0.8</td>
</tr>
<tr>
<td>Total</td>
<td>1.5</td>
</tr>
</tbody>
</table>

In Paper II, nineteen different experiments were conducted in a full factorial design to analyze the effect of different chemical activation conditions on the resulted activated carbons. Four different specific conditions/variables (the temperature of activation ($X_1$), time for activation ($X_2$), concentration of H$_3$PO$_4$ ($X_3$), and flow rate of N$_2$ ($X_4$)), were investigated, as shown in Table 2.7. Three different responses ($Y_n$): the median pore size ($Y_1$) determined from the pore size distributions (calculated in a DFT model), BET surface area ($Y_2$) and yield ($Y_3$), were analyzed using a polynomial function. The final parameterized model (Eq.2) shows the relationship between the response of median pore size ($Y_1$) and the experimental variables ($X_i$), and the interactions ($X_{ij}$, $i\neq j$) between variables.

$$Y_1 = 2.864 - 0.304X_1 - 0.256X_2 + 0.645X_3 - 0.293X_4 + 0.059X_{12} - 0.227X_{13} - 0.182X_{14} - 0.147X_{23} - 0.166X_{34} + 0.216X_{34}$$  \hspace{1cm} (2)
Table 2.7 Activation conditions for hydrothermally carbonized beer waste II by chemical activation using H$_3$PO$_4$, from Paper II

<table>
<thead>
<tr>
<th>Factors</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low level (-1)</td>
</tr>
<tr>
<td>$X_1$: temperature of activation(°C)</td>
<td>600</td>
</tr>
<tr>
<td>$X_2$: activation time (h)</td>
<td>1</td>
</tr>
<tr>
<td>$X_3$: H$_3$PO$_4$ concentration (wt %)</td>
<td>40</td>
</tr>
<tr>
<td>$X_4$: N$_2$ flow rate (dm$^3$/h)</td>
<td>17</td>
</tr>
</tbody>
</table>

Figure 2.15 Plot of the effects of the variables ($X_n$) on the response to median pore size ($Y_1$) for the activated carbons prepared by chemical activation of hydrothermally carbonized beer waste II by H$_3$PO$_4$. Interaction effects are double digits. From Paper II
Figure 2.16 Plots of observed values vs. the predicted response for the median pore size of chemically activated HTC beer waste II by H$_3$PO$_4$. From Paper II

The calculated effects of the parameters and their combinations (the coefficients) with the corresponding estimation of errors are presented in Figure 2.15. The concentration of H$_3$PO$_4$ ($X_3$) turned out to positively affect the median pore size of the activated carbons ($Y_1$) the most. The other variables ($X_1$, $X_2$, and $X_4$) had smaller and negative effects on the median pore size. The interactions of the parameters ($X_{ij}$) have smaller effects than the single ones ($X_i$). Moreover, the model in Eq 2 could predict the median pore sizes of activated quite well, as shown in Figure 2.16. The analyses of the BET surface areas ($Y_2$) and yields ($Y_3$) were done as well using full factorial design, the details of which are presented in Paper II.
3 Activated carbon disc from hydrothermally carbonized beer waste by pulsed current processing

In Paper III, we prepared and studied strong and dense activated carbon discs (ACDs). The ACDs were prepared by physically activating precursor tablets with \( \text{CO}_2 \), the precursor tablets had been prepared by pulsed current processing (PCP) of hydrothermally carbonized beer waste (HTC-BW). More specifically, the HTC-BW powders were put in a graphite die with a diameter of 12 mm, and a uniaxial pressure of 50 MPa was applied under dynamic vacuum conditions using a Dr Sinter 2050 device. In this device, the HTC-BW powders were rapidly heated up to the desired temperature by applying pulsed direct currents. The precursor discs were formed at temperatures of 100 and 150 °C, and at room temperature. A maximum temperature of 150 °C was chosen to avoid any degradation of HTC-BW. After being cooled down to room temperature by natural convection in air, the discs were activated at 800 °C in \( \text{CO}_2 \) using the same procedure described in Chapter 2. (Figure 3.1 shows the schematic of PCP.)

![Figure 3.1 Schematic of pulsed current processing (PCP)](image-url)
3.1 Morphology, density and mechanical strength

The HTC-BW powder contained 22 wt.% of tar that could be extracted by acetone in a Soxhlet setup. Discs were prepared from both acetone extracted HTC-BW (HTC-D-E-X) and regular HTC-BW without extraction (HTC-D-X). The resulted activated carbon discs are denoted as ACD-E-X-Y or ACD-X-Y. “E” is “acetone extracted”, “X” stands for pressing temperature (25, 100, 150 °C) in the shaping step. “Y” is the activation time in the activation step (1 – 7 h). The photos of Figure 3.2 show the discs HTC-D-150 and ACD-150-2. The disc shrunk after activation, but kept well their original shape.

![Figure 3.2](image)

**Figure 3.2** Photos of discs of hydrothermally carbonized beer waste without extraction, prepared by pulsed current processing at 150 °C before activation (a and b are HTC-D-150) and after activation in a flow of CO₂ at a temperature of 800 °C for 2 h (c and d are ACD-150-2). From Paper III

Although the outer shape of the HTC-Ds did not change during activation into ACDs, the microscopic morphology did change. The SEM image in Figure 3.3a shows that HTC-D-E-150 contained highly packed carbon particles and tar, while the image in Figure 3.3b displays a lot of pores in the ACD-E-150-2.
Figure 3.3 Scanning electron microscopy (SEM) images of a) precursor disc of hydrothermally carbonized beer waste prepared by pulsed current processing at 150 °C under a uniaxial pressure of 50 MPa (HTC-D-E-150), and b) activated carbon disc prepared from HTC-D-E-150 in a flow of CO₂ at a temperature of 800 °C for 2 hours (ACD-E-150-2). Redraw from Paper III

High density is one of the requirements of ACD in certain gas storage and gas separation applications. Hence, we measured the densities of the ACDs as well as the precursor discs in the study of Paper III. These values are presented in in Table 3.1. Both the precursor and activated discs pressed at 150 °C had higher densities (1.38-1.42 g/cm³) than those pressed at 100 °C (0.69-0.83 g/cm³). This difference was related to the tar components that acted as binders in the PCP. These binders worked better when the temperature was high and, consequently led to highly dense discs at 150 °C. Others have reported that related tar compounds are mixtures of large varieties of organic condensed compounds, part of which can be removed by acetone. The same appeared to be true for the HTC biomass studied in Paper I and III. Tar compounds seem to have been fluidized for HTC-D-150 and HTC-D-E-150 and increased their densities by filling voids. Interestingly, the densities of HTC-D-100 and HTC-D-E-100 decreased after activation at 800°C; however, HTC-D-150 and HTC-D-E-150 did not change densities, basically. It seems that the dense HTC-D-150s discs hindered the volatiles to evaporate during activation at 800 °C. The density of 1.42 g/cm³ is the highest value for activated carbon discs that has been reported. Such discs could improve the volume efficiency of carbon based natural gas storage, especially if the microporous volume could further be improved.
The mechanical strength is another important parameter in many applications where ACD could be used. In Paper III, such strengths were measured using diametral compression test. It seems as the mechanical strength of the ACDs is related to the density. ACD-150-2 and ACD-E-150-2 have mechanical strength around 7 MPa. Such strong ACDs could reduce the pressure drop and have long life time in gas separation processes.

Table 3.1 The densities (g/cm$^3$) of discs of the hydrothermally carbonized beer waste (acetone extracted (HTC-D-E-X) and without extraction (HTC-D-X)), pressed at X °C, and the corresponding discs of activated carbon (ACD-E-X-2/ACD-X-2), activated at 800 °C for 2h. From Paper III

<table>
<thead>
<tr>
<th>X (°C)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.08</td>
</tr>
<tr>
<td>150</td>
<td>1.36</td>
</tr>
<tr>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td>150</td>
<td>1.39</td>
</tr>
<tr>
<td>100</td>
<td>0.83</td>
</tr>
<tr>
<td>150</td>
<td>1.38</td>
</tr>
<tr>
<td>100</td>
<td>0.69</td>
</tr>
<tr>
<td>150</td>
<td>1.42</td>
</tr>
</tbody>
</table>

The mechanical strength is another important parameter in many applications where ACD could be used. In Paper III, such strengths were measured using diametral compression test. It seems as the mechanical strength of the ACDs is related to the density. ACD-150-2 and ACD-E-150-2 have mechanical strength around 7 MPa. Such strong ACDs could reduce the pressure drop and have long life time in gas separation processes. Table 3.2 shows the corresponding mechanical strengths for the ACDs prepared from precursor discs pressed at 100 and 150 °C. (The ACDs from the HTC-BW pressed at room temperature were not strong enough to hold together, they fell apart during the activation.)

Table 3.2 Mechanical strengths of the discs of activated hydrothermally carbonized beer waste II (ACD-X-2/ACD-E-X-2). The mechanical strength was measured by diametral compression test. The test was repeated on four identical discs of activated carbon. From Paper III

<table>
<thead>
<tr>
<th>ACD-X-2</th>
<th>Mechanical strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No extraction 100 °C</td>
<td>3.2 ± 0.6</td>
</tr>
<tr>
<td>Acetone extracted (E) 100 °C</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>No extraction 150 °C</td>
<td>7.2 ± 1.0</td>
</tr>
<tr>
<td>Acetone extracted (E) 150 °C</td>
<td>6.7 ± 1.0</td>
</tr>
</tbody>
</table>

$^a$ ACD-X-2 / ACD-E-X-2 are activated carbon discs from the discs of hydrothermally carbonized beer waste extracted by acetone (E) or without extraction, pressed at X °C, activated at 800 °C for 2 h in a flow of CO$_2$.
3.2 Porosity

The porosity of ACDs was affected by both the temperature of PCP and the activation time. As shown in Table 3.3, the ACDs of Paper III had a lower surface area than the activated carbon powder in Paper I, II and IV. The surface area (calculated from N\textsubscript{2} adsorption data using BET model) of the ACDs originated from HTC-Ds pressed at different temperatures optimized with different activation times. The ACDs pressed at 25 °C and 100 °C had the maximal BET surface areas of 527 m\textsuperscript{2}/g and 567 m\textsuperscript{2}/g, when they were activated for 2 hours. However, the highest surface area (533 m\textsuperscript{2}/g) was reached with the activation time of 5 hours for the ACDs pressed at 150 °C.

Table 3.3 Specific surface area (m\textsuperscript{2}/g) of activated carbon discs prepared from hydrothermally carbonized beer waste II without acetone extraction (ACD-X-Y).\textsuperscript{a} From Paper III

<table>
<thead>
<tr>
<th>Pressing Temperature (X / °C)</th>
<th>Activation Time (Y / h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>518</td>
</tr>
<tr>
<td>100</td>
<td>514</td>
</tr>
<tr>
<td>150</td>
<td>401</td>
</tr>
</tbody>
</table>

\textsuperscript{a} “X” is the temperature of the pulsed current processing (PCP), “Y” is the activation time (h)

The evolution of porosity could also be reflected by the change of mass after activation. The HTC-Ds lost a significant amount of weight during the activation at 800 °C. Figure 3.4 from Paper III shows that the ACDs had 8-38 % of mass remaining after activation, and the mass remaining decreased when increasing the activation time. With the same activation time, those dense discs pressed at 150 °C had larger mass remaining than those pressed at lower temperatures, which is probably because the dense discs prevent the organic volatiles from evaporating during the activation.

Not only the surface areas of the ACDs were studied, but also the pore volume and pore structure. The ACDs was characterized both by N\textsubscript{2} adsorption and mercury intrusion in Paper III. N\textsubscript{2} adsorption can characterize the pores in micropore (\(<2\) nm) and mesopore (between 2 and 50 nm) region. However, mercury intrusion is good at measuring the pores with larger sizes, such as large mesopores and macropores (\(\geq50\) nm). In Table 3.4 from Paper III, both the total pore volume determined by N\textsubscript{2} adsorption and the macroporosity determined by mercury intrusion showed that under the same
activation condition the ACDs got higher pore volume when the HTC-Ds were pressed at lower temperature.

![Figure 3.4](image)

**Figure 3.4** Mass remaining for discs of hydrothermally carbonized beer waste II, without acetone extraction, after the activation in a flow of CO$_2$ at a temperature of 800 °C for different activation times (ACD-X-Y). “X” is the pressing temperature, “Y” is the activation time. Pulsed current processing was used for the discs pressed at a temperature of 100 and 150 °C. From Paper III

**Table 3.4** Total pore volume, micropore volume, and external pore volume as determined by N$_2$ adsorption analyses, and porosity as determined by mercury intrusion porosimetry, of the discs of activated carbons (ACD-X-2 / ACD-E-X-2).$^a$ From Paper III

<table>
<thead>
<tr>
<th>Discs</th>
<th>No extraction</th>
<th>Acetone extracted (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>100 °C</td>
</tr>
<tr>
<td>$V_{\text{tot}}$ (cm$^3$/g)</td>
<td>0.354</td>
<td>0.250</td>
</tr>
<tr>
<td>$V_{\text{mic}}$ (cm$^3$/g)</td>
<td>0.171</td>
<td>0.149</td>
</tr>
<tr>
<td>$V_{\text{ext}}$ (cm$^3$/g)</td>
<td>0.183</td>
<td>0.101</td>
</tr>
<tr>
<td>Macroporosity (%)</td>
<td>---</td>
<td>40.20</td>
</tr>
</tbody>
</table>

$^a$ ACD-X-2/ ACD-E-X-2 are activated carbon discs from the discs of hydrothermally carbonized beer waste II extracted by acetone (E) or without extraction, pressed at X °C, activated at 800 °C for 2 h in a flow of CO$_2$.
Figure 3.5 Macropore size distributions of discs of activated carbons (ACD-X-2/ACD-E-X-2), prepared from discs of hydrothermally carbonized beer waste II, with extraction by acetone (E) or without extraction. Activation was in a flow of CO\textsubscript{2} at 800 °C for 2 h. “X” is the pressing temperature (100 and 150 °C). From Paper III

The ACDs studied in Paper III had hierarchical porous structures, with the pore sizes covering a very large region. Figure 3.5 shows the macropore size distribution of the ACDs as determined by mercury intrusion. The pores size of the ACDs distributed from 50 nm to 10 µm. ACD-150-2s have smaller pores than the ACD-100-2s, which could be explained by that the dense nature of the ACD-150-2s restricted the evaporation of volatiles to form large pores. The existence of acetone extractable tar also affected the porosity. ACD-100-2 had the center of the peak at 400 nm, while ACD-E-100-2 had smaller pores than ACD-100-2.

N\textsubscript{2} adsorption was used to characterize the miro pores and mesopores of the ACDs in Paper III. Figure 3.6 from Paper III shows the adsorption and desorption isotherms and pore size distributions of the ACDs. From the isotherms in Figure 3.6b, we could see that when the HTC-BW was extracted by acetone, the ACD-Es had similar shapes for the isotherms. However, without such extraction, the isotherms of ACDs pressed at high temperatures were different from the one pressed at room temperature (Figure 3.6a).
Figure 3.6 $\text{N}_2$-adsorption and desorption isotherms (a, b) and pore size distributions (c, d, using DFT model; e, f, using BJH model) of discs of activated carbon prepared in a flow of CO$_2$ at 800 °C for 2 h (ACD-X-2/ACD-E-X-2), “X” is the pressing temperature (25, 100, and 150 °C). From Paper III.
Different models for analyses of gas sorption have their own domains of applicability, especially when it comes to different pore sizes. For the micropore analysis in Paper III, we used DFT and the slit model, with a medium amount of regularization during analysis. Figure 3.6c-d shows the micropore size distribution. The ACD-Es have very unique pore size, while the ACEs have multiple pore sizes in this region. The slit model is in our opinion not suitable for larger pores, hence, we relied on the more traditional BJH model for such larger mesopores. For activated carbons, mesopore sizes are usually quite broadly distributed. Both the adsorption and desorption data for the BJH model are used for the analysis, as they inform on different aspects. The desorption information are used to discuss pore blockage and cavitation. In Figure 3.6e-f, all the ACDs show the pores with the size of 4 nm in the desorption branches, but not in the adsorption branches, which could be attributed to cavitation of liquid N₂.
4 Applications of activated carbons from hydrothermally carbonized biomass

Gas-phase and liquid-phase applications as sorbents are the two major uses of activated carbons today. As mentioned in section 1.2.1, nearly 80% of the activated carbons are used for liquid-phase applications, and the gas-phase applications consume about 20% of the total production. In this thesis, we have assessed the ability for the activated carbons to separate CO$_2$ from N$_2$, and to take up the dye methylene blue (MB) from water.

4.1 CO$_2$ separation

Global warming is widely accepted being caused by the enormous emission of greenhouse gas (mainly CO$_2$) into the atmosphere in the latest decades. Carbon capture and storage (CCS) is one of the promising solutions to reduce the amount of CO$_2$ from releasing into atmosphere. Carbon dioxide in flue gas from the fossil fuel burning power plant is the main source of CO$_2$. Flue gas contains mainly CO$_2$ and N$_2$, from which CO$_2$ can be separated by using adsorbents and stored underground. There are different techniques for CO$_2$ separation using adsorbents, for example pressure swing adsorption (PSA) and temperature swing adsorption (TSA). A robust adsorbent plays a crucial role in those adsorption processes. An ideal adsorbent should have high CO$_2$ uptake capacity, high selectivity of CO$_2$/N$_2$, good cyclic performance, fast adsorption speed, low economical cost. Activated carbons have a lower price than the many other adsorbents, in general. In Paper IV, we investigated CO$_2$ separation form N$_2$ using four physically activated carbons (PAC) made from HTC grass cuttings, horse manure, beer waste I and biosludge, and one chemically activated carbon (CAC) from HTC beer waste II as the adsorbents. CO$_2$ uptake capacity, CO$_2$/N$_2$ selectivity, kinetic performance and cyclic performance are within our study.

The CO$_2$ uptake capacity is one of the most important parameters for an adsorbent for CO$_2$ separation. Without a high CO$_2$ uptake capacity, an adsorbent cannot be used in the separation process. Aspects of the CO$_2$ adsorption of five different ACs are presented in Figure 4.1a and Table 4.1. PAC grass cuttings and PAC horse manure have the highest uptake according to the isotherms in Figure 4.1a. Flue gas from power plant contains around 90% of N$_2$ and 10% of CO$_2$. Hence, the working pressure of CO$_2$ is under
around 10 kPa. As presented in Table 4.1, PAC grass cuttings and horse manure have the highest CO₂ uptake at this pressure, which are 1.45 mmol/g and 1.36 mmol/g. In Paper IV, we found that large ultramicropore volume benefits a lot in the CO₂ separation. Ultramicropores have a size smaller than 0.7 nm. As shown in Table 4.1, PAC grass cuttings and PAC horse manure have high ultramicropore volume, which results in the high CO₂ uptake capacity of them. CAC beer waste has very high surface area, but it did not show high CO₂ uptake, due to its small ultramicropore volume.

Figure 4.1 Adsorption and desorption isotherms of a) CO₂ and b) N₂ recorded at 0 °C. Physically activated carbon (PAC) from hydrothermally carbonized (HTC) biomass: grass cuttings, “■ (black)”; horse manure, “▲ (green)”; biosludge, “● (red)”; beer waste I, “▼ (blue)”. Chemically activated carbon (CAC) from HTC beer waste II, “♦ (cyan)”. From Paper IV
High CO\textsubscript{2}/N\textsubscript{2} selectivity is another requirement of a good adsorbent in CO\textsubscript{2} separation process. In an adsorption process, it is preferred to maximize the CO\textsubscript{2} adsorption and minimize the N\textsubscript{2} adsorption. A high CO\textsubscript{2} selectivity could result in pure CO\textsubscript{2}, and the CO\textsubscript{2} capacity will not be compromised by the adsorption of other gases. In Paper IV, we also recorded the N\textsubscript{2} adsorption at the same temperature of 0 °C, as shown in Figure 4.1b. The uptake of N\textsubscript{2} was much lower than that of CO\textsubscript{2} for all the samples, which could be largely attributed to the differences in the boiling point of N\textsubscript{2} (l) and the sublimation point of CO\textsubscript{2} (s). From the isotherms in Figure 4.1, we could calculate the relative adsorption of CO\textsubscript{2}-to-N\textsubscript{2} under the working pressure (10 kPa), which could give a clue to the CO\textsubscript{2}/N\textsubscript{2} selectivity in flue gas. Table 4.1 from Paper IV shows that CAC beer waste had the CO\textsubscript{2}/N\textsubscript{2} selectivity of 26.7 at 0 °C, which is the highest among the studied ACs, even though it did not have high CO\textsubscript{2} uptake. PAC horse manure also has a CO\textsubscript{2}/N\textsubscript{2} selectivity of 19.4 at 0 °C. Please, note that these selectivities were conservative estimates, in many studies one typically reports another estimation of selectivity (N(CO\textsubscript{2})/N(N\textsubscript{2}))/p(N\textsubscript{2})/p(CO\textsubscript{2}).

<table>
<thead>
<tr>
<th>Activated HTC biomass</th>
<th>Uptake of CO\textsubscript{2} (0 °C, 10 kPa) (mmol/g)</th>
<th>Apparent selectivity n(CO\textsubscript{2})/n(N\textsubscript{2})</th>
<th>Specific surface area (m\textsuperscript{2}/g)</th>
<th>Specific pore volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC\textsuperscript{b} horse manure</td>
<td>1.36</td>
<td>19.4</td>
<td>749</td>
<td>344</td>
</tr>
<tr>
<td>PAC grass cuttings</td>
<td>1.45</td>
<td>14.5</td>
<td>841</td>
<td>742</td>
</tr>
<tr>
<td>PAC beer waste</td>
<td>1.31</td>
<td>16.4</td>
<td>622</td>
<td>573</td>
</tr>
<tr>
<td>PAC biosludge</td>
<td>0.84</td>
<td>14</td>
<td>489</td>
<td>291</td>
</tr>
<tr>
<td>CAC\textsuperscript{c} beer waste</td>
<td>0.80</td>
<td>26.7</td>
<td>1073</td>
<td>238</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ultramicropore volume determined by CO\textsubscript{2} adsorption at 273 K, using DFT model; \textsuperscript{b} CAC stands for chemically activated carbon; \textsuperscript{c} PAC stands for physically activated carbon
For the application of ACs in the separation of CO\textsubscript{2} from flue gases, it is also crucial that the adsorption process can be fast. In a PSA process, there is usually very short cycle time for each adsorption. In Paper IV, we studied the uptake kinetic of CO\textsubscript{2} on the produced ACs. A small amount of CO\textsubscript{2} was released into the system, and the adsorbed amount was recorded in the function of time. As shown in Figure 4.2 from Paper IV, the AC from HTC grass cuttings had a rapid adsorption speed. Within 25s, 90\% of the released CO\textsubscript{2} molecules had already adsorbed on the AC. A rapid adsorption by the adsorbent could make the separation process more efficient.

**Figure 4.2** Uptake kinetics for CO\textsubscript{2} physically activated carbon (PAC) produced from hydrothermally carbonized (HTC) grass cuttings, recorded at 0 \degree C by subjecting the sample to a small amount of pure CO\textsubscript{2}. From Paper IV
A CO$_2$ adsorbent that can run many cycles without a drop of adsorption capacity has a long lifetime. By using an adsorbent for a long time, the CO$_2$ separation process could reduce the cost of both adsorbent and operation. In activated carbons, the loss of capacity is caused by CO$_2$ entrapment by narrow pores, or the loss of porosity. In the ACs produced from HTC biomass, there are no functional groups that can chemically adsorb CO$_2$ molecules, no extremely narrow pores were found in the ACs that can entrap CO$_2$ molecules. The porous structure of AC is also very stable. Hence, the ACs produced from HTC biomass in this thesis probably have long lifetime for CO$_2$ separation. Figure 4.3 from Paper IV shows that, after 9 cycles of CO$_2$ adsorptions performed without any heat regeneration after each adsorption, the AC from HTC grass cuttings lost only 2% of its capacity.

4.2 Water treatment

Waste water may certainly contain different contaminants, depending on the pollution source. Ionic heavy metals and organic compounds are two main types of pollutants. Heavy metal pollution typically arises from industrial sectors. Organic compounds, on the other hand arise from industrial and municipal waste, rural and urban runoff, natural decomposition of animal
and vegetable matter, and from agricultural practices. Even in drinking wa-
ter, it has been found that there are small amounts of a large number of syn-
thetic organic compounds such as phenols, pesticides, herbicides, aliphatic
and aromatic hydrocarbons, and their halogen derivatives, dyes, surfactants,
organic sulfur compounds, ethers, amines, and nitro compounds. Many
methods, including chemical and biological methods have been tried to re-
moval of organic compounds from waste water. But they have achieved lim-
ited success, due to the complex composition of the waste water. Removal of
organic compounds using activated carbons is considered to be an effective
and efficient method. Activated carbons have the advantage of high surface
area, highly porous structure, and high reactivity of the surface, and are in-
deed potential adsorbent materials for the cleaning waste water also on a
large scale.

Methylene blue dye (MB) is a common organic pollutant from textile in-
dustry, with a relatively large molecule size. MB is also used as probe mole-
cule for an adsorbent to test the capacity of removing organic compounds
from water phase. In Paper I and II, we tested two physically activated car-
bons (PAC) and one chemically activated carbon (CAC) as the adsorbents
for removing MB molecules from water. In general, the removal capacity do
not only depend on the property of the adsorbent, but also the condition of
the water phase such as the concentration of the pollutant and the pH of the
waste water. In Paper I and II, we studied the adsorption capacity of the
three ACs produced from HTC biomass, the adsorption isotherm and adsorp-
tion kinetic of CAC beer waste, and influence of pH.

Table 4.2 shows the adsorption capacity of MB on physically activated
HTC grass cuttings and horse manure, chemically activated HTC beer waste
I, and a commercial activated carbon, when the pH of the solution is 7.
When the concentration of MB is low, the ACs studied could remove almost
of the MB molecules from the solution (from 18 mg/L reduce to 0.01 mg/L).
The amounts of MB adsorbed per gram of different ACs at equilibrium ($q_e$)
were quite similar. When the concentration of MB is high, $q_e$ differed among
different ACs. CAC from HTC beer waste had a $q_e$ of 303.47 mg/L, which is
higher than the PACs, but lower than the commercial AC.
Table 4.2 The batch equilibrium methylene blue dye (MB) adsorption test (pH= 7) on physically activated HTC\(^a\) grass cuttings and horse manure, chemically activated HTC beer waste, and a commercial activated carbon. Reproduced from Paper I and II.

<table>
<thead>
<tr>
<th>AC(^b)</th>
<th>CAC(^c) from HTC</th>
<th>PAC(^d) from HTC</th>
<th>PAC(^d) from HTC</th>
<th>Commercial activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_0) (mg/L)</td>
<td>18.23</td>
<td>121.33</td>
<td>18.23</td>
<td>110.39</td>
</tr>
<tr>
<td>C(_e) (mg/L)</td>
<td>0.01</td>
<td>54.56</td>
<td>0.01</td>
<td>55.50</td>
</tr>
<tr>
<td>q(_e) (mg/g)</td>
<td>80.96</td>
<td>303.47</td>
<td>80.89</td>
<td>267.77</td>
</tr>
</tbody>
</table>

\(^a\) HTC stands for hydrothermally carbonized; \(^b\) AC stands for activated carbon; \(^c\) CAC stands for chemically activated carbon; \(^d\) PAC stands for physically activated carbon.

\(C_0\) is initial concentration of MB solution, \(C_e\) is the equilibrium concentration of MB solutions in mg/L, \(q_e\) is the amount of MB adsorbed per gram of adsorbent at equilibrium.

The adsorption isotherm could help us understand how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption reaches an equilibrium state. It can provide qualitative information on the nature of the solute-surface interaction at a certain temperature. There are various models describing the adsorption results, for example Langmuir model, Freundlich model, Temkin model. Different models are based on different assumptions.

Langmuir model assumes that the adsorption happens on a homogenous surface, and is monolayer adsorption. A linear form of the Langmuir model is expressed by: \(^{118}\)

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
\]  

(3)

where \(C_e\) is the concentration at equilibrium, \(q_e\) is the amount of dye adsorbed by the adsorbent, \(q_m\) is the maximum adsorption capacity associated with complete monolayer coverage, and \(K_L\) is the equilibrium constant of adsorption.

Freundlich model is derived on the assumption that the adsorption is on a heterogeneous surface, with a formation of a multilayer. A linear version of the Freundlich isotherm is: \(^{119}\)

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F
\]  

(4)
where $K_F$ and $n$ are constants, $q_e$ is the uptake on the carbon, $C_e$ is the equilibrium concentration in the aqueous phase.

Temkin model assumes the heat of adsorption of all the molecules in the layer decrease linearly with coverage, which shows the effects of some indirect adsorbate-adsorbent interactions. A linear version of the Temkin equation can be expressed by:

$$q_e = B \ln A + B \ln C_e$$  \hspace{1cm} (5)

where $B = \frac{RT}{b}$, $b$ is the Temkin constant related to heat of sorption, $A$ is the Temkin isotherm constant, $R$ is the gas constant, and $T$ is the absolute temperature (K).

Figure 4.4 from Paper II shows the experimental result of the MB adsorption equilibrium points on the CAC from HTC beer waste, obtained at 25 °C and regression analysis was performed with different models. The adsorption result had the lowest summed squared deviations with the Langmuir model, which indicates that the adsorption of MB on the CAC occurred as a homogenous monolayer.

**Figure 4.4** Adsorbed amounts of methylene blue (MB) (■) onto chemically activated carbon prepared from hydrothermally carbonized beer waste II. The pH value of the MB solution is 7. Regression lines to the Langmuir (solid line), Freundlich (dashed line), and Temkin (dotted line) models are presented. From Paper II
Figure 4.5 Adsorbed amount of methylene blue (MB) on the activated carbon as a function of time. The chemically activated carbon was prepared from hydrothermally carbonized beer waste II. (Initial concentration of MB = 400 mg/L, pH=7). From Paper II

The adsorption rate of an adsorbate on an adsorbent is important for the efficiency of the adsorption process. Figure 4.5 from Paper II shows the adsorption kinetic of MB by CAC from HTC beer waste. From the kinetic curve, the adsorption equilibrium appeared in around 2 hours, and 90% of the MB was adsorbed within 1 hour.
Adsorption on AC in aqueous phase is affected by the pH condition of the aqueous solution. The surface charge of an adsorbent could be changed by changing the pH value of a solution, which influences the adsorption of a certain adsorbate molecule. Figure 4.6 from Paper II shows that the uptake of MB on the CAC is higher when the pH value of the solution is higher than 7, which is because the MB adsorption capacity is related to the zero charge point of the AC ($\text{pH}_{\text{PZC}}$). When $\text{pH} < \text{pH}_{\text{PZC}}$, $\text{H}^+$ in the solution will compete with MB molecule to be adsorbed on the AC, reducing the MB adsorption capacity. When $\text{pH} > \text{pH}_{\text{PZC}}$, the surface of the AC is negatively charged, which could increase the adsorption of the positively charged MB molecule.
Conclusions

Four different HTC biomass (horse manure, grass cuttings, biosludge, beer waste) were investigated and successfully refined into activated carbon related materials in the papers of this thesis. The resulting activated carbons showed good potential as adsorbents for $\text{CO}_2$ and methylene blue.

The HTC biomass were characterized by different techniques and found to be relatively well carbonized during the hydrothermal treatment. The cells and fiber structure kept the original shape and some carbon spherical particles formed during hydrothermal treatment. The HTC biomass contained around 20% of acetone extractable tar content, which influenced the properties of the activated carbons produced.

Powdered activated carbons were produced from HTC biomass by both physical activation using $\text{CO}_2$ and chemical activation using $\text{H}_3\text{PO}_4$. In physical activation, the better carbonized biomass as the HTC grass cuttings and HTC beer waste were easily activated into microporous carbons. The less carbonized biomass such as HTC horse manure and HTC biosludge tended to also get large pores during activation. Long activation time led to high porosity and large flow rate of $\text{CO}_2$ led to low porosity. In chemical activation using $\text{H}_3\text{PO}_4$, HTC beer waste was activated into activated carbons with large pores. Full factorial design helped us to find out that the ratio of $\text{H}_3\text{PO}_4$ to HTC carbon was the most important parameter for such chemical activation. A large $\text{H}_3\text{PO}_4$/carbon ratio resulted in large pores. Physical activation by $\text{CO}_2$ did not change the shape of the HTC biomass; however, chemical activation by $\text{H}_3\text{PO}_4$ changed the microstructure of HTC biomass significantly. Moreover, chemical activation created larger porosity than did physical activation.

Iron oxide nanoparticles were embedded in the activated carbons when the iron containing precursor was physically activated in $\text{CO}_2$. The iron was introduced into the precursor during the hydrothermal treatment, and got crystallized into $\text{Fe}_3\text{O}_4$ nano particles. The porosity developed during activation in $\text{CO}_2$. The resulted iron oxide and activated carbon composite showed both superparamagnetism and ferrimagnetism, which was caused by the iron oxide nano crystals with sizes of 20 - 40 nm. Electro-tomography showed that the iron oxide nano particles were well embedded in the studied activated carbon particle. The activated carbon with embedded iron oxide nanoparticles could be easily separated from a water suspension by a magnet. We
assume the magnetic composites with high surface area would be beneficial to several applications in liquid phase, such as water treatment.

Strong and dense activated carbon discs were prepared from HTC beer waste by pulsed current processing and physical activation using CO$_2$. The tar compound in the HTC beer waste worked as a binder and filled the voids between the particles. The density of the disc is as high as 1.4 g/cm$^3$, mechanical strength as high as 7.2 MPa. Such strong and dense activated carbon discs can improve the volume efficiency and have long life time in gas adsorption such as methane storage.

The powdered activated carbons prepared from HTC biomass showed high CO$_2$ uptake capacity and good CO$_2$/N$_2$ selectivity. It could be used for many cycles with very small drop of adsorption capacity. The activated carbons also showed good performance in methylene blue adsorption. The adsorption isotherm fit the Langmuir model well, which suggest a monolayer adsorption of MB on the activated carbon made from HTC beer waste.

There is a lot of work I have not done due to the limited time in my PhD study. Future research could be on preparing activated carbon discs by chemical activation using KOH and H$_3$PO$_4$. The physical activation procedure we applied did not achieve very high porosity of the activated carbon discs. Chemical activation is supposed to make higher surface area and porosity of activated carbons than the physical activation, which should produce activated carbon discs with higher porosity. A study on the gas adsorption application, such as methane storage, should be done on the activated carbon discs we produced. The high density of the discs will improve the volume efficiency; however, the storage capacity at increased pressures should be studied.

There are many other applications of the activated carbons and the composites produced from HTC biomass that need to be investigated; for example, adsorption of heavy metals in water as well as their use as electrodes in electrochemistry and electrotechnology.
Acknowledgement

This thesis work could not have done without the help and support from many people. I would like to take this chance to express my appreciation to them.

My sincere gratitude to my supervisor Niklas*. Thank you for providing me the opportunity to work on this project. You have been a tremendous mentor for me. I would like to thank you for encouraging me to grow as a research scientist. Your advice on both research as well as on my career have been priceless. My thanks to Prof. Lennart Bergström as my co-supervisor. Your supervision and guidance have been invaluable for my work.

I owe thanks to my coworkers. Eva*, you gave me a lot of support since the beginning of this project, and I learned a lot from you. Thanks! Malte, thanks for providing the samples, you gave me another perspective of research. Yifeng, you did a great job in TEM, I liked the video of tomography very much. Neda, thanks for the contribution towards the paper, the carbon discs you produced were really strong. Adrien, you did good work as a summer student, and contributed to the paper.

I am grateful to the help from colleagues during the thesis work. Zoltán* and Ocean*, thanks for the help in adsorption measurement and a lot of discussions. Zoltán*, for the help in the measurements of mercury intrusion. Ocean*, for the help in atomic absorption spectrophotometry. German, for the help in the measurement of magnetism. Erik, for the help in the calculation of magnetism.

To my group members: Ocean*, Zoltán*, Mikaela and Orlando, you have been nice office roommates, we had lots of nice chat and badminton time. Ocean*, thanks for organizing a lot of after-work activities. It is good to see that your mandarin is improving. Zoltán* and your wife Vicky, I like the Marhapörkölt bográcsban you made, and also the moment when Zoltán* started playing air guitar. Baroz, Qingling, Chao*, Fredrik and Przemyslaw, Lihong, you made a warm atmosphere in the group, I really enjoy. Qingling, I still remember the first day when I arrived in Stockholm and you met me at the central station, thanks!

*Special thanks to those people for reading and improving my thesis.
I also owe a huge vote of thanks to all the administrative and technical personal. Gunnar, thanks for taking care of PhD students like me. It was nice to visit India with you. Ann-Britt, I really appreciate that you arranged housing for me so that I did not sleep in the street during the first cold nights in Stockholm. Daniel, Anita, Karin, Pia, Hanna, Tatiana, Ann, Anna-Karin, for a lot of practical things. Per, Hans-Erik, in the workshop, you are magic fellows. You are always able to solve the problems for my experimental setup. Per, thanks for the reactor you made. It was fantastically made. Kjell, I am thankful to the training and help for operating the SEM. Hillevi, for the help of literature searching.

To the other colleagues at MMK. Special thanks to Xiaodong, thanks for introducing me to this PhD position. Zhijian (James), Sven, Mats, Junliang, Feifei, Wei Wan, Su Jie, Jianfeng, Shiliang, Bernd, Zou Ji, Shichao, Chen Hong, Han Guang, Zhong Yuan, Guo Peng, Yunxiang, Shen Yang, Bertrand, Erik, Changhong, Michael, Valentina, Kamran, Li Duan, Arto, Christina, Yulia, Korneliya, Amber, Jon, Cheuk-Wai, Liang jie, Zhang Yi, Justin, Daniel, Yanhang, Yunchen, Yuan Ning, Cecilia, Daqing, Yin Ge, Chen Qiang. You made this department an enjoyable place to work.

My gratitude to Prof. Ruifeng Li and Prof. Jinghong Ma in Taiyuan University of Technology, thanks for introducing me into the world of porous material.

Getting through my dissertation required more than academic support, and I have many, many people to thank for helping me beyond academic work and making my life more fun.

Football group in the department: Zoltán, German, Leifeng, Haoquan, Chao, Dickson, Arnau, Farid, Guido, Leifeng, Julien, Ken, Petr, Changjiu, Junzhong, Fabian, and many other guys in the football field. We had good time on Wednesdays. I always felt fresh when I got back to work after the football games.


Lennart Kjellander, thanks for helping me with my life in Sweden, and listening to the stories of my work and life. One loyal friend is worth ten thousand relatives.
I would like to thank the CSC scholarship from Chinese government for supporting my study, and the staff from the Education Section in Chinese Embassy: Mr. Dou Chunxiang, Mr. Zhang Ning, Mr. Wang Wei, Mr. Zhang Hong, thanks for a lot of assistance and taking care of my studies in Sweden.

A special thanks to my family. Words cannot express how grateful I am to my mother and father for all of the sacrifices that you’ve made on my behalf. Thank you for your endless love and support. To my uncle and aunt, I am thankful to your encouragement and your support for so many years.

Wenming Hao
Stockholm, October 2014
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