

Alternative material use of fast pyrolysis char and its impact on the bioliq® process chain

Muhammad Mujtaba Abbas

Thesis to obtain the Master of Science Degree in

Energy Engineering and Management

Supervisors: Prof. Filipe José da Cunha Monteiro Gama Freire

Prof. Jörg Sauer

Examination Committee

Chairperson: Prof. Francisco Manuel da Silva Lemos

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Declaration

I **Muhammad Mujtaba Abbas**, student at **Instituto Superior Técnico** No. **79797**, author of dissertation for the degree of **Master of Science Degree in Energy Management and Engineering**, with title **Alternative material use of fast pyrolysis char and its impact on the bioliq® process chain** impart the Instituto Superior Técnico a perpetual, but not exclusive to use this thesis for the purpose teaching or research and authorize him to enter it and your extended abstract in pdf format on your page the internet, with address www.tecnico.ulisboa.pt to allow its dissemination to all who access that page, and with the same purpose of disclosure to respond favourably to requests from institutions education or research and documentation centres or libraries, sending them those same files pdf format, but making an explicit statement, whether on their website or when the aforementioned shipment the obligation of those who go to that so my dissertation and their extended abstract to safeguard my copyright in these documents, which I conferred by the Code of Copyright and Related Right.

Lisbon, the 23rd of September 2014

Muhammad Mujtaba Abbas

Abstract

Biochar is a significant by-product of bioliq® fast pyrolysis plant concept developed by KIT, Germany amounting up to 28 % of reaction products. Given its quantity, it would be a good prospect to find an alternative use of biochar on industrial scale. After exploring a number of prospective solutions and applications, activated carbon has been chosen as the focus of this work. In this work, biomass based precursor (biochar) was demineralized and further used for production of activated carbon by using two different methods of activation: physical and chemical activation in which steam and potassium hydroxide were used, respectively. Activated carbon was analysed to check its physical and chemical characteristics by using experimental methods such as N₂ adsorption, iodine adsorption and scanning electron microscopy. The results indicated that biochar from wheat straw is promising for this purpose. The effective Brunauer-Emmett-Teller (BET) surface and iodine number were determined to be 2900 m²/g and 2567 mg/g, respectively, in case of chemical activated carbon. The bulk densities of powdered chemical activated carbon and pelleted physical activated carbons are 0.128 t/m³ and 0.239 t/m³ respectively. In this work, the proposed solution for integration of activation into fast pyrolysis process on industrial scale. The utilization of waste thermal energy of flue gas to dry biomass and the the usage of waste thermal energy from hot char to produce steam for physical activation process. Physical activation process will be used for production of pelleted activated carbon.

Keywords: Biochar, demineralization, activated carbon, chemical activation, physical activation, and adsorption

Abstrato

Biochar é um dos mais importantes sub-produtos das unidades bioliq® de pirólise rápida desenvolvidas pelo KIT, chegando a atingir 28 %. Dada a elevada quantidade produzida será interessante encontrar uma utilização alternativa para este produto à escala industrial. Após a exploração de um certo número de possíveis soluções e aplicações, foi escolhida a produção de carvão ativado como foco para este trabalho. Assim, os precursores baseados em biomassa foram desmineralizados e posteriormente utilizados para a produção de carvões ativados por dois métodos de ativação: física e química, respetivamente com vapor e com hidróxido de potássio. As propriedades físico-químicas dos carvões foram analisadas por métodos experimentais como a adsorção de N₂, adsorção de iodo e a microscopia eletrónica de varrimento. Os resultados indicaram que o biochar produzido a partir de palha é promissor. A maior área BET e número de iodo que foram obtidos foram 2900 m²/g e 2567 mg/g, respetivamente, para o caso do carvão ativado quimicamente. As densidades a granel do carvão ativado quimicamente em pó e em pellets foram de 0.128 t/m³ e 0.239 t/m³ respetivamente. Neste trabalho foi proposta uma solução para a integração da ativação numa unidade industrial de pirólise rápida que inclui a utilização de energia térmica residual dos gases de escape para secar a biomassa e a utilização do conteúdo térmico do carvão quente produzido para produzir vapor para o processo de ativação física. O processo de ativação física pode ser utilizado para produção de carvão ativado em pellets.

Palavras chave: biochar, desmineralização, carvão activado, activação química, física ativação, KOH, a adsorção

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Abbreviations and Nomenclature

Abbreviation	Definition
AC	Activated Carbon
AWWA	American Water Works Association
ASTM	American Society for Testing and Materials
ANG	Adsorbed Natural Gas
APac	After Physical activated carbon
BET	Brunauer, Emmett and Teller Surface Area
BPac	Before Physical activated carbon
Cac	Chemical activated carbon
DOC	Dissolved Organic Carbon
Dbc	Deminerlized biochar
db	Dry basis
daf	Dry ash free
EDX	Energy Dispersive X-ray analysis
FE-SEM	Field Emission Scanning electron Microscope
GAC	Granular Activated Carbon
HHV	Higher Heating Value
KIT	Karlsruhe Institute of Technology
MCL	Maximum Contaminant Level
MJ	Mega Joule
PAC	Powdered Activated carbon
PDU	Process Demonstration Unit
Phac	Physical activated carbon
Rbc	Raw biochar
SSDs	Superheated Steam dryers
SEM	Scanning Electron Microscopy
TGA	Thermo Gravimetric Analysis

Abbreviation	Definition
TEM	Transmission Electron Microscopy
USEPA	US Environmental Protection Agency
UNICEF	United Nations International Children's Emergency Fund
WS	Wheat Straw
WHO	World Health Organization
wt. %	Weigh percentage

Chemical Formulas	Definition
AgNO ₃	Silver nitrate
CO ₂	Carbon dioxide
H ₃ PO ₄	Phosphoric acid
HCl	Hydrochloric acid
H ₂ SO ₄	Sulphuric acid
H ₂ S	Hydrogen sulphide
KOH	Potassium hydroxide
K ₂ CO ₃	Potassium carbonate
N ₂	Nitrogen gas
NaOH	Sodium hydroxide
SO ₂	Sulphur dioxide
ZnCl ₂	Zinc chloride

1 Introduction

In recent years, Countries around the world showed interest and increasing focus on cleaner technologies to move away from fossil fuel derived power. Germany also signed the Kyoto Protocol and they are trying to achieve targets with clear intentions to diversify the country's power generation and automotive industry by including biomass as a renewable resource for electricity generation or as a fuel alternative in the automotive industry. Woody biomass and associated forestry residues in particular could potentially be used as such a renewable resource. Wheat crop can be cultivated in almost every part of the world, in Germany after harvesting wheat crop, wheat straw is left as a residual or waste material, in world-wide, mostly farmers burnt it on the field and some farmers just sold it as a feedstock for animals. By burning wheat straw on field emissions are emitted into environment. Burning residue on the field is not an eco-friendly because we are adding emissions directly to atmosphere by burning on field. We can do pyrolysis on it in a reactor and produce different useful products like tar, gas and bio char. Biochar is a fine-grained and highly porous charcoal made from renewable biological material (biomass) by using Thermal process (pyrolysis), its high in carbon content. The bioliq® concept developed by KIT (Karlsruhe institute of Technology) is a three step conversion process for the production of 2nd generation drop-in biofuels from biomass waste such as e.g. wheat straw. First, biomass is converted by fast pyrolysis to yield energy dense bio-synchrude®, a mixture of bio-oil and char. This slurry is fed to gasifier for production of syngas through Fischer-Tropsch synthesis.

The aim of this work is to investigate the alternative use of biochar on industrial scale application. Because now-a-days within bioliq® the three products tar condensate, fraction char and aqueous condensate are mixed and gasified together to recover most of the energy [1]. There is also an alternative way to use these products separately on Industrial scale, which will be more beneficial for plant economy. There are a lot of applications of biochar which are discussed in upcoming chapter but most promising ones are Biochar as a soil conditioner or as a fertilizer and activated carbon used as adsorbent material in aqueous and gas phase applications. In this work biochar used as precursor for production of activated carbon.

1.1 Research objective

The objective of this study are as follows:

- a) To investigate the alternative uses of biochar in industrial scale and see their economic feasibilities.
- b) To reduce the ash content of biochar by doing demineralization of biochar.
- c) To prepare activated carbon from wheat straw biochar by using chemical and physical activation.
- d) To investigate the maximum BET surface by varying different optimum parameters.
- e) To investigate the adsorption capacity of activated carbon by doing aqueous and gas adsorption experiments.
- f) To investigate the activated carbon through water treatment (DOC) test.

- g) To investigate the impact of application on existing process chain.

1.2 Scope of research

The scope of this study are as follows:

- a) BET surface area and pore size distribution state the usage of activated carbon in respective application.
- b) Iodine no and BET surface area are best sources to compare it with industrial activated carbons.
- c) Activated carbon, which is prepared from wheat straw biochar has been used as an adsorbent material for removal of contaminants from drinking water or waste water.
- d) New implications in existing design bioliq plant process chain will make it economically feasible and technically suitable for large scale production.

1.3 Thesis layout

This thesis has six chapters. Chapter 1 includes a background of study, research objective, scope and significance of study. Chapter 2 is about literature review, which includes pyrolysis process for production of biochar, factors affecting the pyrolysis process, applications of biochar, activated carbon, gas phase and liquid phase applications, worldwide drinking water problem and in the end literature review on production of activated carbon from different methods and materials. Chapter 3, the methodology develops the steps needed for demineralization of biochar, chemical and physical activation of biochar, characterization of activated carbon, iodine number and N₂ adsorption for BET surface area. SEM for analysing the morphology of activated carbon. Chapter 4 will be discussing about the results obtained from experiments. It includes demineralization of biochar, chemical activation of biochar, physical activation of biochar, N₂ adsorption and iodine adsorption results and SEM images. Chapter 5 is about optimization of bioliq fast pyrolysis plant. One suggestion is proposed for optimizing of bioliq plant by utilizing exhaust waste heat thermal energy for drying of biomass and waste heat recovery from hot char to produce steam for physical activation process. Chapter 6 will provide concluding remarks of this research and also provide recommendation for further research to achieve optimum operating conditions for activation and other processes.

2 Literature review on production and potential uses of biochar

This chapter provides a review of fast and slow pyrolysis, factors affecting the product yields of slow and fast pyrolysis, biochar technology and biochar applications. In addition it describes the production methods of activated carbon, gas and liquid phase applications of activated carbon and worldwide drinking water problem issues. The last part of this chapter discusses about literature review on previous research work by different researchers.

In photosynthesis, plants and trees use CO₂ combined with water and sunlight to produce sugar. By this process, we can store CO₂ in plants in a natural way. Until a plant or tree dies, it will continue to use and store CO₂ as a fuel for growth. Upon death, plant or tree will start to decompose in air as microbes and fungi begin to break it down. This process releases CO₂ back into the atmosphere within a few years, so it only acts as a carbon sink for a relatively short time.[2]

2.1 Pyrolysis

Pyrolysis defined as the thermal decomposition of organic material through the application of heat without the addition of extra air or oxygen. Some authors define it as the thermal decomposition “in the absence of oxygen” [3].

2.1.1 Fast pyrolysis

Overview

In literature, it is mentioned that the overall fast pyrolysis reaction have very short reaction times of up to 2 s [4],[5]. After volatilization and secondary cracking of product vapours, vapours and solid product separated through cyclone before rapid quenching of vapours into a liquid product called bio-oil. Basically short hot vapour residence times of typically less than 2 s is to minimize the secondary reaction [5]. The rate of thermal decomposition depends on biomass particle size and type as well as the heating rate, final temperature, reactor configuration and presence of impurities. Major products of pyrolysis are liquid, char and gas.

Reactor configuration

Reactor configuration is an important parameter and it has received a lot of attention in literature and reviewed by various authors [4],[5],[6],[7]. The fluidized bed reactor is the most common fast pyrolysis reactor used in both industrial scale and for research purposes, due to better heat transfer and mixing conditions that can be achieved. It is also most convenient for scaling-up. Other reactor configurations can also be used for different purposes including transported bed, circulating fluidised bed, rotating cone, ablative, screw and microwave reactors [5]. Every reactor has its own advantages and disadvantages, but they should adhere to the requirements set for fast pyrolysis:

- Moderate reactor temperature (typically around 500 °C)
- Vapour residence time below 2 seconds.
- High particle heating rates ($> 10^2$ K/min)
- Short solid residence time
- Rapid quenching of product vapours to yield bio-oil.

Reactor temperature

Temperature is one of the key variables affecting pyrolysis reaction. Fast pyrolysis is mostly conducted in the temperature range of between 400 °C – 600 °C [5],[6],[8] where the liquid phase comes out as a main product yielding between 60 wt. % to 75 wt. % on a dry basis depending on the feedstock used. In the literature from kinetic data, thermal degradation of hemicellulose and cellulose may start at lower temperatures. At higher temperature (> 600 °C) the thermal decomposition of biomass continues to such extent that the main products at the end are incondensable gas and char [9]. Reactor temperature is not only affecting the yield of products but also the quality of products like (porosity and ash content of char) [10].

Vapour residence time

Vapour residence time plays an important role in the case of thermal degradation of product vapours during pyrolysis. Residence time below 2 seconds limits the secondary reaction of vapour [8] and is a typical criterion for fast pyrolysis process where the main product focus lies in the liquid component [7]. When char is desired as the main product then long residence times are employed [4]. The char produced during pyrolysis has catalytic effects on vapour phase condensation reactions [5] and should have separated immediately from vapour phase after formation.

Particle size and heating rate

The particle-heating rate is a dynamic parameter, it can be manipulated during pyrolysis by varying the size of biomass feed, heat transfer medium used to heat up particle or by alternating reactor temperature and by mixing conditions (with heating medium). The heating rates in case of fast pyrolysis are higher than as compared to slow pyrolysis and usually estimated based on reactor temperature, particle size and residence time of particle within the reactor. As mentioned residence time for fast pyrolysis is less than 2 seconds to obtain a high liquid product yield and limit secondary cracking; therefore, the heating rate must be as high as possible.

Van de Velden et al. [8] showed that the heating rate of particle depends on the Biot number of particles; biomass particle size theoretically should not exceed 200 μm . To obtain a fast heating of whole particle, it is appropriate to use small particles (e.g. < 200 μm for saw dust). On a laboratory scale, particle size is used in the range of 100 μm to 3000 μm [5]. It was analyzed that by increasing the particle size between 300 μm to 1500 μm the yield of bio oil will decrease, but further increase in particle size will not affect the yield of bio-oil [11]. It was showed that particle size used affects the yield of pyrolytic water

formed during fast pyrolysis where larger particles tend to increase the yield of pyrolytic water yield [12],[13].

Studies also show that the char produced under high heating rates are more reactive to oxygen and have larger surface areas and more reactive sites [14],[15].

2.1.2 Slow pyrolysis

Overview

Slow pyrolysis has been used mostly for the production of charcoal in past years and therefore it is referred as carbonization or conventional pyrolysis [4],[6]. Mostly in the production of charcoal, a limited amount of oxygen is used, but slow pyrolysis takes place in the complete absence of oxygen, the main product at the end is usually char. Packed bed reactors are used for slow pyrolysis experimental work and run under nitrogen or other inert atmosphere [14],[16],[17]. Slow heating rates of typically less than 25 °C/min and long vapour residence time, typically a few seconds or minutes are preferred to slow pyrolysis to produce a high yield char product.

Reaction temperature

Temperature is a key factor affecting the product yields of reaction. Different temperatures investigated in literature for slow pyrolysis ranging from 300 °C to 1000 °C [10],[14],[18],[16],[19]. Studies show that reaction temperatures used in literature for slow pyrolysis have a significant effect on product yield of bio-char. The char yield decreases with increasing in reaction temperature (300 °C to 500 °C) due to the degradation of cellulose to a more stable an hydrocellulose, which gives higher biochar yield is dominant reaction at temperature less than 575 K and at temperature greater than 575 K, cellulose depolymerizes, producing volatiles [20]. Bio-oil yield first increases and then decreases above 450 °C in the same temperature range [18],[16].

In different studies, a decrease in char yield was observed with increasing reaction temperature, but it showed that quality of char product improved by increasing the reaction temperature, especially with regard to BET surface area, calorific value and fixed carbon content of char [18],[14],[21]. The focus of slow pyrolysis is usually the production and characterization of solid product (char) but it was shown that reaction temperature also influences the chemical composition of bio-oil. A study by [10] showed that the formation of acidic compounds decreased with increasing reaction temperature while production of phenolic and neutral compounds increased with increasing temperature (350 to 550 °C).

Heating rate

An observation was made by Kumar et al. [22] for acacia nilotica and eucalyptus globulus, where higher heating rates resulted in increased bio-oil yield and decreased in char yield. It was also reported by a study on slow pyrolysis of sugarcane bagasse [18], that the heating rate was insignificant towards liquid yield and various other properties like calorific value, BET surface area of char and water content of bio-oil.

Hold time

During a slow pyrolysis experiment, the biomass is heated until the desired (maximum) temperature is reached. Once it reached to desired temperature, then reactor and its contents allowed to stay at that temperature for specific hold time before allowing the system to cool down. In a study on Thuja (*Tetraclinis articulata*) wood samples by [23] it was shown that under isothermal pyrolysis conditions, hold time had a significant effect on char yield only up to 120 minutes. After 120 minutes char yield increased marginally for isotherms investigated (330,360,390 and 420 °C).

Table 2.1: Comparison of product yields for Fast and slow pyrolysis (wt. % dry) as reviewed by [4]

Process Parameters		Liquid yield	Char yield	Gas yield
Fast Pyrolysis	Short residence time & High heating rate	75	12	13
Slow Pyrolysis	Long residence time & Low heating rate	30	35	35

2.1.3 Chemical composition influencing on pyrolysis

Structure and composition of lignocellulosic biomass

Lignocellulosic biomass is a composite material in which the main constituents cellulose (~ 50 wt. % (dry basis)), hemicellulose (~ 25 wt. % (db)) and lignin (~ 25 wt. % (db)) are linked together to obtain structural strength in combination with flexibility. In addition, biomass also contains water and minor amounts of extractives and inorganic compounds (ash).

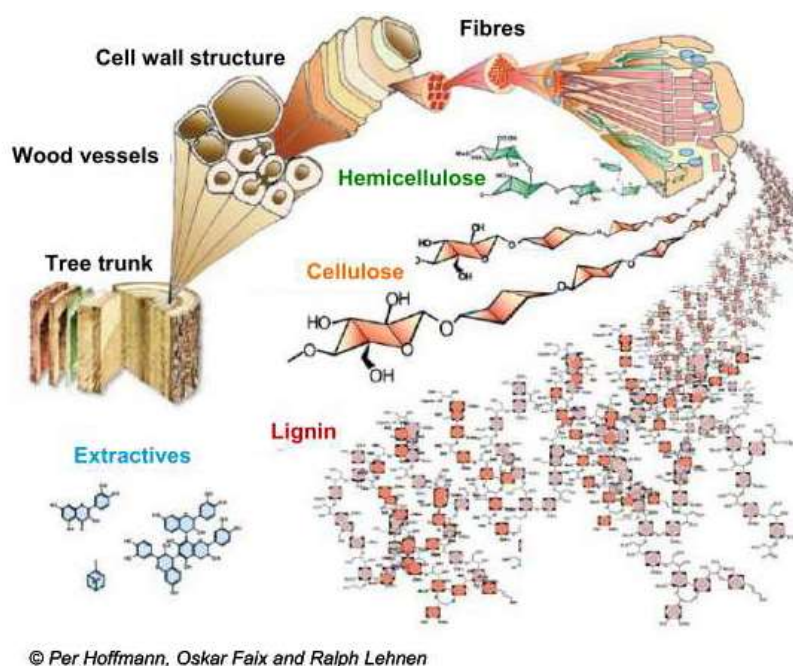


Figure 2.1: Composition of wood, illustrating the structure of lignocellulose biomass

A study by [24] investigated the effects of the lignocellulosic composition of different types of biomass using a TGA. Two reaction phases were observed which were attributed towards volatilization of cellulose (fast) and lignin (slow) components of biomass. It was reported that as the cellulosic content of biomass increased, the liquid yield also increased and the reaction rate increased while the opposite was observed for lignin. Alkali and alkaline earth metals were found to increase the char yield under gasification.

Table 2.2: Typical values for the composition of biomass [25]

	Cellulose	Hemicellulose	Lignin
Soft wood	45	25	30
Hard wood	42	38	20
Straw stalks	40	45	15

2.2 Bio char technology

The term biochar known as charcoal is a carbon rich product that results from the thermal treatment of natural organic feedstock (crop waste, wood chips, municipal waste or manure) in an oxygen-limited environment [25]. The process named as pyrolysis in which Bioenergy also produced [4] which is already explained in detail **Pyrolysis**. Due to its aromatic structure biochar is chemically and biologically more stable than carbon(C) source from which it produced. This makes bio-char difficult to breakdown and scientists have shown that the mean residence time of stable fraction is estimated to range from several hundreds to few thousands of years [26]. Biochar is not a single material, its characteristics vary depending upon biomass and production method. Most of bio chars have small labile fraction but in addition to much larger stable fraction [27].

Biochar concept

In the natural carbon cycle, plant decomposes rapidly after the plant dies. With this, process CO₂ is released back to atmosphere to neutral the overall carbon cycle. Biochar technology is designed to uncouple the natural carbon cycle. Instead of allowing plant residue to decompose, biochar technology sequesters carbon in a stable form and resistant to decomposition. Biochar technology slows the return of CO₂ from soil to the atmosphere, stores it in biochar and making it negative carbon cycle [28].

Importance of biochar

The biochar looks impressive, when you see how much and how quickly CO₂ actually released in to the atmosphere by plants, animals and humans. CO₂ released by human activities makes up 70% of greenhouse gas emissions. Currently, the world could annually harvest more than 6.5 GtC y⁻¹ of biomass. This amount of biomass can be converted to 3.25 GtC y⁻¹ (biochar) and biofuels with heating value equivalent to that of 6500 million barrels of crude oil. Biochar is not digestible to microorganisms and can be used in soil amendment as permanent carbon sequestration agent in soils for thousands of years. By storing 3.25 GtC y⁻¹ of biochar, which means capturing of 11.9 Gt of CO₂ per year in to soils or underground reservoirs. It would offset the world's 8.67 GtC y⁻¹ of fossil fuel CO₂ emissions by about

38%. The worldwide maximum capacity of storing biochar in agricultural soils (1411 million hectares) is estimated to about 428 GtC [29]. Aside from lowering individual energy use and producing electricity from green or renewable energy, efforts should be taken to decrease the amount of CO₂ in the atmosphere. It needs to be trapped, there are few technologies to trap CO₂, biochar technology is among them [2].

During pyrolysis, approx. 50% of the carbon locked in the biomass is converted into biochar and the rest is converted to syngas, which can captured and used to produce heat and power. The biochar produced is chemically and biologically more stable than the original carbon. It can remain stable in soil for hundreds of thousands of years [26],[27],[29] . Therefore, biochar has potential to play an important role as a long-term carbon sink, sequestering the carbon from the atmosphere and partially offsetting greenhouse gas emissions produced by burning fossil fuels [2].

Biochar has valuable property of high stability in the environment relative to other types of organic C-substances. Biochar had estimated for a mean residence time of 10,000 years in soils [30]. The biochar stability is closely related to the temperature of pyrolysis [25].

2.2.1 Applications of biochar

There are a lot of biochar applications depending on characteristics of biochar. Biochar can be used in animal farming, composting, building sector, textile, cosmetics, paints and energy production without any improvement in physical or chemical property. But few applications need specific improvements in physical and chemical properties of biochar for respective applications includes soil conditioner, decontamination, biogas production and treatment of water.

Key possible applications of char are solid fuels, activated carbon and biochar for soil amendment [31]. Studies have shown that high heating rates favour pore formation in pyrolysis chars and under the correct operating conditions char may be produced that exhibit favourable BET surface area, good adsorption properties and high reactivity for combustion [14],[19],[32].

The cascaded use of biochar in animal farming

We can use biochar as silage agent, feed additive / supplement, litter additive, slurry treatment, manure composting & water treatment in fish farming.

According to research, at present 90 % of the biochar used in Europe goes into animal farming [33] . Different in its application to fields, a farmer will notice its effects within few days. Whether used in feeding, litter or in slurry treatment, so that the farming field can have less odour. Used as a feed supplement, the incidence of diarrhea rapidly decreases, feed intake is improved, allergies disappear and animal become calmer [34].

Schmidt proposed, it can be used as a silage, charging biochar with malolactic bacteria and add 1 % biochar will reduce mycotoxins and butyric acid & adsorption of pesticides and herbicides. Used as a feed additive, 1 % biochar for feeding carbon-feed will increase energy efficiency of digestion,

decreases milk cells, adsorption of gram-positive bacteria (botulism), pesticides and herbicides, can be used for reducing odours, fixation of nutrients and improvement of barn climate [35].

The red colobus monkeys, *procolobus kirkii* eat charcoal [36]. These endangered animals have specially adapted stomachs which enable them to feed principally on leaves. They eat charcoals from burnt tree stumps and branches to detoxify poisons (mainly phenolic) obtained from their leafy diet and convert them into proteins.

Schmidt proposed, it can be used as a litter additive, 5 – 10 % biochar in a litter will reduce humidity and odour, NH₃ and CH₄ emissions, ameliorates hygiene and hoof infection. Biochar can be used for manure composting and the compost used for plant growth. During composting of manure with 10 – 20 % biochar, large reduction in nitrogen losses were shown in few experiments [35].

Use as a Soil Conditioner

Biochar can be used as a carbon fertilizer, compost, substitute for peat in potting soil, plant protection and compensatory fertilizer for trace elements.

Soil depletion may occur through a variety of other effects, including over tillage, which damages soil structure, overuse of inputs such as synthetic fertilizers and herbicides, which leave residues and build up that inhibit microorganisms and salinization of soil [37]. In addition, plants remove nutrients from the soil as they grow, so these nutrients must be replaced in order for the soil to remain productive. For these reasons Farmers enhance the soil by adding fertilizer, a material that contains one or more of the nutrient plant needs.

The strongest evidence for using high concentrations of charcoal in soil, can be proved from the soil test from the Amazonian Dark Earths and charcoal from respective region rich soils containing about three times more soil organic matter, N and P than other soils with twice productivity [38].

The best method of loading nutrients is to co-compost the biochar. This involves adding of 20-30% biochar to the biomass for composting. The compost can be used as a highly efficient substitute for peat in potting soil, greenhouses and nurseries. Through mixing of biochar with such organic waste as wool, molasses, ash and slurry, organic fertilizers can be produced [33].

The biochar contain all the trace elements originally contained in the pyrolised biomass. During pyrolysis, the crucial trace elements become part of the carbon structure, thereby preventing them being leached out and making them available to plants via root exudates and microbial symbiosis.

Use in the building sector

Some biochar properties give us a clear indication that it is the right material for insulating buildings and regulating humidity. The physical properties such as its low thermal conductivity and its ability to absorb water up to 6 times its weight makes it ideal for building sector. In a ratio 50 % biochar can be added to clay, lime and cement mortar to create indoor plasters with excellent insulation and comfortable breathing environment, to maintain humidity levels in a room at 45-70 % in both summer and winter. Such biochar mud plasters adsorbs smell and toxins, a property not just benefiting to smokers, it's also

good for houses, factories, warehouses, schools and agricultural buildings which are frequently visited by people [39].

Biochar can also be sprayed mixing with lime through jet spray technique at outside of building up to 20 cm thickness as a thermal insulation, it's also a substitute of "extruded polystyrene foam". By this method, houses become carbon sinks and healthy indoor climate. Biochar mud plaster can also be recycled as a valuable compost additive.

Decontamination

Biochar can be used as a soil additive for soil remediation, e.g. in particular former mine works, military bases and landfill sites. Biochar can be used as a barrier preventing pesticides getting into surface water. Fields and ponds can be equipped with 30-50 cm deep barriers made of biochar for filtering out pesticides. Biochar can be used in treating pond and lake water like biochar is a good absorber of pesticides and fertilizers as well as for improving water aeration. [33]

Biogas production

Biochar can be used as a biomass additive and a biogas slurry treatment. The test shows that by adding biochar to a fermenter's biomass, methane and hydrogen yield is increased, while at the same time decrease in CO₂ and ammonia emissions is observed. It may be possible to use the "activated" biochar as an inoculant to further enhance biogas production. [40]

Wellness

Biochar also used for filling mattresses and pillows. Biochar adsorbs perspiration and odours, shields against electromagnetic radiations and removes negative ions from skin. Moreover, it can be used as thermal insulator reflecting heat, enabling comfortable sleep without any build-up heat in summer. In Japan pillows have been filled with biochar for a long time just by preventing from insomnia and neck tension [33].

Textiles

Biochar also has a good future in textile industry, it can be used as fabric additive for functional underwear, thermal insulation for functional clothing and deodorant for shoes. In Japan and China bamboo based bio chars are already being introduced in the textile industry [41] to gain better thermal and breathing properties and to reduce the development of odours through sweat. The same aim is pursued through inclusion of biochar in inlay soles and socks.

Activation of biochar for active carbon filters

Active carbons are produced from carbonaceous materials (e.g. lignocellulosic materials, coal, wood, coconut shell) and have a well-developed porous structure [42]. Due to their microporous structure and chemical nature of their surface with acidic functional groups they have been considered as a potential adsorbent for removal of pollutants and nutrients from industrial and sewage waste water [43].

In this work, activated carbon is finally selected as an alternative use of biochar on industrial scale after reviewing all possible biochar applications. Production methods and applications of activated carbon will be discussed. Activated carbon used in different industrial and domestic applications and has a bright future in upcoming years.

2.3 Activated carbon

The American Water Works Association (AWWA) defines activated carbon as “a family of carbonaceous substances manufactured by processes that develop internal porosity, thereby creating adsorptive properties”. Activated carbon is manufactured through thermal decomposition of carbonaceous material followed by activation with chemicals, steam or CO₂ at temperature 700 to 1000 °C.

Activated carbon is a fine black, odourless and tasteless powder made from coal, char and other materials that have been processed to make it extremely porous and thus to have a very large surface area available for adsorption. One gram of activated carbon has a surface area of approximately 500 m² (or about 2 tennis courts) as determined typically by nitrogen gas adsorption [44]. Humans started using carbon materials as purifying agent before 1500 B.C. [45]. In World War 1, activated carbon used in gas masks as adsorbents [46], as a catalyst support [45] as well as in many adsorption processes for removal of impurities from liquids and gases.

The quality of the resulting activated carbon is considerably influenced by starting material. The activation method employed mainly determines the chemical nature of surface oxides and surface area of resulting product, whereas the structure of pores and pore size distribution is largely predetermined by the nature of starting material. The choice of precursor is largely dependent on its availability, cost applicability and purity.

There are two industrial processes used to maximize the adsorption potential of a parent organic material, natural or synthetic: The carbonisation of raw carbonaceous materials in an inert atmosphere and the activation of carbonized product. The purpose of carbonization is to enrich the carbon content and to create an initial porosity and activation helps to enlarge pores [47]. In Physical activation, the precursor is activated in an inert atmosphere by using oxidizing agents such as e.g. steam or carbon dioxide. Whereas in chemical activation, the precursor is impregnated with chemical agents such as phosphoric acid (H₃PO₄), zinc chloride (ZnCl₂), or potassium hydroxide (KOH) and activated in an inert atmosphere [48]. Advantages of the chemical activation over physical activation are lower activation temperature and shorter time. Furthermore, the activated carbon obtained from chemical activation have mesopores and micropores with a larger surface area [49].

2.3.1 Thermal or physical activation

Two gasifying agents' carbon dioxide and water vapour (steam) either singly or together used for modification in char. These agents “extract” carbon atoms from the structure of porous carbon. This method of activation of solid char takes place, entirely within the gas phase and is named **physical activation** [50].

Because of blockage of the pores by tar [51],[52], the internal surface area of char is too low and porous structure is yet to develop. Physical activation involves high temperature activation using oxidizing agents steam or carbon dioxide, which produces activated carbon with high porosity [45],[53],[51]. Porosity development is due to penetration of oxidizing agents in to internal structure of char and removal of carbon atoms by reaction, which results in opening, and widening of inaccessible pores [53],[51]. Activation using steam, first opens the blocked pores in char and developed micropores and followed by widening of the developed micropores. At the end, this results in larger development of mesopores and macropores and less development in micropores [51]. In case of activation with carbon dioxide, only micropores are attainable [54], [45], ([55]).

2.3.2 Chemical activation

Second, suitable modifications are made to the activation process by additions of such material as phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), or potassium hydroxide (KOH). Such activation process is named **chemical activation** [50].

In literature, it is given that some operating parameters such as temperature and heating rate can affect the development of micropores. [56]. The chemical activation is considered as suitable method for production of activated carbons with a higher fraction of micropores. After heat treatment of impregnated precursor with chemical agent, the impregnating agent is eliminated by washing with acid/water. The washing step makes the pore structure available by removing impregnating agent.

Zinc chloride ($ZnCl_2$) is used as an activating agent but due to environmental concerns associated with zinc compounds, it displaced with other activating agents. Activated carbon produced by zinc chloride is mostly micropores dominant [57]. The use of phosphoric acid (H_3PO_4) increased in industry as an activating agent, especially for improvement in process of acid recovery in recent years. This method produces activated carbon with fine pores in comparison with $ZnCl_2$ [45],[58].

Activated carbon with highly developed micropores and BET surface area of more than $3000\text{ m}^2/\text{g}$ can be produced by KOH activation [57],[59], [60]. The surface area is a function of percentage of KOH to precursor weight ratio. However the higher cost for chemical agent recovery and low bulk density are main problems for commercializing this process [53] ([55]).

2.3.3 Classification of activated carbon

Activated carbons are complex products, which are different to classify on the base of their behaviour, surface characteristics and preparation methods. Properties such as pore size distribution, surface area, iodine number, bulk density, particle size, hardness and mechanical strength gives an idea about the applicability of activated carbon on industrial scale [50]. However sometime they can be classified according to physical characteristics.

Powdered Activated Carbon (PAC)

When activated carbons are made in particular form as powders or fine granules less than 1.0 mm in size, with an average diameter between 0.15 mm to 0.25 mm, they are called powdered activated

carbon (PAC). They present a large surface to volume ratio and PAC are made-up of crush and ground particles, 90 to 95 % of which will pass through designated mesh sieve. ASTM classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins and clarifiers [61].

Granular Activated Carbon (GAC)

Granular activated carbons has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface area. GAC is used as a filter medium, water treatment and deodorization. GAC can also be used in gas phase applications. [62]

Extruded Activated Carbon

Extruded activated carbons are defined by the opening diameter through which carbon is extruded. Diameter in case of pellet is slightly small. The length of pellet is typically twice the diameter. Extruded activated carbons are mainly used in air and gas phase applications. [62]

Impregnated Activated Carbon

Activated carbons are impregnated with chemicals to stimulate chemisorption. Impregnation is important for enhancing its capacity in air purification applications. This kind of activated carbons can be used for water purification processes, when impregnated with antimicrobial agents. [62]

Pellet Activated Carbon

Pellet activated carbons are used where high pressure and high volumetric adsorption required. These pellets are made by applying 200 bar pressure, activated carbons structures are compact, hard and suitable for adsorption. The main advantage to use these pellets for adsorption are of its unique pore distribution. Enhanced porosity have a great effect in gas adsorption processes.

Porous structure of Activated Carbon

The porous structure of activated carbon is formed by three types of pores, which are categorized as follows [50]:

Table 2.3: Types of Pores

Pore	Width
Micropores	< 2 nm
Mesopores	Between 2 to 50 nm
Macropores	> 50 nm

2.3.4 Gas phase applications

For gas phase applications, activated carbon is generally used in the form of hard granules, hard pellets, fibres, cloths and monoliths, because these avoids excessive pressure drop, when gas passes through

adsorbent (activated carbon) bed. The activated carbons should have a well-developed micro-porosity to insure a high adsorptive capacity for gases and organic vapours. Normally the surface areas lies between 1000 and 2000 m²/g [50],[63],[53].

There are a number of gas phase applications for activated carbon. Marsh *et al.* have outlined a few applications which have been widely explored [50]. Activated carbon can be used for personal protection, cigarette filters, industrial gas masks, chemical warfare agent protection (including clothing and gas masks), effluent gas purification and industrial off-gas purification like (removal of SO₂, H₂S etc.). Activated carbon have also useful contribution in petroleum refineries, sewage and geothermal plants, solvent recovery, separation of gas mixtures using carbon molecular sieves, adsorption of radionuclides, natural gas storage and purification, control of gasoline emissions and generally for odour control recovery. Carbons impregnated with caustic materials such as KOH and NaOH are widely used to control odours of H₂S and organic mercaptans in sewage treatment plant [50].

Mochida *et al.* reviewed the applicability of activated carbon for removal of SO_x and NO_x. The highest activity for SO₂ removal in the presence of water at 25°C can be reached with pitch-based activated carbon and this activity could also be improved by heat treatment of activated carbon in nitrogen at 600 to 900 °C [64].

Control of gasoline emissions

Activated carbons for automobile industry have different characteristics such as AC must adsorb gasoline vapours efficiently and must be able to release during regeneration cycle. The most promising pores for this application lie in mesopores. They have surface area between 1400 m²/g to 2000 m²/g and apparent density of 0.2 to 0.35 g/l. The fuel vapours vaporised from carburettor or from the fuel tank are adsorbed in a canister containing (0.5 to 2 L) AC. During regeneration cycle, fuel is recovered by passing air stream through canister. Desorbed fuel put in to engine with air and burnt during normal operation. [50]

Methane storage

Major problem recognized as storage of natural gas, when natural gas is used as a fuel in vehicles. Although having higher hydrogen to carbon ratio than other fuels and greater energy per unit mass, it cannot be stored at same density [65]. Activated carbon can be used as an adsorbent material for storage of natural gas at relatively low pressure and adsorbed natural gas (ANG) is stored with help of adsorbent at pressures ranging between 3.5 to 4 MPa. The density of natural gas in adsorbed phase is higher than in the gaseous phase and easy to store in storage container [50],[65]. Adsorbed natural gas uses adsorbents and operate at much lower storage pressure (500 psi) than Compressed natural gas (3000 psi), thus has relatively lower maintenance cost. In commercial granular activated carbon, the volumetric methane gas storage (V_m/V_s) is 70 (cm³/cm³) [66].

The adsorbent having high micro porosity and high density are important requirements for achieving optimal storage capacity [67]. In this application, natural gas is adsorbed at room temperature, higher than its critical temperature (191 K) and the adsorption of supercritical gases occurs predominantly in

micropores (less than two or three molecular diameter in width) [68]. For enhancing the adsorption storage of methane, micropores should be maximized [50].

Solvent recovery

The major industrial contribution of activated carbon is to adsorb solvent vapours from air streams in recovering method. This method has superiority on water scrubbing that it can be applied to water insoluble solvents. The solvents, which can be recovered by activated carbon, are acetone, benzene, ethanol, ethyl ether, pentane, methylene chloride, tetrahydrofuran, toluene, xylene, chlorinated hydrocarbons and aromatics. The recovery methods by activated carbon are used in the paint, petrochemical, printing, rubber, synthetic fiber, paper, adhesives, metal fabrication, solvent manufacturing and coating industries [69],[50].

2.3.5 Liquid phase applications

For liquid phase applications, Activated carbon is used in both forms such as granular or powdered. Almost 60% powdered activated carbon used in USA is for liquid phase application. AC for liquid phase applications should have larger pores as compared to gas phase ones, in order to allow for rapid diffusion of liquid in to the interior of carbon particles. Three different liquid phase applications for AC like odour, colour, or taste removal from a solution and concentration or solute recovery from solution includes water purification and sugar and sweetener decolourization. [50]

Water treatment

The pollutant organic compounds like NOM (natural organic compounds), synthetic organic compounds and by-products of chemical water treatment produce bad odour, taste and become a source of infection. Due to its adsorptive property and selectivity, AC is widely used for liquid phase application. Both powdered and granular can be used for water treatment, for low dosage of contaminants in water, powdered AC is preferred due to cost and it can last for one year to adsorb contaminants or high dosage of contaminants, granular AC is preferred due to regeneration capability [56],[53],[50].

Activated carbon is also used in treatment of industrial wastewater for upgrading to reuse or discharge in to rivers and streams. AC does not only remove biodegradable organic compounds but also chemicals, which are toxic and not responsive. AC is also used to treat with effluents wastes from chemical factories, rubber factories, fabric dyeing, fertilizer plants, pulp and paper mills etc. Another important use of AC is the removal of oil from effluent water in petrochemicals, petroleum refinery and metal extraction.

Decolourizing in sugar industry

Activated carbon is also used for the removal of colour from sugar during refining process. The last step in decolourization of sugar is completed with activated carbon for the removal of dyes, caramels and iron oxide, that ends as white product and helps in crystallization and separation of sugar crystals [56],[55].

Chemicals and pharmaceuticals

Activated carbon contributes to control product quality by removing toxic chemicals and impurities in chemical processes. Activated carbon is used for the extraction of pharmaceuticals from the process involves fermentation. Antibiotics, vitamins and steroids are adsorbed and recovered by solvent extraction through distillation process [50].

In this work, activated carbon will be used in liquid phase applications especially focussed on drinking water treatment. Clean water availability is a crucial issue in developing countries. World is facing critical drinking water quality problems. In many parts of world, heavy metal concentrations in drinking water are higher than international guideline values. The main threats to human health from heavy metals are associated with exposure to cadmium, lead, mercury and arsenic. Utilization of activated carbon for removal of heavy metals from water will minimize health related diseases.

2.4 Worldwide drinking water problem

Availability of clean water for drinking is a crucial problem in African and Asian countries. According to different reports and research, more than 3.4 million people die each year from water and hygiene related causes and nearly 99% deaths occur in developing countries [70]. 884 million people don't have access to clean and safe water, 37% of those people live in Sub-Saharan Africa [71]. According to Human development (2006), 443 million school days are lost each year due to water related diseases and half of the world's hospital beds filled with people suffering from a water related disease. According to a statement by UN secretary general Koffi Annan (June 2003), in developing countries, as much as 80% of illness are linked to poor water and sanitation conditions. Nearly one out of every five deaths under the age of five worldwide is due to water related diseases.

2.4.1 Removal of water pollutants and their effects on living organisms

Activated carbons are the most important commercial adsorbents. Their high surface area and together with their chemical surface structure allows them to be used in a wide range of industrial applications, some of most important dealing with environmental field and particularly with water purification and industrial waste water cleaning [61].

Due to discharge of large amounts of metal contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb and Zn are most hazardous among the chemical intensive industries. Because of their high solubility in the aquatic environment, heavy metals can be absorbed by living organisms. Once they enter in drinking water and food, large concentration can accumulate in the human body. If someone ingested beyond permitted concentration, they can cause serious health diseases [72].

Heavy metals are generally considered those whose density exceeds 5 g per cubic centimetre. A large no of elements fall in this category, but those who have relevance to environmental context are mentioned in **Table 2.4**. Arsenic is usually regarded as a hazardous heavy metal even though it is a

semi-metal. Heavy metals cause serious health effects, included reduced growth and development, cancer, organ damage and in extreme cases, death [73].

Table 2.4: The MCL (maximum contaminant level) standards, for those heavy metals established by USEPA (US environmental protection agency) [45].

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys and nervous system	0.0003

2.4.2 Arsenic in ground water: a worldwide problem

The world health organization has estimated that long term exposure to arsenic in ground water, at concentrations up to 500 $\mu\text{g/L}$, causes death in 1 in 10 adults. In Europe the focus on arsenic problems is currently confined to countries with higher concentration of arsenic level in their ground water like such as Serbia, Hungary and Italy. In most European countries, the natural occurring concentration of Arsenic in ground drinking water is less than 10 $\mu\text{g/L}$ [74].



Figure 2.2: Arsenic affected countries in (red) of the world, [46]

The world health organization estimated in 2001 that about 130 million people worldwide exposed to arsenic concentrations above 50 $\mu\text{g/L}$ [75]. Affected countries include Bangladesh (> 30 million exposed people), India (40 million), China (1.5 million) and the United States (2.5 million). The problem of arsenic contaminated water not only confined to these countries as illustrated in **Figure 2.2**. According to United

Nations synthesis report, arsenic poisoning is the second most important health hazard related to drinking water [75] Only contamination by pathogenic microorganisms has a bigger impact worldwide.

2.5 Literature review

Rajeshwarisivaraj et al. prepared activated carbon from cassava peel by using physical (steam) and chemical (H_3PO_4). AC used for removal of heavy metals and dyes. Characteristics of AC shows BET surface from physical (steam) at 700 °C is 270 m²/g and from Chemical (H_3PO_4) is 490 m²/g. The results showed 57 % removal of Cr by using Steam AC and 99.83 % removal of Cr by using H_3PO_4 from Cr contaminated water [76].

Mohan and Chandler used activated carbon of Bagasse pitch (raw bagasse), which is produced by chemical activation (800 to 850 °C) for 30 min. Characteristics of AC shows BET surface is 960 m²/g. They used AC for adsorption of metal ions (Cd and Zn). From results, adsorption capacity of AC on Cd is 38.03 mg/g and on Zn is 31.11 mg/g [77].

Basso et al. produced activated carbon from canes (*Arundo donax*), a rapidly growing Renewable Biosource by using phosphoric acid under four different activation atmospheres (self-generated, air, CO₂ and N₂) up to 500 °C. Characteristics of AC shows BET surface between 1000 m²/g to 1100 m²/g. and AC used for adsorption of Cd and Nickel. The result showed 90% removal from aqueous solution [78].

Hayashi et al. prepared activated carbon from corncob by using H_3PO_4 , $ZnCl_2$, K_2CO_3 , KOH and NaOH. The maximum surface area obtained with (H_3PO_4 and $ZnCl_2$) was more than 1000 m²/g at 600°C and were as large as commercial activated carbons. The Micropores were well developed. In comparison, the maximum surface area about 2000 m²/g was obtained with K_2CO_3 activation at 800°C and it was generally larger than commercial activated carbons [79].

Yang and Lua prepared activated carbon from pistachio-nut shells in granular form by KOH. The pistachio-nut shells considered as a good raw material for developing activated carbons with well-developed pore. The best optimum conditions observed during his work was impregnation ratio 0.5 (KOH to raw material on mass basis), an activation hold time of 3 h, nitrogen flow rate (150 ml/min) and an activation temperature of 800 °C. With these optimum conditions, the BET surface area 2259.4 m²/g and total pore volume 1.10 cm³/g was obtained [80].

Budinova et al. prepared activated carbon from woody biomass birch by using various activation procedures like: a) treatment with H_3PO_4 and pyrolysis at 600 °C in inert atmosphere, b) same as in a) but followed by steam activation at same temperature, c) treatment with H_3PO_4 and direct pyrolysis in a stream of water vapour at 700 °C. Activated carbon, prepared by impregnation with treatment with H_3PO_4 and followed by steam pyrolysis had highly well-developed porous structure and largest surface area among other procedures. The BET surface area 1360 m²/g and iodine number 1280 m²/g was noticed in this work. The adsorption capacity for Hg at 293 K was 160 mg/g [81].

Chandra et al. prepared activated carbon from durian shell and used for the removal of methylene blue from aqueous solution. The activated carbon was prepared using chemical activation with KOH as an activating agent. The activation conducted at 400 °C, for 1 h with impregnation ratio 2:1 (KOH to precursor on mass basis). Characteristics shows that the BET surface was 991.82 m²/g. The adsorption experiments was carried out with Langmuir and Freundlich isotherms. The results indicated that the Langmuir isotherm fitted best and showed positive results for removal of methylene blue by using activated carbon as an adsorbing material [82].

Hameed et al. prepared activated carbon from rattan saw dust from furniture factory, used for adsorption phenol from aqueous solution. The activated carbon was prepared using KOH as an activating agent, the char produced by carbonization at 700 °C for 1 h in inert atmosphere. The char used for pre-treatment, using 1:1 impregnation ratio. After pre-treatment the char used for chemical heat treatment in stainless steel vertical reactor at 850°C for 2 h under high purity nitrogen (99.995 %) flow of 150 ml/min. After heat treatment precursor was washed with 0.1 M hydrochloric acid solution to remove KOH and then with distilled water to remove chlorides and to maintain the PH within 6.5 – 7. Equilibrium data fitted well to to Langmuir model with a maximum adsorption capacity of 149.25 mg/g [83].

Lozano Castelló et al. used Spanish anthracite for the preparation of activated carbon using chemical activated carbon with KOH. In his work, different parameters varied to check their effect on BET surface area of activated carbon. All parameters studied, among of them the main factor affecting the final porous structure is KOH/ anthracite ratio. Mostly nitrogen flow rate was not considered as an affecting parameter in previous studies, but in this work result indicates nitrogen flow rate has a vital role and important effect on porosity development. Higher nitrogen flow rate produces higher micro pore volume. The optimum parameters from this work is chemical activation at 800 °C for 1 h under high purity nitrogen flow of 800 ml/min. From this work, it's clear that in case of higher impregnation ratio, washing should be preferred with both HCL and water. Characteristics shows the BET surface area is 3290 m²/g [84].

Azargohar and Dalai used biochar as a precursor from pyrolysis plant for production of activated carbon using physical (steam) and chemical (potassium hydroxide). The effects of operating conditions for each activation method on BET surface area and reaction yield was analyzed by central composite design. For both processes, quadratic models were developed by Design-Expert Software for BET surface area and reaction yield. In physical (Steam) activation, by increasing temperature, the BET surface area increases and reaction yield decreases. In chemical (KOH) activation, by increasing activation temperature and nitrogen flow rate, the BET surface area increases. By increasing KOH to char ratio up to certain limit have same effect on BET surface area. The activated carbon produced by steam at optimum conditions, T = 792 °C, S/C = 1.06, and t = 1.39 h. The BET surface area predicted one is 643 m²/g and observed one is 664 m²/g. For chemical activation, the optimum conditions T = 680 °C, KOH/biochar = 1.23, Nitrogen flow rate = 240 ml/min. The BET surface area predicted one is 783 m²/g and observed one is 836 m²/g. Potassium hydroxide had an excellent ability to produce highly well-developed micro pore activated carbon with total surface area more than 1500 m²/g [85].

Viboon Srirachoenchaikul et al. used waste as raw material for production of porous carbon. Physic nut (*Jatropha curcas* L.) residue from oil extraction for biodiesel production was pyrolyzed at 400 – 800 °C with holds times of 15, 120 and 240 min to obtain char for activation. Activated carbon produced by soaking char with KOH, H₃PO₄ and a pure CO₂ gas flash activator. Activated carbon prepared by chemical activation of Physic nut pyrolyzed char at 800 °C with KOH and attained a maximum surface area of 530 m²/g [49].

Dimitrios Kalderis et al. produced activated carbon from bagasse and rice husk using chemical activation in a short retention time (30-60 min). Chemicals used in this work were ZnCl₂, NaOH and H₃PO₄ for temperatures of 600, 700 and 800 °C. The maximum BET surface area achieved by ZnCl₂ up to 750 m²/g with using impregnation ratio of (1:1) ZnCl₂: Rice husk. The maximum BET surface area obtained from bagasse was up to 674 m²/g using (0.75:1) ZnCl₂ : bagasse ratio [86].

3 Materials and methods

This chapter includes the experimental procedures used in this work for production of biochar, demineralization of biochar, chemical activation, physical activation, iodine adsorption analysis and N₂ adsorption analysis.

3.1 Materials

Table 3.1: Information about apparatuses used in this work

Apparatus		
Name	Application	Details
Muffle Oven	Chemical activation	Heraeus, Tiegelofen Type 11/12 R
Freezer Mill	Milling / Grinding	6800 Freezer Mill
TGA	Determination of organic or inorganic contents in sample	Leco, TGA-701 S4CR Makro, Model No- 604-100-700
FE-SEM	surface morphology	Type DSM 982 Gemini, Carl Zeiss Ltd., Oberkochen, Germany
EDX	For Elemental analysis	Type INCA Penta FET ; 30 mm ² crystal size; oxford instruments, UK
Nova 2000e	For BET surface area	Quantachrome Partikelmesstechnik GmbH
Retech	For sieving Purposes	AS 200
Sieve 150 µm	For Sieving	VWR , CAS NO: 510-0720
Filter paper	Grade 40, for Filtration	VWR, CAS NO: 512-0311

Table 3.2: Details for reagents used in this work

Reagents		
Name	Application	Details
0.1 N Iodine Solution	For Iodine adsorption test	VWR , CAS NO: 7553-56-2
0.1 N Sodium Thiosulphate	For titration during Iodine adsorption	VWR , CAS NO: 7772-98-7
Starch	As an indicator in Iodine adsorption	E.Merck 64271 Darmstadt.
KOH	As an activating agent	Flake, pure, Merck 105012
HCl	For demineralization and washing	37 %, Merck, KR 1039517
H ₂ SO ₄	Same as above	97 %, Merck, KR 3005631

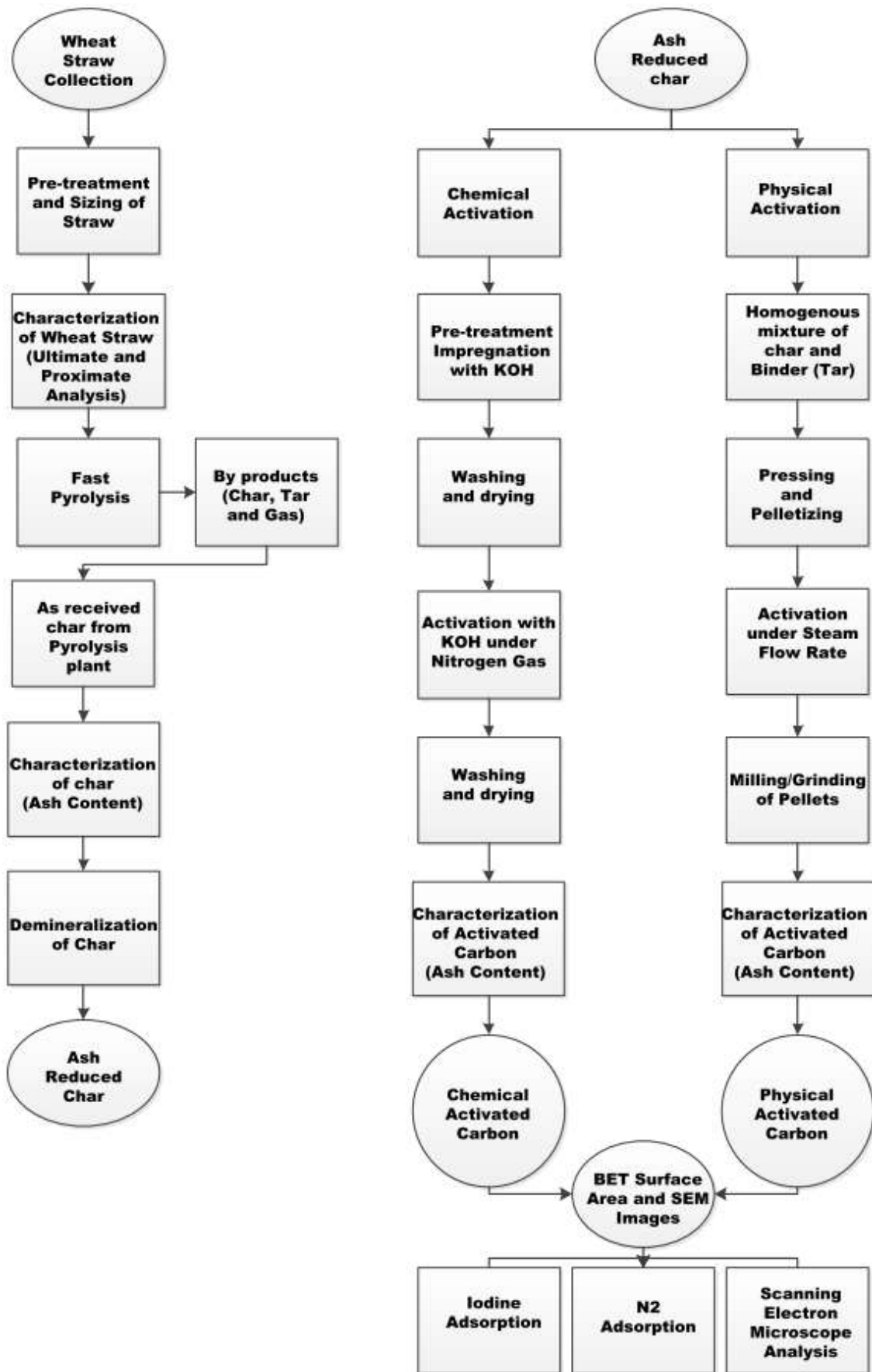


Figure 3.1: Methodology of project

3.2 Methods

Biomass feedstock

Wheat straw was sourced from the stems received from summer wheat supplied by Dörrmann (Kraichtal-Münzesheim Germany).

3.2.1 Biochar production

Biomass was fed through biomass container (approx. capacity 0.7 m³), which is situated on screw feeder. The screw feeder has a small reservoir for biomass material and it is separated from container by way of pressure lock. Prior to feeding, biomass is flushed with nitrogen. Twin screw mixers are used in reactor to provide axial movement with good radial mixing of heat carrier and cold biomass. The whole heat carrier/ reactor system is well-gasketed and there is constant supply of nitrogen gas in order to prevent the ingress of air to system. Biomass is fed to reactor by feeding rate of 6 kg/h. Biomass particles are transported to reactor where a hot carrier (stainless steel balls $\varnothing = 1.0$ and 1.5 mm) is added at 510-550 °C. The heat carrier stream (approx. 1.2 t/h) is mixed with biomass particles and within seconds particles are disintegrated in the forms of gas, tar vapours, reaction water and char. Most of the char is milled to fine particles due to friction between heat carrier and rotating screws. During an experiment, a stream of neon gas is constantly added to reactor as a reference gas stream for determination of pyrolysis gas yield. In recovery step, char is separated in cyclones and subsequently cooled in the steel barrels under nitrogen atmosphere in a controlled manner. Powdered char is highly flammable material and barrels can be exchanged, weighted and sampled for analysis or further experimentation. **Table 3.3** gives an overview on most important properties of for plant operation and calculation of mass and energy balances.

Table 3.3: Results of the proximate and ultimate analysis performed KIT internally by using feedstock

Proximate and ultimate analysis of wheat straw Results on dry basis (db)		
Water content	wt.%	9.1
Ash content at 550 °C	wt.%	7.4
Ash content at 815 °C	wt.%	6.1
C	wt.%	46.1
H	wt.%	5.7
O	wt.%	38.9
N	wt.%	1.0
S	wt.%	0.2
HHV _{with wet}	MJ/kg	16.89
HHV _{with dry}	MJ/kg	18.6
Bulk density	g/cm ³	0.13
Compaction density	g/cm ³	0.185

Particle size distribution is complex procedure. Take an oven dried biochar sample that weighs about 100 g and prepare a stack of sieves. Sieves having larger opening sizes (400 μm) are placed above and the ones having smaller opening sizes (80 μm). The pan is placed under 80 μm sieve to collect the portion of char passing through it. Weigh all sieves and pan separately. Pour the biochar in to the stacks of sieves from top and place the cover, put the stacks in sieve shaker and fix the clamps, adjust the time on 10 to 15 minutes and the shaker going on. Stop the sieve shaker and measure the mass of sieve and retained char. After measuring, we can easily calculate the particle size in % through sieve sizes in μm . considering the bigger size particles, 95% particles were below 400 μm , and bulk density of powdered char is 0.15 and 0.25 kg/m^3 . From **Table 3.4**, 9.2 % ash content in the biomass and 39.8% ash content in biochar. The flow sheet of bioliq fast pyrolysis is displayed in **Figure 3.2**, proximate and ultimate analysis performed for biomass feedstock results are shown on dry basis in **Table 3.3**. Mass yields of products received from PDU (Process Demonstration Unit), Version II (Hot Gas Cyclone and organic condensate) including ash content (%) in **Table 3.4**. Further experimental details are given elsewhere [87].

Table 3.4: Mass yields of products as received in PDU Version II; ash content

Wheat Straw biomass	
Water content biomass (ar), %	9.6
Ash content biomass (ar), %	9.2
HHV (ar), MJ/kg	16.8
Wheat straw char	
Char (ar), %	18.2
Ash content in char (ar), %	39.8
HHV (ar), MJ/kg	19.6

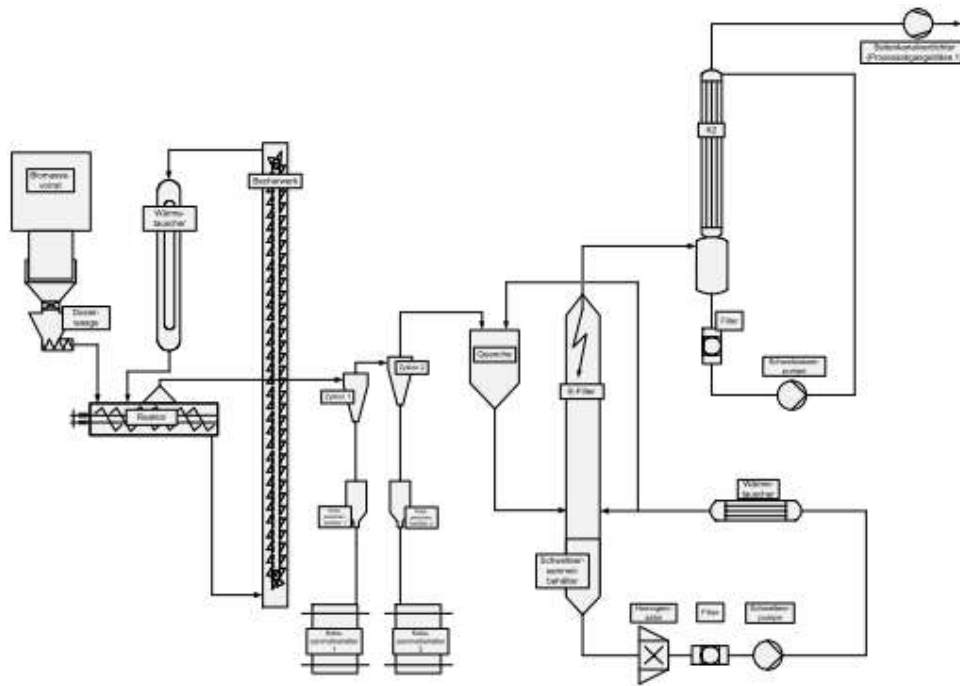


Figure 3.2: Schematic flow sheet of the bioliq fast pyrolysis plant [2]

Biochar is used as a precursor in this work. Biochar was produced from wheat straw using fast pyrolysis process as explained in previous section.

Ash content was determined by Thermo-gravimetric analysis (TGA). Equipment details producer (Leco), Type (TGA-701 S4CR Makro), Model-No (604-100-700). The analysis performed at 3 different temperatures (550, 815 and 1000 °C) to insure the percentage of ash content.

3.2.2 Demineralization of biochar

Dried biochar was soaked in a 1 N solution of HCl : H₂ SO₄ (1:1) for 2 days in order to reduce ash content of biochar and then washed with distilled water (Millipore ultrapure water system) and dried at 110 °C for about 14 h. Ash reduced biochar was used for production of activated carbon.

3.2.3 Chemical activation

Ash reduced biochar activated by using KOH activating agent under nitrogen atmosphere. Ash reduced biochar was sieved. The particles having mesh number 60 (250 μm) size were collected for activation. The equipment Retech (AS 200) was used for sieving. In pre-treatment, biochar was impregnated with KOH having impregnation ratio of 2.34:1 (KOH/Biochar) in a 500 ml volumetric flask containing 250 ml demineralized water with different amount of biochar (2, 5, 10 and 15 g). Impregnated mixture was stirred on a magnetic stirrer for 2 h at 60 °C in a water bath. The resulting mixture was washed with demineralized water to remove KOH. The resulting slurry was dried at 110 °C overnight in an oven. The activation was carried out in a vertical electric muffle furnace (**Table 3.1**). In this work, activation was conducted at different temperatures (450, 675 and 700 °C) with impregnation ratios such as 1.63:1 and 4:1 (KOH/Biochar) ("to clarify for chemical heat treatment ground KOH is used with biochar

to prepare a homogenous mixture in a reactor material- (X6CrNiMoTi17-12-2,1.4571) but for pre-treatment prior to chemical heat treatment KOH pellets are used with biochar in distilled water’), under high purity nitrogen (99.995 %) with different flow rates 150, 258 and 800 ml/min for 1 h and 2 h. Time duration was noted, once the final temperature was reached. The reactor was cooled down in an ice tub and activated carbon first washed with demineralized water to remove chemicals. For better removal of potassium compounds, activated carbon was washed with 250 ml (0.1 M HCl) solution. After washing with HCL, activated carbon was repeatedly washed with demineralized water until the pH of washing solution reached 6.5-7. Washed solution was cross checked with two drops of AgNO₃ (Merck 101512) to check the presence of chlorides with formation of clouds. The resulting activated carbon was dried at 110 °C in an oven. Activation burn-off percentage and chemical recovery were estimated by equations 1 and 2 [88][89]. **Figure 3.3** shows the general flow sheet of chemical activation.

$$\text{Chemical recovery} = \frac{\text{Wt}_{\text{product}}(\text{before washing}) - \text{Wt}_{\text{product}}(\text{after washing})}{\text{Wt}_{\text{chemical agent}}} \times 100 \quad (1)$$

$$\text{Activation burn - off \%} = (\text{Mass loss (g)}) / (\text{Original mass of char (g)}) \times 100 \quad (2)$$

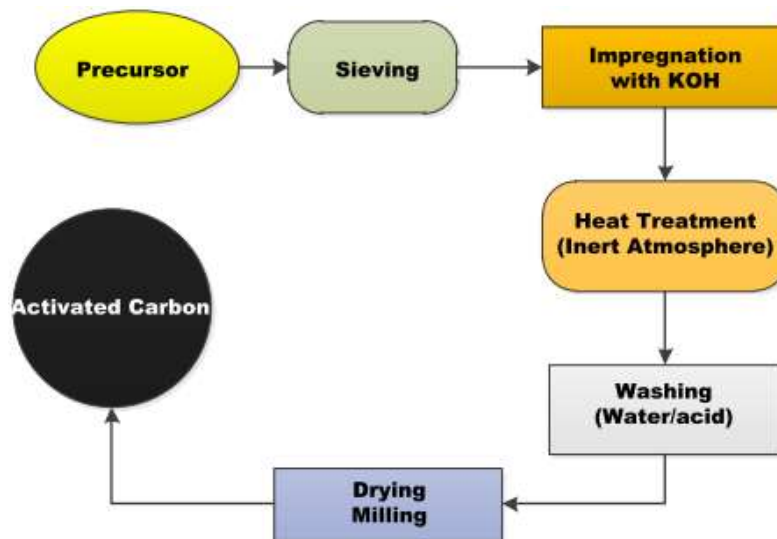


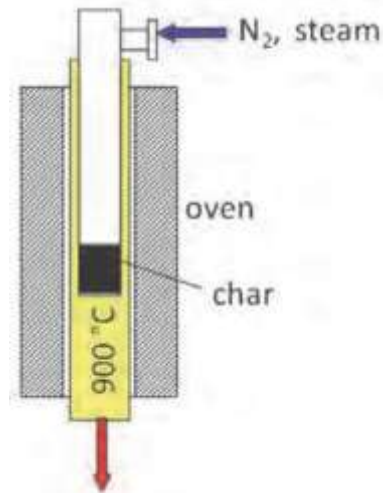
Figure 3.3: Flow sheet for chemical activation

3.2.4 Physical Activation

Activation reactor consists of a vertical furnace which can be heated up to 1200 °C. Inside of a furnace a tube with small case at bottom is inserted. The case contains char and has a porous bottom to ensure the incoming steam/N₂ (Gas) flows through the char bed. In this work, case porous bottom with 100 μm holes was used, but char has different size particles, particles having size less than 100 μm can easily pass through case and it creates mass loss. There are two possibilities to avoid this problem, by using

0.5 μm holes case or by using pellets. In this work it was preferred to do steam activation with pellets due to reduce the pressure drop for steam during reaction through porous plate and pellets are easy to handle, store and transport. The tube can be taken out from the furnace.

Figure 3.4: Scheme of activation reactor [5]



3.2.5 Pellets formation

Char had to be milled before pelletizing to make homogenous mixture of char and binder. To form stable pellets the use of binder is necessary. State of art is to use molasses as binder to form pellets prior to pyrolysis [88]. From economic point of view high viscous pyrolysis oil or tar is preferred to use as a binder to form pellets. In this work, pyrolysis oil was used as a binder to form stable pellets. The mixture of char and binder should be homogenous to form stable pellets, which can easily sustain during activation process. Pressing conditions for stable pellets required pressure between 150 bar - 350 bar. The binding ratio for stable pellets was 1:0.65 (Pyrolysis char/Pyrolysis oil). Pelletizing method explained in **Figure 3.5**.

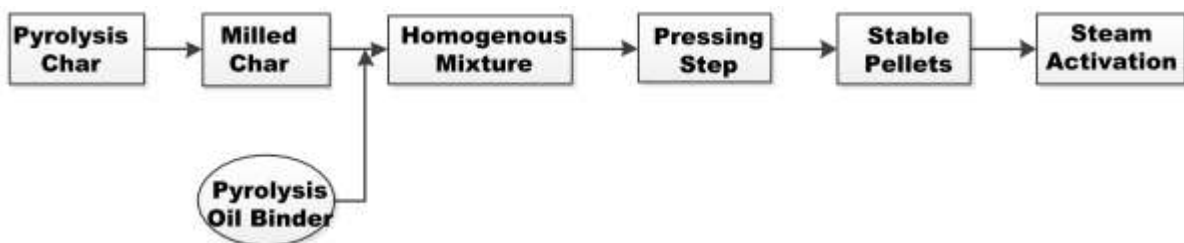


Figure 3.5: Scheme for pelletizing of char

In the beginning, 5 – 10 g pellets were inserted in to case with porous bottom, afterwards the case was fixed to the reactor tube. The tube was inserted in to hot furnace and the pellets were kept under nitrogen. When the desired temperature was reached then nitrogen gas was substituted by steam flow. In this work, the pellets were activated at 750 °C in a vertical tube reactor, the nitrogen flow rate (500 ml/min) passing through pellets bed in the start and at the end of activation and the steam flow rate (75 ml/min) passing through bed during activation. A retention time of 1 h was kept for all samples. After desired time, steam flow was replaced with nitrogen gas and the reactor tube was taken out of the reactor and cooled down with small fan under nitrogen flow rate.

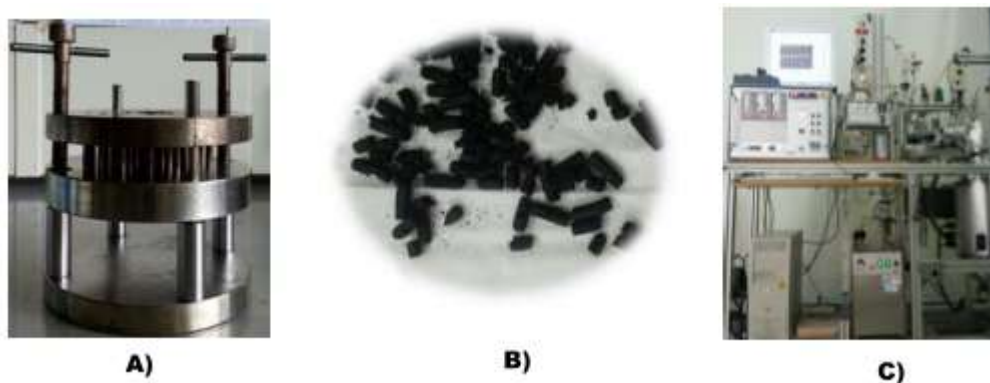


Figure 3.6: A) Pressing Matrix, B) Pellets, C) Physical activation Equipment

3.3 Characterization of activated carbon

The activated carbon is characterized by its surface area, porosity, surface topography, adsorption of iodine, adsorption of nitrogen gas, pH and ash content. The determination of surface area can be analyzed with adsorption of iodine and nitrogen gas but porosity analyzed with adsorption of nitrogen gas.

Adsorption properties of activated carbon

3.3.1 Iodine adsorption (Liquid phase adsorption)

Iodine adsorption is a simple and fast adsorption method to analyze the adsorption capacity of activated carbon and also known as Iodine number. In this work, all samples of activated carbon were analyzed using the standard test method for the determination of iodine number of activated carbon (ASTM, D4607-94) which is shown in **Appendix C**. In determining the iodine number, 10 ml of 5 % by weight HCl was added to calculated amount of carbon dosage in Erlenmeyer (250-mL) flask and was allowed to boil for 30 seconds. After the solution was cooled to room temperature, 100 ml of 0.1 N iodine solution added and start shaking vigorously for 30 seconds. Gravity filtration equipment should be prepared prior to shaking so no delay is encountered in filtering the samples. For each filtrate, use first 20 to 30 ml to rinse pipet and discard this rinse portion. 50 ml filtrate collected in a clean beaker and titrated with 0.1 N sodium thiosulphate in the presence of starch as an indicator (ASTM, D4607-94).

3.3.2 Nitrogen gas adsorption (Gas phase adsorption)

The BET surface area of activated carbon were measured by standard BET method [89] (Brunauer, Emmett, Teller) with automated gas adsorption analyzer, Nova 4000e from Quantachrome Partikelmesstechnik GmbH. After degassing (24 h) of activated carbon sample in a measurement cell at 140 °C to a vacuum. Activated carbon is exposed in nitrogen atmosphere at the boiling temperature (77.2 K) of liquid nitrogen. The BET method involves the determination of the amount of the adsorptive gas required to cover the external and accessible internal pore surface of a solid with a complete monolayer. According to theory, the nitrogen gas only adsorbed physically by weak bonds at the surface of the solid (Van der-wall forces) and can be desorbed by a decrease of pressure at same temperature.

3.3.3 Scanning Electron Microscopy (SEM) & Elemental analysis

A scanning electron microscope (SEM) that images an activated carbon sample by scanning it with a high energy beam of electrons in a raster scan pattern. The activated carbons having higher surface area were chosen for measuring SEM analysis. SEM studies the surface morphology and verify the presence of porosity. The SEM analysis was examined by FE-SEM (Field Emission Scanning Electron Microscope) type DSM 982 Gemini, Carl Zeiss Ltd., Oberkochen, Germany. For Elemental analysis EDX (Energy Dispersive X-ray analysis) is used and it is connected to FE-SEM.

4 Results and discussion

4.1 Demineralization of char

The ash content of the raw biochar (Rbc), demineralized biochar (Dbc), chemical activated carbon (Cac) and physical activated carbon (Phac) is compared in **Table 4.1**. As it is seen from **Table 4.1**, the raw biochar exhibits the maximum ash content and minimum BET surface area. Demineralized char showed higher effective BET surface area and minimum ash content up to 50 % less than raw biochar. The acid treatment significantly reduces the ash content of char. Acid treatment of char resulted in about 50 % removal of ash.

Table 4.1: Properties of Char and Activated Carbon, db (dry basis)

	Elemental analysis, wt. %			Surface area, m ² /g	Ash Content, wt. %
	C	O	Si		
Raw biochar	65.14	19.12	6.06	4.1	39.8 (db)
Demineralized biochar (1 N)	72.81	18.26	6.51	23.5	20 (db)
Demineralized biochar (2 N)	72.67	18.23	6.27	-	22.2 (db)
Chemical activated carbon	91.61	8.21	0.71	2900	0.7 (db)
Physical activated carbon	70.99	14.75	7.12	545	38.2 (db)

The inorganic element distributions in ash chars before and after the acid treatment and also in activated carbon before and after the activation showed substantial reductions in different main elements (**Table 4.2**). It is clearly seen from **Table 4.2** that all elements were significantly decreased instead of S, results were taken by EDX measurements. Basically in case of Dbc (1 N) the percent of sulphur was increased instead of Chlorine by treating with HCl: H₂SO₄. But in Dbc (2 N), both sulphur and chlorine were increased after acid treatment. Washing of char after acid treatment effects the wt.% of sulphur and chlorine in demineralized char and also changes the EDX measurements.

The BET surface area of biochar is generally related to their activation process parameters as well as their ash content. It is clear from **Table 4.1**, that reduction of all inorganic elements and chemical activation step lead to maximum surface area like in case of Cac having 0.7% ash content. Higher amount of inorganics in biomass led to formation of biochar having low surface area due to filling up pores by fusion of molten ash [90].

In this work demineralization was done with 1 N acidic solution. But in case of 2 N, ash reduction is less as compared to 1 N clearly visible from **Table 4.1**. In **Table 4.2** it's clearly seen that few elements increased or decreased in mass% in case of demineralized biochar with 1 N and 2 N. The variation in mass % can be seen in BPac (Before physical activated carbon) and APac (After physical activated carbon).

Table 4.2: Elements of Char and activated carbons; wt. %

	Mg	Al	P	S	Cl	K	Ca	Fe
Rbc	0.36	0.22	0.36	0.26	0.94	5.63	1.33	0.56
Dbc (1 N)	0.16	0.15	0.22	0.37	0.91	0.36	0.24	0
Dbc (2 N)	0.22	0.12	0.06	0.53	1.32	0.26	0.31	0
Cac	0	0	0	0	0	0	0	0
BPac	0.29	0	0.21	0.45	0.93	3.69	0.92	0
APac	0.48	0.17	0.44	0	0	4.56	1.50	0

It is evident from **Figure 4.1** that biomass chars showed varied surface area characteristics. It is known that activation type (soaking time, impregnation ratio, temperature, washing step, steam flow rate and nitrogen flow rate) greatly influence the surface area of chars generated from biomass [84].

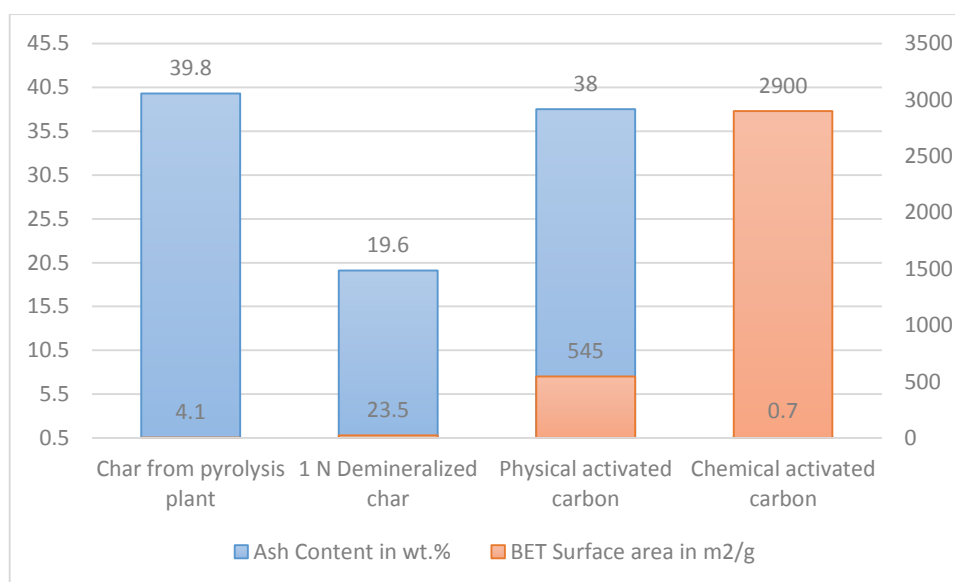


Figure 4.1: Variation in BET surface area and Ash content

4.2 Chemical activation

In chemical activation processes many parameters exist, variation of these parameters will affect the porous texture of the activated carbon. In this present work, the effect of different parameters involved in a chemical activation process on the porosity of the final activated carbon are presented. The nomenclature of samples includes the identification of the wheat straw char (WS). In this work parameters were varied according to findings from the literature study, these parameters were optimum conditions for other precursors to get maximum effective BET surface area. **Table 4.3** contains the porous texture characterization results obtained by applying BET equation to N₂ adsorption at 77 K and liquid phase adsorption by doing iodine adsorption test to check iodine no. it is clearly visible from **Table 4.3** that at higher KOH/Biochar ratio the effect of metallic salt in formation of micro porosity is more pronounced reaching an effective value of BET Surface area of 2857 ± 43.5. From Literature [91],[92] it was shown that in chemical activation there are two different mechanisms: first one is the

formation of micropores which starts with addition of chemicals to raw materials and second one is the widening of pores which is the result of chemical effect inside the opened pores. Increase in impregnation ratio helps to open the pores for second mechanism includes widening of pores.

In this work, WS 1 and WS 2 were optimum conditions for getting maximum surface area considered from study [85],[93], here in the condition were optimized by using Design-expert software. WS 3 was the optimum and ideal conditions for getting effective BET surface area and micropores studied by [84]. Increase in temperature especially above 700 °C enhances reaction between carbon and potassium compounds resulting in porosity development, formation of metallic potassium and its insertion to carbon matrix has a great effect on increasing the porosity [53],[94].

It is observed that optimum conditions reported in literature does not necessarily hold true for wheat straw derived biochar.

Table 4.3: Effect of parameters on yield wt. % and BET surface area (m²/g), db (dry basis)

Sample	KOH/Biochar Ratio	Temperature (C)	Nitrogen flow rate (ml/min)	Time (h)	Yield (%)	Iodine No. (mg/g)	N ₂ BET Surface Area (m ² /g)
WS 1	1 – 4	650 – 700	250 – 800	2	59.72 (db)	1003 ± 56.2	-
WS 2	1 – 4	650 – 700	250 – 800	2	59.36 (db)	1224 ± 68.5	-
WS 3	1 – 4	650 – 700	250 – 800	1	40.16 (db)	2437 ± 129.6	2857 ± 43.5

Nitrogen flow rate is an important factor which results in higher surface area. Activated carbons with much higher adsorption capacities are obtained using higher nitrogen flow rates. These results from **Table 4.3** indicates that a faster removal of gases evolved during activation helps in creation of micropores. Another informative explanation to higher nitrogen flow rate is given by [84], that study is related to production of potassium during activation process. At 700 °C the deposition of potassium on cooler parts of reactor was seen. This potassium is developed gradually during reaction between carbon and KOH. If potassium is removed from the reaction place by using higher nitrogen flow rates from reaction place results in the production of further potassium, then an increase in reaction will occur between carbon and KOH. It can be said that nitrogen flow rate is an important parameter for considering during preparation of activated carbon after drastically increase in BET surface by increasing nitrogen flow rate because from **Table 4.3** it is clearly visible, the increase in iodine number with varying nitrogen flow rate in WS 1 and WS 2 by keeping same impregnation ratio.

4.2.1 N₂ gas adsorption

In physical adsorption studies, the experimental information dominance is *adsorption isotherm* which is a plot of equilibrium amounts adsorbed (n_m^a in mmol g⁻¹) against the relative pressure (p/p^0) of the adsorbate. The problem with the use of computerized equipment is that it is programmed to re-assemble adsorption data into the coordinates of the Brunauer-Emmett-Teller (BET) to provide the best straight line through data, and to obtain a value of surface area. [50] The adsorption isotherm results from controlled physical adsorption of a gas in to activated carbon showed in **Appendix**.

The physisorption of nitrogen at 77 K, on non-porous surfaces, resulted in multilayers being formed. The BET equation does not predict surface areas; it predicts monolayer coverage (units of cm³ g⁻¹, mmol g⁻¹ of adsorbate). In some activated carbons, adsorption may occur such that several layers of adsorbate molecules adsorb together. This is named as *volume filling* and occurs in the largest of the micropores. It is termed *capillary condensation*. When it occurs in mesoporosity. Such capillary condensation must not be included in values of n_m^a (monolayer capacity in mmol g⁻¹). Any value beyond 1000 m² g⁻¹ must be associated with micropore volume filling and capillary condensation and should be treated with caution. [50].

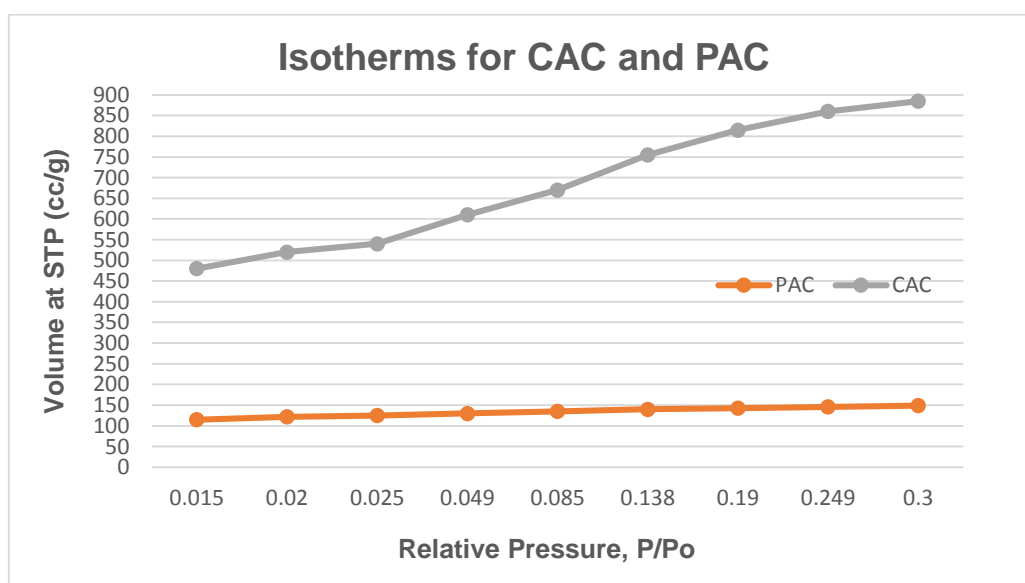


Figure 4.2: Nitrogen adsorption isotherms of activated carbons at 77 K

The adsorption isotherms of CAC and PAC are shown in **Figure 4.2**. Both isotherms displayed a very large difference in volume, indicating the presence of mesopores in case of PAC and micropores in case of CAC. This is the reason for the smaller BET surface area and iodine number for the PAC.

4.2.2 Iodine adsorption

Iodine adsorption is a quick method to check adsorption capacity of activated carbon. In this work standard methods from ASTM D4607 were followed. According to standard method least squares fit calculated for three points and iodine number. The regression coefficient for least squares fit should be greater than 0.995.

From **Figure 4.3** it is seen that regression coefficient for least squares fit in WS 1 case is 0.9998 which satisfies the standard value. From this plot iodine number is the value at $C = 0.02$ which is normally the mean of values. According to standard D4607, precision of test in the determination of iodine number of activated carbon ranging from 600 to 1450 iodine number is 5.6 % of the average value measured in (mg/g or X/M). In this work iodine number is 1003 ± 56.2 which can be seen from **Figure 4.3**.

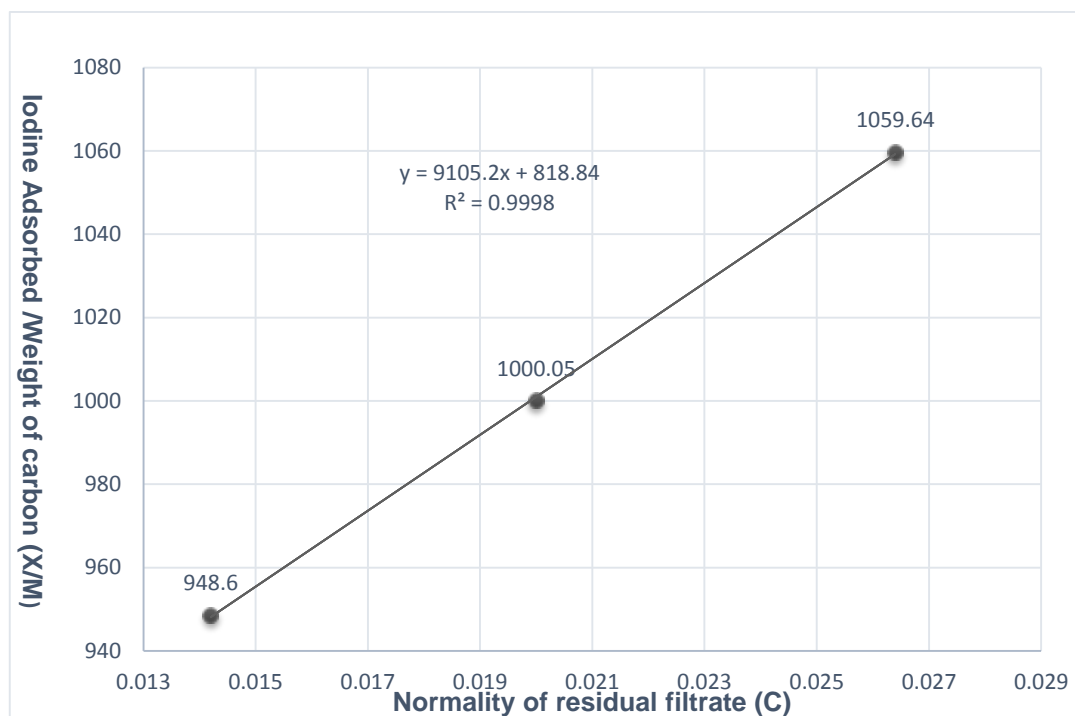


Figure 4.3: Least squares fit plot for iodine adsorption on WS 1

4.2.3 Physical activation

In physical activation, many parameters can be varied for getting the optimum conditions for higher BET surface area. In this work, few promising conditions are considered for physical activation of wheat straw. The parameters used in this work is chosen from work done by [85],[95]. If major objective is to obtain activated carbon with higher surface area from specific amount of char, then the level of yield should be in range between 50 – 60 (dry basis) wt. %. Activation should be low as much as possible to increase the yield of a batch process [85]. Mostly the yield of activation carbon will decrease with increase in temperature. The activation burn-off will occur due to steam reforming reaction of char, and will emit carbon monoxide and hydrogen [96]. This reaction takes place on outer surface as well as inner surface of char. The reaction on outer surface results in generation of new pores and reaction on

inner surface in micro pores results in widening of generated pores. As explained above, activation burn-off will increase with increase in temperature results in higher BET surface area but with further increase in temperature pore wall became thinner and started breakdown. Due to breakdown of pores wall results in reduction of number of pores also decrease in BET surface area and iodine number.

According to different studies the steam flow rate have a great influence on yield and surface of activated carbon. Activation burn-off occurs due to steam reforming of char and in excess of steam flow rate the yield of activated carbon will start decreasing. Within limiting time of 1 h micropores starts converting in to macropores and results in reduction of BET surface area and iodine number. Pore volume can be controlled by controlling steam flow rate because high steam flow rate increases the burn-off results in fragile structure of pores and results in lower surface area. From study by [95], maximum surface area and iodine number achieved at lower steam flow rate (75 mg/min).

From **Table 4.4**, according to results there is a 48 % yield and maximum surface area of 545 ± 26.97 which fulfils our prerequisite for use as an adsorption material in cleaning of drinking water because according to American water works association (AWWA) surface area should be greater than $500 \text{ m}^2/\text{g}$. However, it is noted that two of the three experiments are below $500 \text{ m}^2/\text{g}$ and exhibit a nearly identical surface area. It cannot be excluded that the maximum BET observed is an outlier.

Table 4.4: The values of BET surface area and yield of physical activated carbon prepared at $T = 750 \text{ }^\circ\text{C}$, steam flow rate $300 \text{ mg}/\text{min}$, time = 1 h and binder ratio (char /bio=oil) = 1:0.65, db (dry basis)

	n = 3
BET Surface Area (m^2/g)	510 ± 26.97
Iodine number (mg/g)	485 ± 27.72
Yield (wt. %) (db)	48 ± 0.362

4.3 Scanning electron microscope

SEM are used to check the images of samples at microscopic level. Images are used to determine the structure and distribution of pores that are present on surface of activated carbon. The pore size that can be measured through images mostly depends on magnification of image. In this work, the pores cannot be observed through images because the sample which has surface area greater than $2900 \text{ m}^2/\text{g}$ have micropores ($< 2 \text{ nm}$) it is an assumption because from other studies, if surface area is more than $1000 \text{ m}^2/\text{g}$ then it will be micropores, which is very difficult to see through SEM. Transmission electron microscope (TEM) can be used to see micropores. But in case of **Figure 4.4 (D)**, it is observed that significant increase in physical activated carbon pores (macro). From **Figure 4.5**, it is seen that significant change in surface morphology before and after the pellets of biochar.

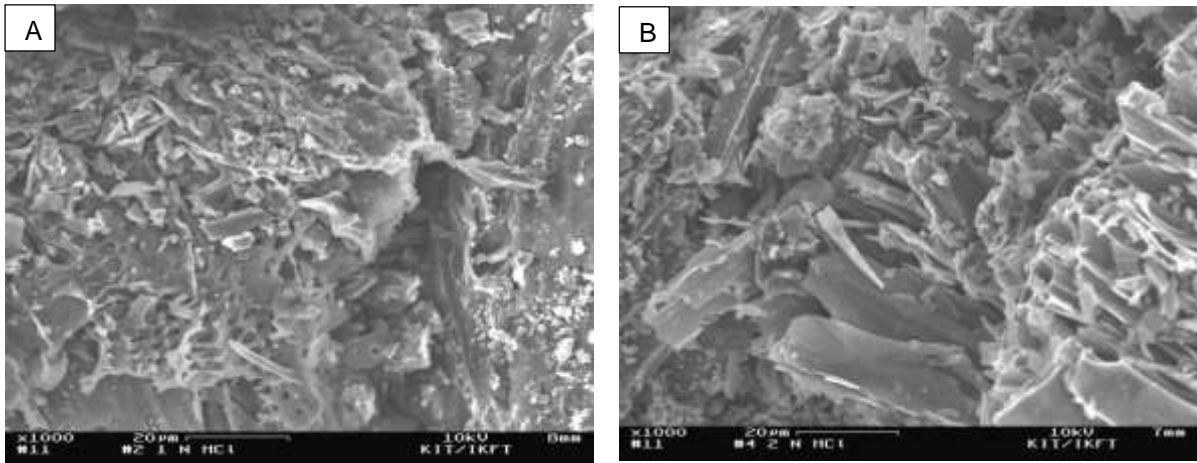


Figure 4.4: SEM images (A) represents 1 N ash reduced Biochar and (B) represents 2 N ash reduced Biochar

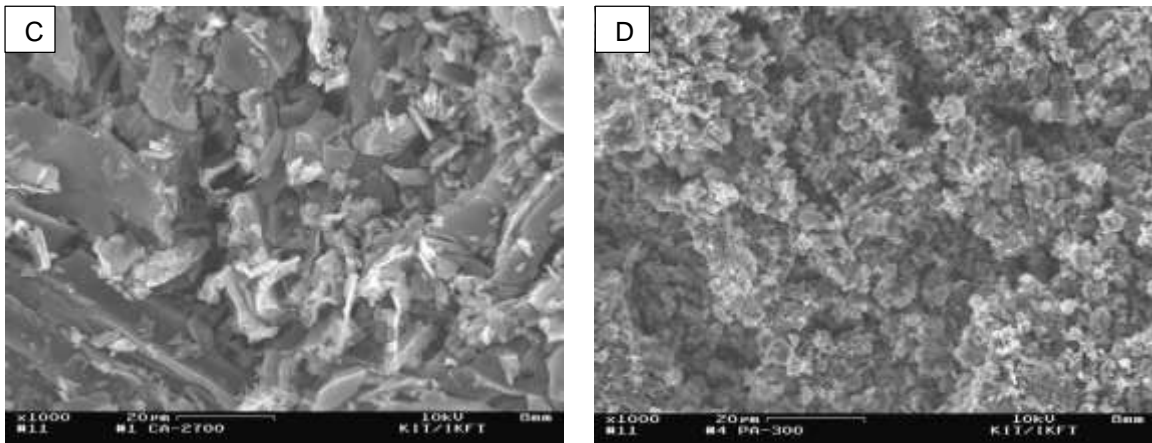


Figure 4.5: SEM images (C) represents the Chemical activated carbon having surface area 2900 m²/g and (D) represents Physical activated carbon of 1 N ash reduced Biochar having surface area 400 m²/g

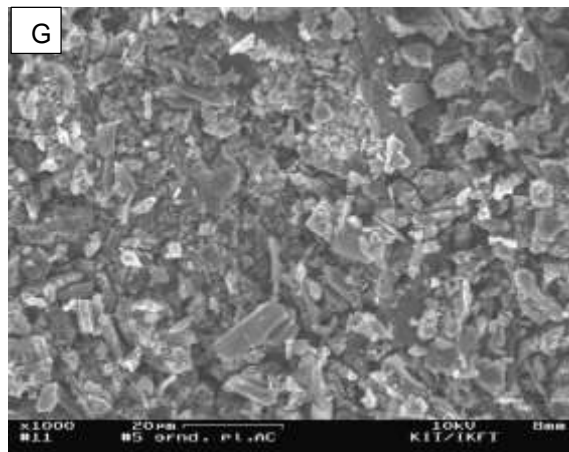
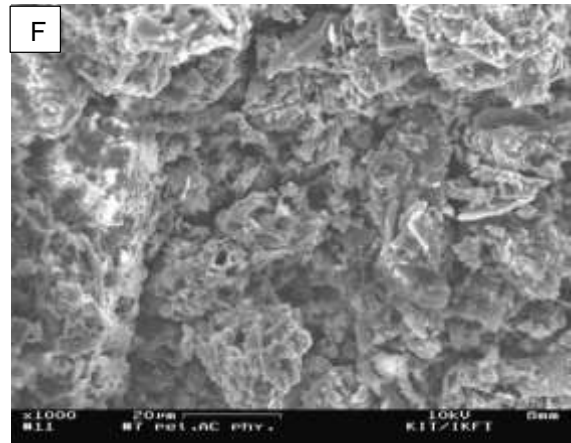
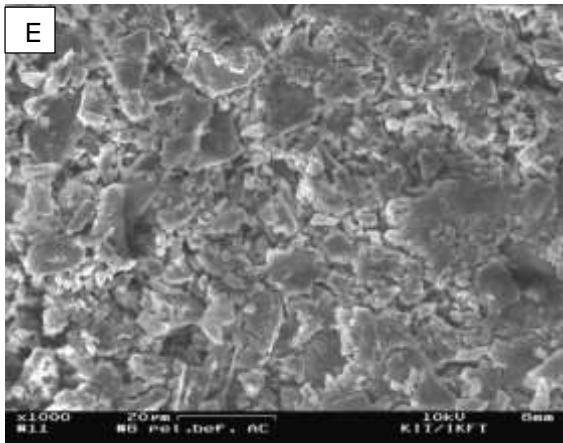


Figure 4.6: SEM images (E) represents 1 N ash reduced pellets before physical activation, (F) represents physical activated carbon pellets having surface area 545 m²/g and (G) represents Physical activated ground pellets having surface area of 545 m²/g

5 Optimization of bioliq plant

The bioliq concept, which is currently working at Karlsruhe Institute of Technology and converting low-grade lignocellulosic biomass (wheat straw) to synthetic fuels and other organic chemicals. Recently fast pyrolysis pilot plant is equipped with twin screw reactor and pneumatic heat carrier loop with sand is used as the heat carrier medium. Air dried wheat straw having size up to 10 mm is fed to reactor. In this work, optimized design concept of pyrolysis plant will be discussed with different required and beneficial changes. This plant is fed by 400 kg h⁻¹ (wheat straw) on dry basis (9.72 % water content). Dried biomass reduces the thermal energy and time required to evaporate the water content from biomass in twin screw reactor. Drying process of biomass increases relative % increase in biochar production.

In this work, optimized pyrolysis plant can be divided in to six units which can be seen in **Figure 5.1**. First, there is storage of biomass (wheat straw) and secondly the pre-treatment of biomass includes drying and sizing of biomass. Third, there is heat carrier loop with steel balls for pyrolysis process and fourth represents the recovery of hot pyrolysis product. Fifth includes the activation of biochar and sixth involves the mixing of bio-synchrude. In this chapter drying process, heat carrier loop with steel balls, recovery of hot pyrolysis product and activation of biochar will be discussed and explained.

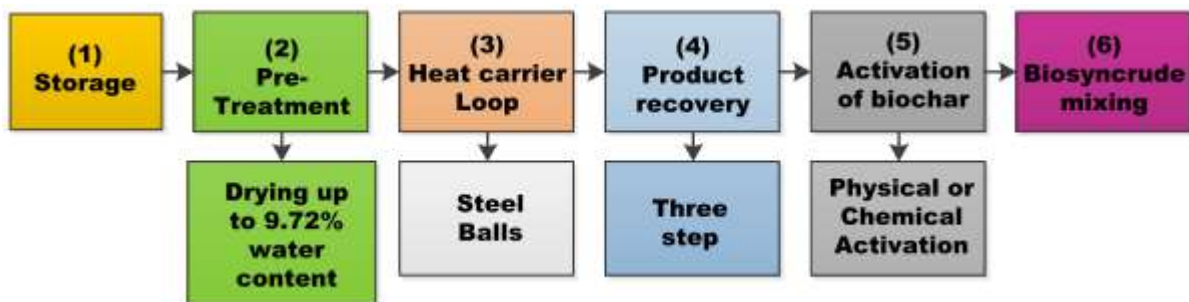


Figure 5.1: Overview of optimized pyrolysis plant

5.1 Pre-treatment of biomass

Pre-treatment involves sizing and drying process. In sizing step, straw bales are broken up and impurities are separated by metal separator and then finally straw is milled by using a two stage cutting mill to size of maximum 10 mm length and 3 mm width [97],[98]. Drying process will be done by exhaust gas.

Available Heat

Biomass pre-treatment involves drying process for reduction of water content from biomass which helps in reducing mass flow and increase in biomass quality by raising its lower heating value. In optimized plant, we will utilize the waste heat within plant for other needed thermal energy demands like drying process. Exhaust gas coming from heat carrier loop heat exchanger having temperature between 350 -400°C will be used for drying process. Thermal energy can be calculated by using specific heat

capacity of flue gas 1.153 kJ/(kg K) [98], density 0.697 (kg/m³), mass flow rate of flue gas 254 (m³/h) and $\Delta T = 200$ (K). Thermal energy available for drying process is 11.34 KW. Biomass has 10 % or 15 % water content depending on weather conditions or seasonal changes and we can minimize the water content down to 7.42 % or 12.42 % respectively through drying process by utilizing this waste heat available thermal energy from flue gas. Drying process needs 3960 J/g of water [99].

There are different direct or in-direct drying techniques utilizing air, flue gas or steam as drying medium. In this work, waste heat in the form of flue gas will be used as a drying medium. In the 1970s and 1980s, direct flue gas dryers were used for industrial drying purposes [100]. Mostly flue gas was either taken from plant or generated separately in flue gas burner but in this work, exhaust gas (flue gas) after preheating of air will be used for drying purpose as shown in **Figure 5.4**.

5.2 Dryers

Mostly dryers can be divided in to two categories based on how heat is provided for drying. In direct dryers, the biomass gets heat from direct contact with drying medium in form of hot air or steam but in in-direct dryers the material being dried is separated from heat source by a heat exchanger. Directly heated dryers divided into further two more categories: air and superheated steam dryers (SSDs). In air dryers, hot air is contacted with biomass and air loses its sensible heat and provides the latent heat of evaporation to dry material. The air also removes the water vapour that is evaporated and biomass can be agitated by mechanical source or by the flowing air. In SSDs the drying medium is steam instead of air and mechanism is same [101].

There are three requirements for drying [102]:

- A source of heat,
- A method of removing the water evaporated.

5.2.1 Stages of drying or drying curve

In each case, there is representative curve that describes the behaviour of drying process and its phases.

Figure 5.2 shows a typical drying curve.

First Phase or initial period is where sensible heat is transferred to wheat straw chips and contained moisture. This step involves the heating up of chips from initial condition to process condition. The rate of evaporation will increase dramatically in this step. Pre-heating of chips can be replaced this initial period, like if we pre-heated chips through other waste energy then inlet condition of chips will already be at raised temperature [101].

Second phase or constant rate period is when free moisture continuously reducing on the surface and very small variation in rate of evaporation. During this period, drying rates are high and there is gradual and relatively small increase in the chips temperature [101],[103],[104],[105].

Third Phase or falling rate period is the period where migration of moisture from inner surface to outer surface of chips which is the limiting factor that reduces the drying rate and once material is completely dry, it begins to heat up to the surrounding temperature, because water is no longer present to keep its temperature low [101],[103],[104],[105].

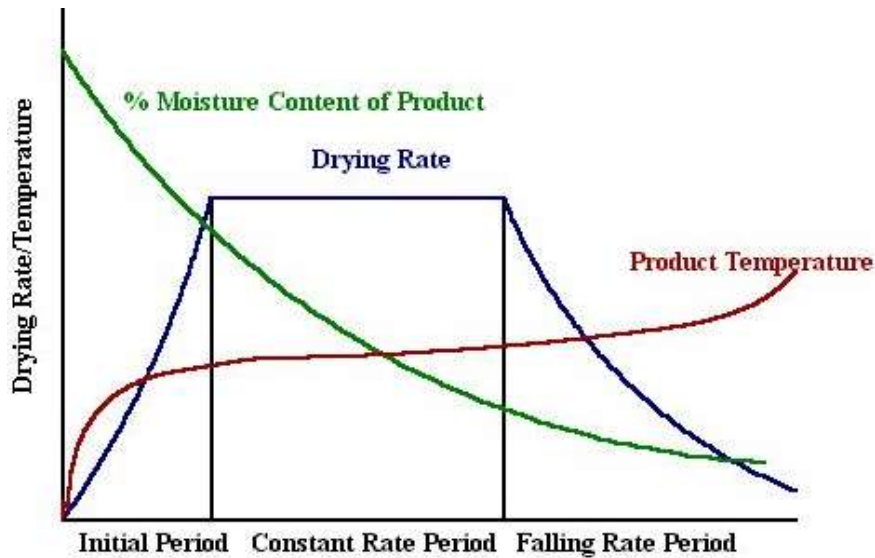


Figure 5.2: Drying Curve

These above mentioned steps are important when drying a combustible material. On other hand, heat transfer can be increased by introducing high temperature by which equipment size will be minimized but at the same time there is possibility that biomass may ignite. Fast drying provided by high temperatures can be exploited with minimal fire risk [101]. Because by doing fast drying, we can minimize the time of hot flue gas contact with biomass which helps in minimizing the fire risk.

There are two points in drying process when there is a significant fire risk. The first occurs after the surface moisture evaporated but before the migration of water from inside of biomass to outer surface. During this very brief migration period of water from inside to outer surface, there is no water vapour near the surface to keep the particle cool and surface can quickly heat up while inside remains cool. If surface remains hot for longer period, the material can ignite even it is not completely dry. The second occurs when biomass is over dried. If biomass losses all its moisture, it will start to warm up and will ignite when it reaches to its combustion temperature. Drying rate decreases as biomass material gets drier [106].

5.2.2 Dryer types

The dryers for biomass can be classified according to drying medium. The most common types of flue gas dryers are rotary and flash dryers.

In this work, flash dryer seems to be more feasible option for drying of biomass. Flash dryers are able to dry biomass rapidly for easy removal of free moisture. There are some benefits and disadvantages of flash dryers as described in **Table 5.1**. With short retention time in the dryer, hydrocarbon emissions

may be slightly lower than for a rotary dryer [107]. In a flash and pneumatic dryer, the intimate contact of solids with a stream of hot flue gases (exhaust gases) results in rapid drying. Flash dryers require smaller biomass particle sizes to suspend and transport the biomass by the fluid stream alone. Because of short drying time in a flash dryer, the equipment is more compact than for a rotary dryer. Flash dryers have a lower fire risk than rotary dryers due to shorter retention time. Gas temperatures are slightly lower for flash dryers than for rotary dryers, but they still operate at temperatures above the combustion point. The solids retention time in a flash dryer is typically less than 30 seconds. ([108],[101]). Flash dryers have been successfully used for drying most biomass materials, including wood, sludge and bagasse [109].

In pyrolysis plant, the biomass particles enter the flash dryer with a water content up to 10%, flue gas and biomass particles separated by using cyclone and flue gases continue through a scrubber to remove any entrained particulate material. A simple flash dryer (without a scrubber) is shown in **Figure 5.3**.

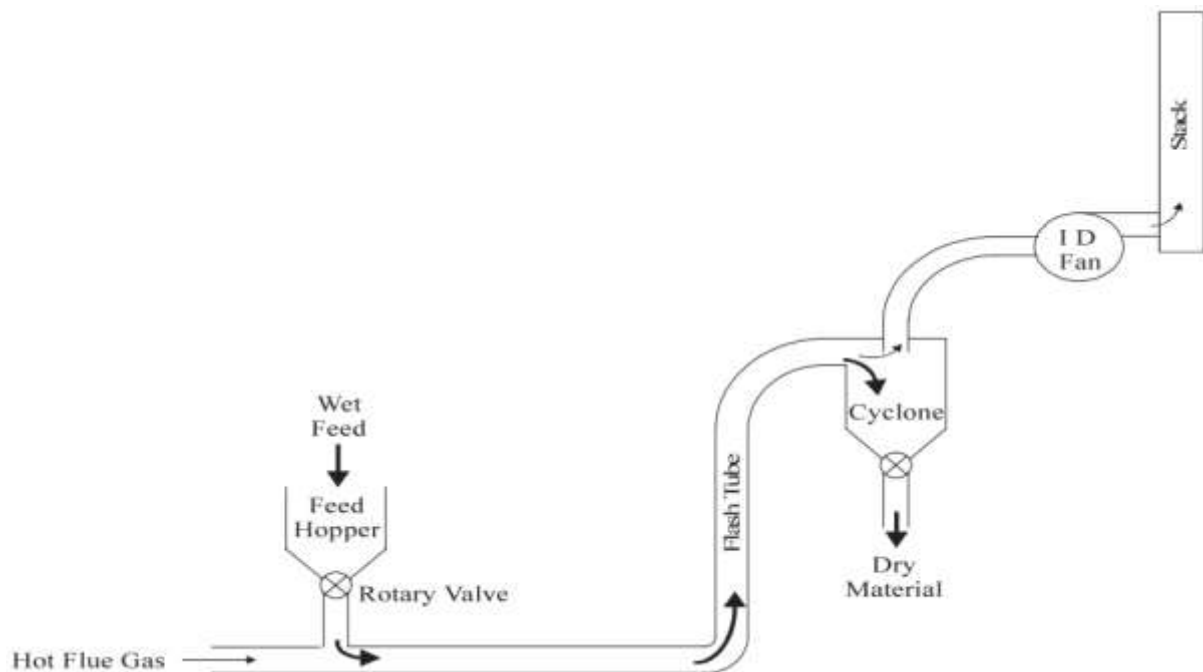


Figure 5.3: Typical Flash Dryer Configuration [5]

In this work, biomass input equals to 400 kilograms per hour with a water content of 15 % and flash dryers have a capacity within a range between 4.4 to 16 (t/h) [108]. Biomass particles dried from 10 % to almost 7.42 % water content, which corresponds to a separation of 10.32 kilograms of water per hour. The idea behind drying the biomass below a water content of about 7.42 % is to reduce mass flow and energy saving in process steps due to no longer needed evaporation of water. The mass flow through subsequent process equipment equals to 389.68 kg/h.

Table 5.1: Summary of advantages and disadvantages of each dryer and considerations when choosing a dryer [5], [12], [4]

	Dryer Type				
	Rotary	Flash	Belt	Fluidised-bed	Superheated steam
Required small particles	No	Yes	No	No	Yes
Heat recovery	Difficult	Difficult	Easy	Easy	Easy
Fire hazard	High	Medium	Low	Medium	Low
Air emissions	Medium	High	Low	Medium	Low
Steam use	Yes	No	Yes	Yes	Yes

5.2.3 Fire or explosion risk

The combustion temperature of Wheat straw is determined by Di Blasi et al. [110], which is in the range of 242-292 °C. Most dryers can be operated at much higher temperatures because the evaporating water vapour keeps the biomass surface temperature lower than flue gas temperature. This increases the drying rate but also increases the fire risk in the dryer, all dryers are designed to minimize the fire risk and are equipped with fire suppression systems [101].

One protection used in most air or flue gas dryers is to maintain a low oxygen concentration in the dryer. This can be done by limiting the excess air or by recirculating exhaust gases to dryer inlet. Flue gas dryers typically operate at higher temperatures than air dryers, because of lower oxygen content of the gas [106],[108]. Higher temperatures can also cause problems, such as increasing both the amount of gaseous emissions and the fire risk [100]. The design of the dryer must take into consideration that the temperature of flue gas at outlet of the dryer should be greater than 100 °C to prevent the condensation of acids and resins [108].

Other cause of fires in biomass dryers is the condensation of resins that are released from wood during drying. If dryer exhaust gases cool, or come in contact with cold surfaces, the resin vapours may condense and then attract dust. This dust and resin mixture is very flammable and can ignite [111],[112].

5.2.4 Environmental control

The exhaust gases from a biomass dryer mostly contains sulphur dioxide, carbon dioxide, carbon monoxide and suspended particulate matter as pollutants. SO₂, CO₂ and CO can be removed by adsorption processes before exhaust is released to atmosphere and particles can be removed by cyclones and wet scrubber [101],[108].

The most common problem in biomass dryers is named as “blue haze”. It is caused by the condensing of resins and organic acids after leaving the dryer stack. It might condense on equipment surfaces and thus cause technical problems [101],[112],[113]. These condensable organics may also be counted as particulate matter in some cases [114]. Blue haze is most common with dryers operated at temperature higher than (260°C- 370 °C) [106],[114].

5.3 Heat carrier loop

Heat carrier loop consists of two separate operations. Firstly, the recycling of heat carrier existing pyrolysis reactor, heating it up to desired temperature and then feeding it into reactor. Secondly, pyrolysis process, decomposition of biomass into three pyrolysis products named as biochar, condensate and gas. The twin screw mixing reactor is used for flash pyrolysis, which has been developed by LURGI Company[115]. In existing plant, sand is used as heat carrier loop in a mass ratio of 10:1. The mass flow of the heat carrier depends on the water content of the biomass. Heat carrier loop of sand is heated directly with hot gas up to 510 – 550 °C. During pyrolysis process, a small fraction of the char sticks to sand, which is burnt in a pneumatic rise pipe and supporting the reheating of sand. The heat exchange in pneumatic rise pipe is direct and concurrent flow. The hot flue gas is leaving the pneumatic rise pipe and heading to gas clean-up. Because in pneumatic rise pipe char is burnt again, which increases the emissions and clean-up gas is mandatory before heading it to drying or to environment. The hot flue gas has a temperature of around 490 °C and is used for preheating of air through heat exchanger before entering into pyrolysis gas burner. There are two disadvantages by using heat carrier loop with sand. First one is increase of emissions in exhaust hot flue gas during heating of sand with fraction of char in pneumatic rise pipe due to direct contact of hot gas with sand. Secondly, when sand leaves the reactor downwards and is separated from light char. But fraction of sand mixed with char and which increase the impurities in char and directly effect on properties of char.

In optimized plant, steel balls will be used as heat carrier loop. Steel balls have lower specific heat capacity as compared to sand so due to this reason steel balls used in a mass ratio of 100:1. Heat carrier mass flow for steel balls is 40 t/h on wet basis (15 % water content) and 38.96 t/h on dry basis (12.42 % water content). Steel balls have a diameter of 1.5 mm and a bulk density of 4800 kg/m³. A mechanical bucket elevator is used to transport steel balls from bottom to top. Steel balls are heated indirectly through heat exchanger, advantage of this option is that hot flue gases will not contact with sand having fraction of char and no flue gas clean-up is needed. Disadvantage is lower heat capacity of steel balls and that is why steel balls to biomass ratio is 100:1. Steel balls take 0.1 h for a whole cycle in heat carrier loop so due to this 38.96 t to 40 t steel balls are needed in inventory. The flue gas has a temperature between 650 and 700 °C after leaving the heat exchanger, which can be used to preheat the air before entering into pyrolysis gas burner [98]. From **Figure 5.4** it is clearly visible that flue gas or exhaust gas having temperature 350-400 °C is available as a heat recovery for drying option.

The required thermal energy in case of heat carrier loop with steel balls is 148.17 kW for dried biomass (12.42% water content). The available thermal energy for pyrolysis process is 167.36 kW [98], which is sufficient for heating up the steel balls for pyrolysis process. Some energy is also available in the waste exhaust flue gas for which can be fulfilled the other required thermal energy demand. In this work that waste exhaust gas is used for drying process in flash dryer.

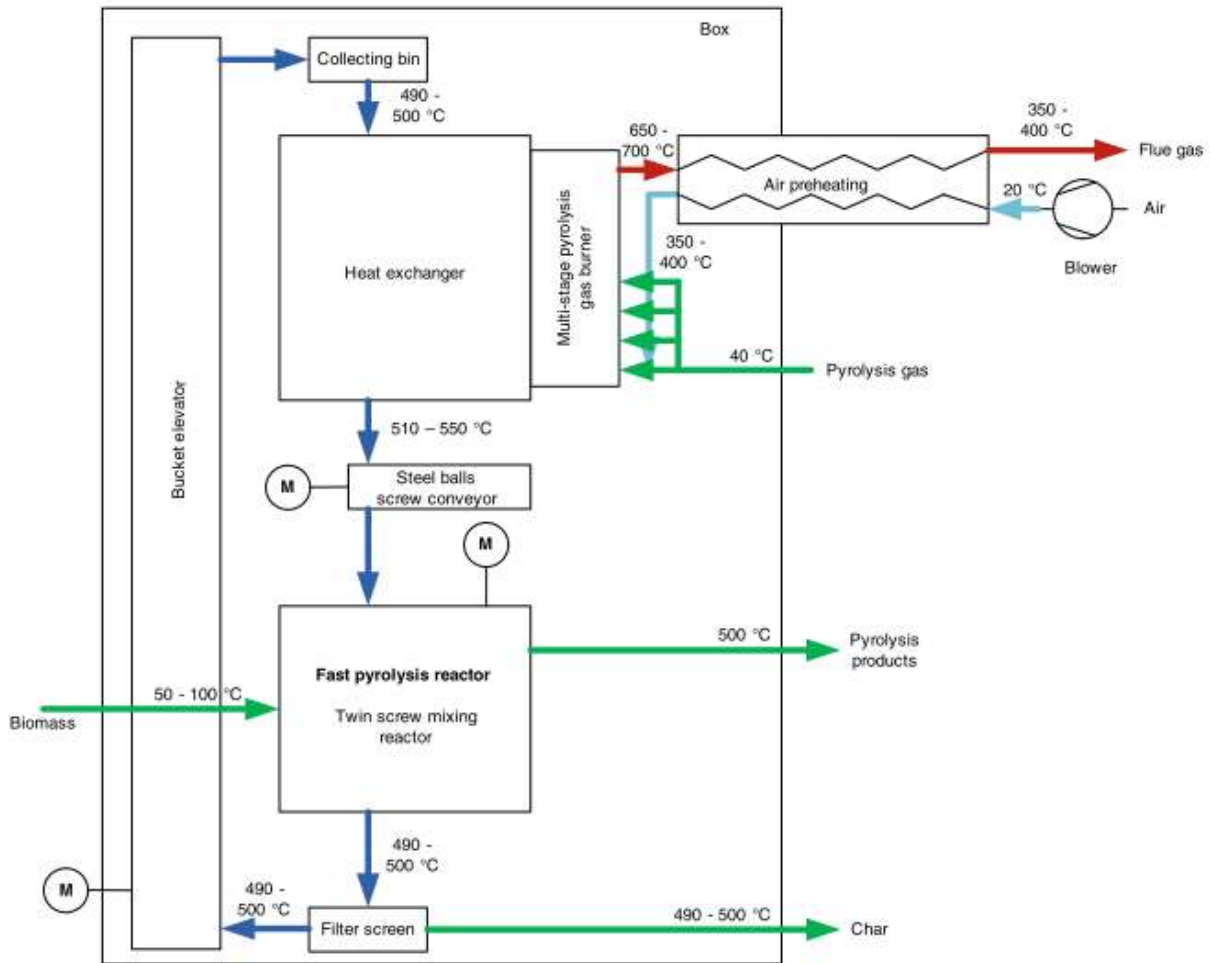


Figure 5.4: Flow sheet of heat carrier loop with heat carrier steel balls [2]

In optimized plant, pyrolysis products consists on solid, liquid and gas, i.e. char, condensate and pyrolysis gas. In this work, pyrolysis gas is used to fulfil the thermal consumption of pyrolysis plant, char is used for production of activated carbon by using (chemical or physical activation) as a precursor and then it will be used for water purification on industrial scale. In bioliq plant, product recovery consists of three step process with a cyclone and two coolers.

The hot pyrolysis products have a temperature of 500 °C after leaving the reactor, when pyrolysis products enter in first stage of three step recovery process, it contains cyclone which removes most of char particles. The char fraction is cooled down to 120°C in a heat exchanger so that waste heat can be used to convert water in to saturated steam that will be further used in production of activated carbon (physical activation). The available waste energy can be calculated by using mass flow rate of char (28 % yield of char) is 112 kg/h, specific heat capacity of biochar is 2556.5 J/(kg K) [116] and $\Delta T = 380$ K. From char particles we can utilize waste heat energy which is 31.81 kW, which can be used in production of saturated steam for physical activation process.

The remaining hot pyrolysis products enters in to quench cooler after leaving cyclone. Heavy organic condensate is recovered that contains most of higher heating value (HHV) of the original biomass. The products are cooled down from 500 °C to between 90 °C and 100 °C to separate the organic condensate. In last stage, products cooled in a gas cooler up to 80 °C in order to separate condensate and water. The recovered aqueous condensate is used again as a quenching medium.

5.4 Activation of biochar

Activation of biochar is comprehensively explained in previous chapter named as 'Materials and Methods'. In this work, temperature required for both chemical and physical activation is 700 °C and which can be provided by burning natural gas because natural gas is cheap non-renewable source among other ones. In this work, I preferred to go for physical activation instead of chemical activation. In comparison, chemical activation process is expensive due to chemical agent used for activation, if chemical recovery is fulfilled then chemical activation process can be preferred on physical activation. In case of physical activation, required thermal energy for steam production will be fulfilled by internal heat recovery up to 43.82% . Chemical activation process requires washing and drying of precursor which requires energy to fulfil this demand. In physical no washing and drying of precursor is required but in some previous work they did washing after physical activation. The precursor should be in powdered or granular form to ensure the homogenous mixture of KOH and precursor for better heat treatment during chemical activation. In physical activation, precursor converted in to pellets by mixing with binder (bio oil). So pellets can be stored and transported easily as compared to powdered or granular activated carbon. In physical activation, we need steam for activation step, steam is produced by extracting waste heat from char particles as explained in hot pyrolysis product recovery. In chemical activation we require heat for drying at different steps, which can be extracted from hot product of activated carbon leaving reactor at 650 °C after chemical activation. Complete description is explained in methodology of project figure 'Materials and Methods' chapter.

Figure 5.5 represents the overview of optimized pyrolysis plant. In plant it is clearly seen that waste heat is used for drying process and steam production. In this work, first required change is basically replacement of sand with steel balls because fraction of char mixed with sand which effects the properties of char and also enhances the emissions problem in exhaust gas. Second required change is implementation of activation step for production of activated carbon as alternative use of biochar on industrial scale. Beneficiary changes are utilization of waste heat of exhaust gas for drying process and the waste heat energy of char can be utilized as thermal energy source for production of steam for activation process. Utilization of exhaust gas in flash dryer for drying process and steam production for physical activation by utilizing char waste heat energy. The waste thermal energy of exhaust gas is utilized in flash dryer for drying process and steam is produced by utilizing waste heat from char for physical activation process.

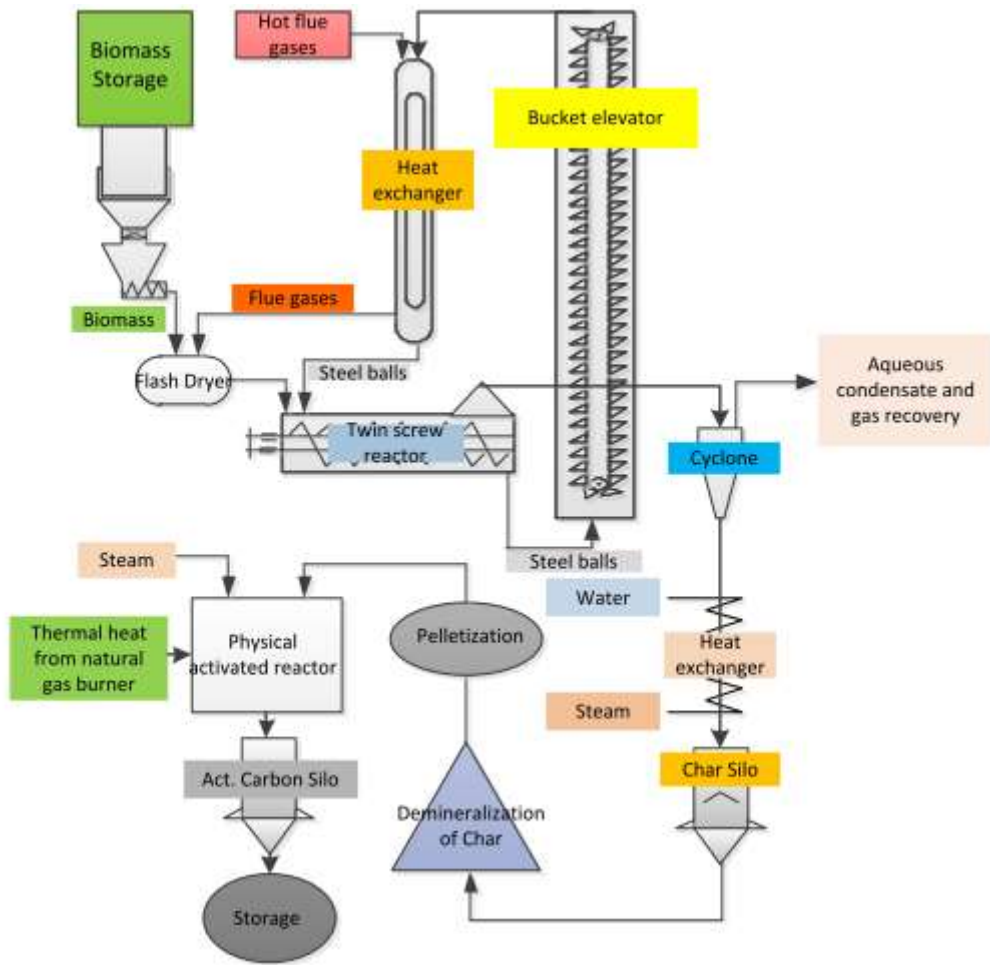


Figure 5.5: Overview of Optimized Pyrolysis plant

6 Conclusions

The results of this thesis include the investigation on demineralization of biochar, chemical activation (KOH) and physical activation (steam) of wheat straw biochar as received from bioliq fast pyrolysis plant. From result of proximate analysis, it could be seen that the biochar had a high percentage of ash content approx. up to 40 % on dry basis. Demineralization of biochar results in reduction of ash content down to 20 % on dry basis. Demineralized char was used as a precursor for production of activated carbon. In chemical activation different operating parameters were varied according to promising conditions such as impregnation ratio, activation temperature, activation time and nitrogen flow rate. BET surface area increased by increasing nitrogen flow rate, impregnation ratio and activation temperature but yield decreased by increasing impregnation ratio and activation temperature in chemical activation process. The effective BET surface area analysed by using N₂ adsorption method is 2900 m²/g and by using liquid phase adsorption named as iodine number is 2567 m²/g. The BET surface area can be controlled by choosing suitable activation parameters. The physical activated carbon was produced by using steam and promising parameters were used in activation of biochar. Investigations were made to prove whether pyrolysis tar can be used as binder material for pelleted activated carbon production. Pellets showed good stability during physical activation process. The effective BET surface area measured by N₂ adsorption method is 510 m²/g. The yield of activated carbon obtained in case of chemical and physical activated carbons were 40 % and 48 % on dry basis respectively. In chemical activation, yield is low due to removal of ash whereas in physical yield decreases due to removal of carbonaceous material while ash content will remained in pelleted activated carbon. Scanning electron microscope was used to determine the surface morphology of activated carbon produced by chemical and physical activation. The scanning electron microscope images gives the comprehensive details of pores present on the surface of activated carbon. The surface morphology of activated prepared from demineralized char had higher number of micropores when precursor char were activated with KOH. The increase in number of pores resulted in higher BET surface area. As an alternative use of biochar, activation step was included in existing bioliq plant. Different heat loads were considered to fulfil the required energy by utilizing waste heat thermal energy. It is proposed that thermal waste heat from exhaust gas is used for drying of biomass by using flash dryer. Thermal waste heat from char could be extracted by using heat exchanger to produce steam for physical activation process.

In summary, highly active powdered activated carbon was prepared, developed and characterised from wheat straw demineralized powder biochar as a precursor by means of chemical activation. In physical activation, highly active pellet activated carbon was prepared and characterised from wheat straw powder biochar as a precursor using bio oil as a binder. This work was aimed to find alternative use of biochar on industrial application and production of activated carbon. Physical activation process has surpassed the chemical activation process because in case of chemical activation process, the big issue was to resolve the problem of chemical recovery after heat treatment. Pellet activated carbon is easy to handle for storage and transportation purposes as compared to powdered chemical activated carbon due to higher bulk density.

For industrial application use activated carbon was proposed to be used in water purification, dissolved organic carbon (DOC) results showed that chemical activated carbon releases 0.05 mg/L impurities during water treatment, which is not so high and could be used for water treatment on industrial scale. The higher micropores and much lower ash content can be obtained by acid washing because all potassium compounds are removed. The washing step has more importance for activated carbons with higher KOH/biochar impregnation ratio.

6.1 Recommendation for further research

1. During chemical activation and physical activation different operating parameters can be varied to just obtain optimum operating conditions for Higher BET surface area.
2. Wheat straw biochar can be activated with different chemical activating agent to check its effect on BET surface area such as H_3PO_4 , $ZnCl_2$ etc. in chemical activation.
3. During chemical activation, nitrogen gas can be replaced by carbon dioxide gas.
4. Wheat straw biochar can be activated with CO_2 gas instead of steam during physical activation to check its effect on surface area.
5. Pelletizing can be done with different binder materials and different binder/char ratios to check its effect on stability and resistance to temperature.
6. Acid washing can be omitted by washing with distilled water, difference can be analysed by treating activated carbons with distilled water.
7. For further research, activated carbon should be used for adsorption of specific compounds such as e.g. heavy metals, pharmaceuticals etc. to check its suitability for an industrial application.
8. It can also be calculated that acid washing could be avoided because results are not different from those obtained with acid washing.
9. In optimization of bioliq plant, different options can be considered. For drying, we can use superheated steam which has a minimal fire risk and latent heat of vaporization from drying can be recovered and no heat losses occur.
10. After physical activation, saturated steam is converted in to superheated steam due to inside reactor temperature and that energy can fulfilled the other requirement within bioliq plant.

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Appendix A

Demineralized biochar ash content TGA results

Appendix Table 1: TGA ash content result for demineralized biochar with 1 N

Analysis	Investigation results		
	Remarks	Unit	results
TV	2.8/2.7	%	2.8
GLR-Fest-550	20.7/19.7	%	20.2
GLR-Fest-815	20.5/19.5	%	20.0
GLR-Fest-1000	20.1/19.1	%	19.6

Appendix Table 2: TGA ash content result for demineralized biochar with 2 N

Analysis	Investigation results		
	Remarks	Unit	results
TV	0.7/0.7	%	0.7
GLR-Fest-550	22.4/22.4	%	22.4
GLR-Fest-815	22.2/22.2	%	22.2
GLR-Fest-1000	21.7/21.8	%	21.8

Appendix Table 3: TGA ash content result for 2900 m²/g chemical activated carbon

Analysis	Investigation results		
	Remarks	Unit	results
TV	-	%	9.9
GLR-Fest-550	-	%	0.7
GLR-Fest-815	-	%	0.7
GLR-Fest-1000	-	%	0.7

Appendix Table 4: TGA ash content result for 510 m²/g physical activated carbon

Analysis	Investigation results		
	Remarks	Unit	results
TV	2.5/2.5	%	2.5
GLR-Fest-550	38.9/38.9	%	38.9
GLR-Fest-815	38.2/38.2	%	38.2
GLR-Fest-1000	38.0/38.0	%	38.0

Appendix B

N₂ Adsorption (BET surface area) results for simple and demineralized biochar

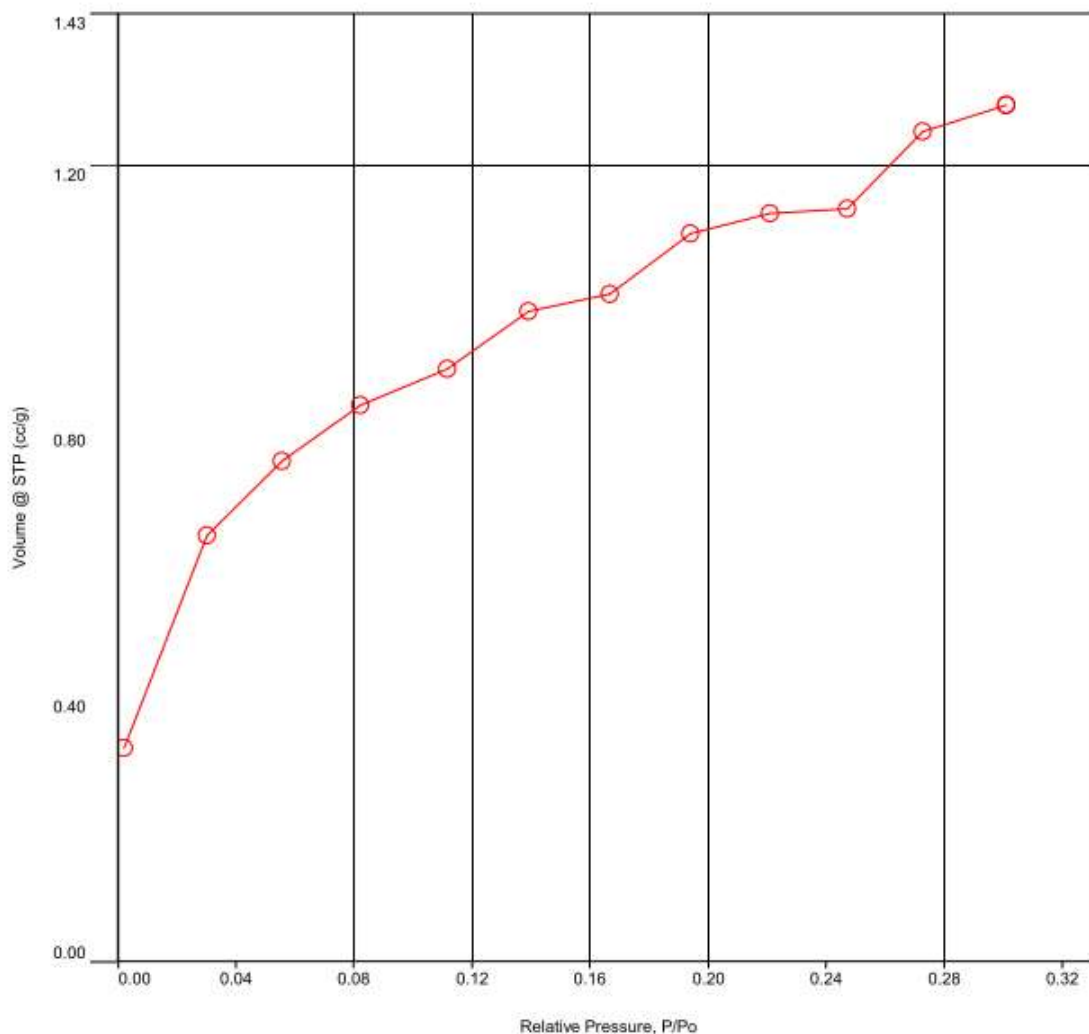
Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
©1994-2010, Quantachrome Instruments
version 11.0



Analysis		Report	
Operator: Quantachrome	Date: 2014/05/13	Operator: Torben	Date: 7/10/2014
Sample ID: Sample-6	Filename:	C:\NOVA-Messungen\Torben Rottgardt\031B_TR_Sample-6.qps	
Sample Desc:	Comment:		
Sample weight: 1.3091 g	Sample Volume: 0 cc		
Outgas Time: 1.0 hrs	Outgas Temp: 350.0 C		
Analysis gas: Nitrogen	Bath Temp: 77.3 K		
Press. Tolerance: 0.100/0.100 (ads/des)	Equil time: 120/120 sec (ads/des)	Equil timeout: 1200/480 sec (ads/des)	
Analysis Time: 86.2 min	End of run: 2014/05/13 8:34:43	Instrument: Nova Station A	
Cell ID: 0		F/W version: 0.00	

Isotherm * Linear

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350K
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²
		Liquid Density:	0.808 g/cc



Appendix Figure 1: N₂ adsorption report for BET surface area 4 m²/g

Analysis

Operator: Quantachrome
Sample ID: Sample-5
Sample Desc:
Sample weight: 1.9556 g
Outgas Time: 1.0 hrs
Analysis gas: Nitrogen
Press. Tolerance: 0.100/0.100 (ads/des)
Analysis Time: 504.3 min
Cell ID: 0

Date: 2014/05/12

Filename:
Comment:
Sample Volume: 0 cc
Outgas Temp: 350.0 C
Bath Temp: 77.3 K
Equil time: 120/120 sec (ads/des)
End of run: 2014/05/12 19:58:09

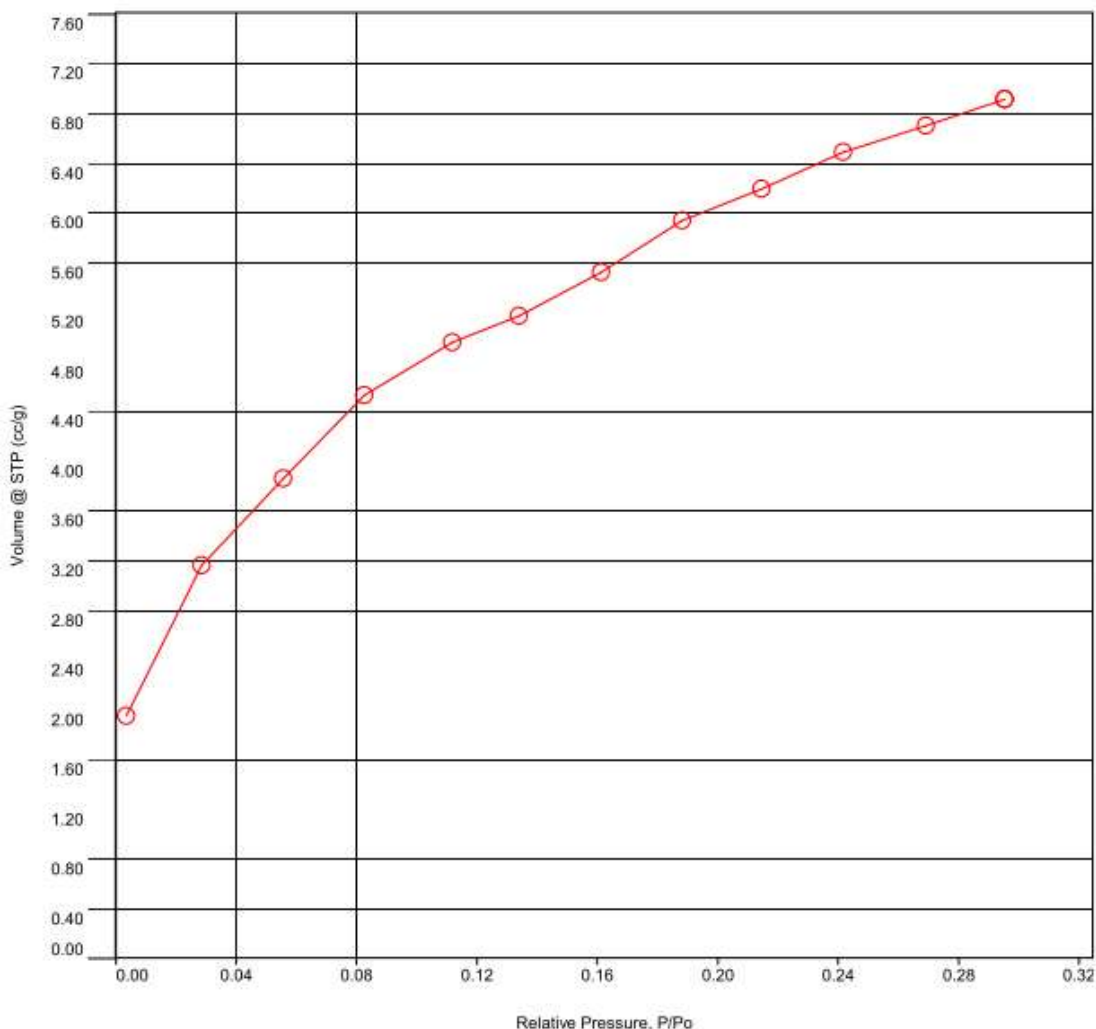
Report

Operator: Torben
Date: 7/10/2014
C:\NOVA-Messungen\Torben Rottgardt\030B_TR_Sample-5.qps

Equil timeout: 1200/480 sec (ads/des)
Instrument: Nova Station A
F/W version: 0.00

Isotherm * Linear

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350 K
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²
		Liquid Density:	0.808 g/cc



Appendix Figure 2: N₂ adsorption report for BET surface area 23.5 m²/g

N₂ Adsorption (BET surface area) results for chemical activated carbon

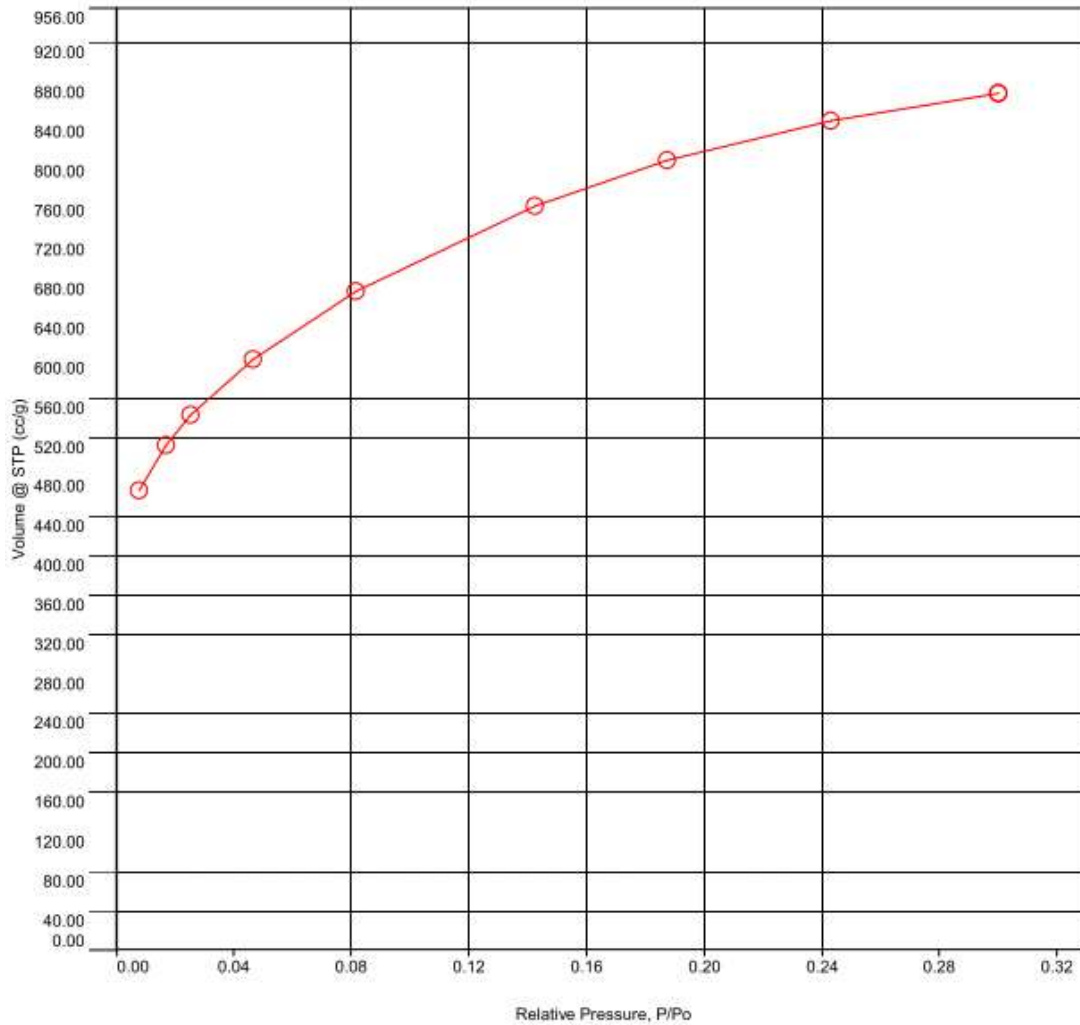
Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
©1994-2010, Quantachrome Instruments
version 11.0



Analysis	Report	
Operator: ES	Date: 2014/07/02	Operator: Torben
Sample ID: Standart	Filename: T:\mujtaba\CA-1 Chemical activated.qps	Date: 7/10/2014
Sample Desc:	Comment: CA-1 Chemical activated	
Sample weight: 0.0145 g	Sample Volume: 0 cc	
Outgas Time: 24.0 hrs	Outgas Temp: 140.0 C	
Analysis gas: Nitrogen	Bath Temp: 77.3 K	
Press. Tolerance: 0.100/0.100 (ads/des)	Equil time: 120/120 sec (ads/des)	Equil timeout: 240/240 sec (ads/des)
Analysis Time: 229.4 min	End of run: 2014/07/02 14:20:31	Instrument: Nova Station A
Cell ID: 67		FW version: 0.00

Isotherm * Linear

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350K
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²
		Liquid Density:	0.808 g/cc

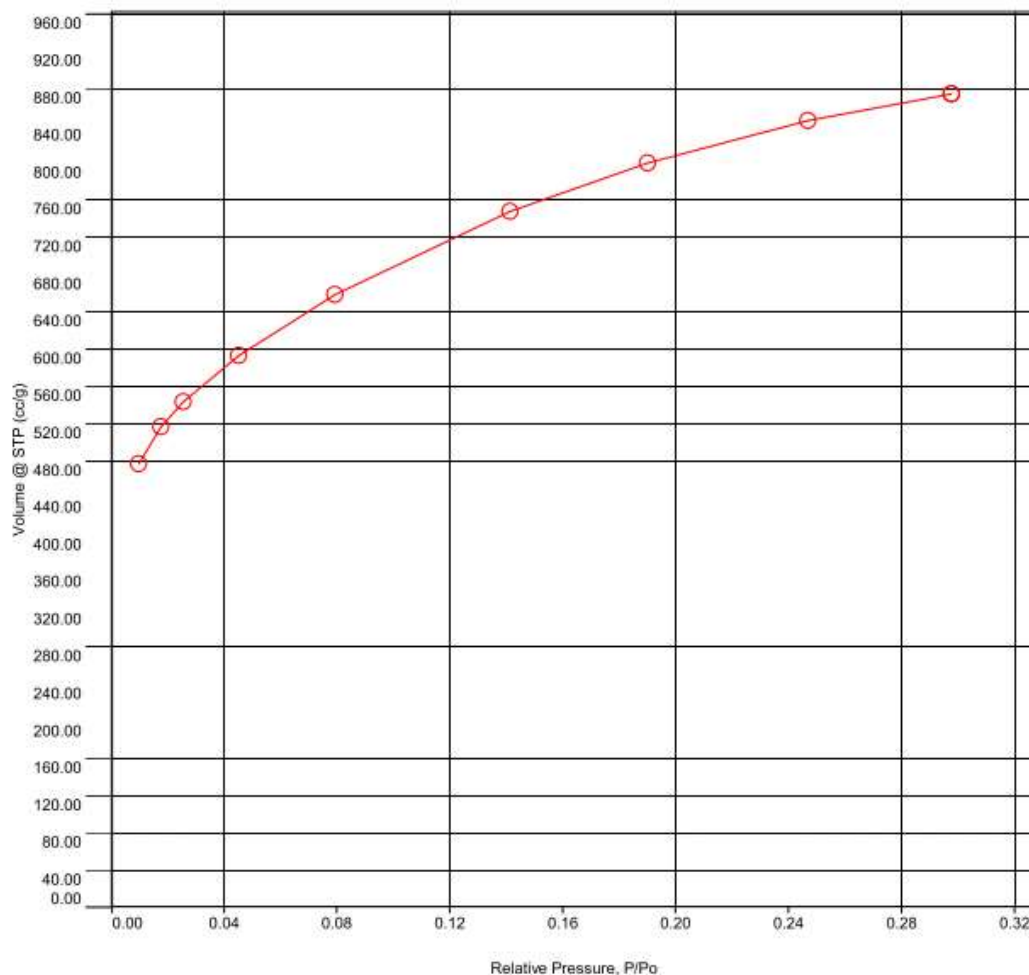


Appendix Figure 3: N₂ adsorption report for BET surface area 2900 m²/g

Analysis		Report	
Operator: ES	Date: 2014/07/02	Operator: Torben	Date: 7/10/2014
Sample ID: Standart	Filename: T:\mujtaba\CA-3 Chemical activated.qps	Sample Volume: 0 cc	
Sample Desc:	Comment: CA-3 Chemical activated	OutgasTemp: 140.0 C	
Sample weight: 0.0169 g	Bath Temp: 77.3 K	Equil time: 120/120 sec (ads/des)	Equil timeout: 240/240 sec (ads/des)
Outgas Time: 24.0 hrs	End of run: 2014/07/02 14:31:56	Instrument: Nova Station C	FW version: 0.00
Analysis gas: Nitrogen			
Press. Tolerance: 0.100/0.100 (ads/des)			
Analysis Time: 240.8 min			
Cell ID: 70			

Isotherm * Linear

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350K
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²
		Liquid Density:	0.808 g/cc



Appendix Figure 4: N₂ adsorption report for BET surface area 2886 m²/g

Analysis

Operator:ES
Sample ID: Standart
Sample Desc:
Sample weight: 0.0145 g
Outgas Time: 20.0 hrs
Analysis gas: Nitrogen
Press. Tolerance: 0.100/0.100 (ads/des)
Analysis Time: 235.2 min
Cell ID: 64

Date:2014/07/02

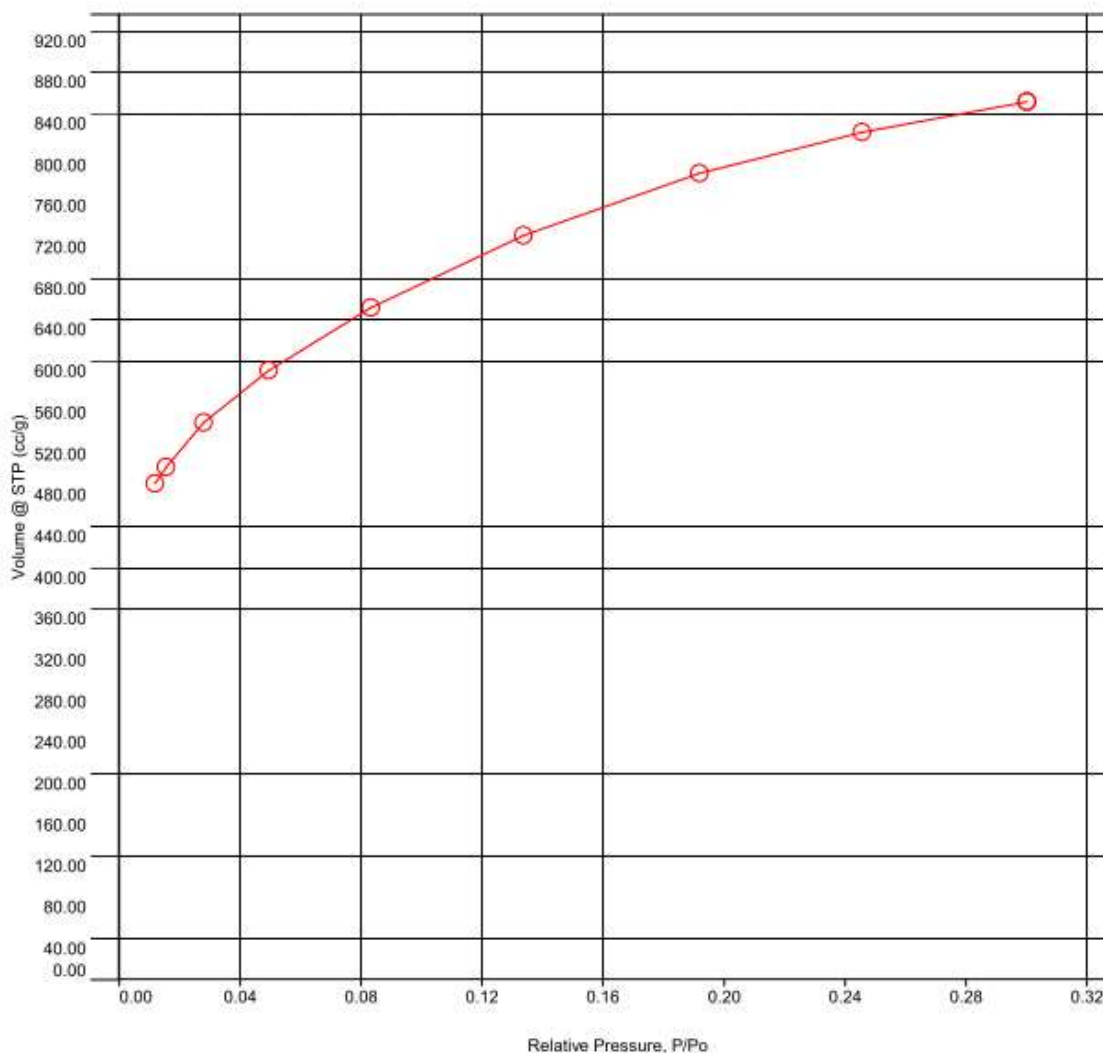
Filename:
Comment: CA-2 Chemical activated
Sample Volume: 0 cc
OutgasTemp: 140.0 C
Bath Temp: 77.3 K
Equil time: 120/120 sec (ads/des)
End of run: 2014/07/02 14:26:20

Report

Operator:Torben
Date:7/10/2014
T:\mujtaba\CA-2 Chemical activated.qps
Equil timeout: 240/240 sec (ads/des)
Instrument: Nova Station B
F/W version: 0.00

Isotherm * Linear

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350K
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²
		Liquid Density:	0.808 g/cc



Appendix Figure 5: N₂ adsorption report for BET surface area 2813 m²/g

N₂ Adsorption (BET surface area) results for physical activated carbon

Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
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version 11.0



Analysis

Operator: ES
Sample ID: Standart
Sample Desc:
Sample weight: 0.1296 g
Outgas Time: 24.0 hrs
Analysis gas: Nitrogen
Press. Tolerance: 0.100/0.100 (ads/des)
Analysis Time: 233.0 min
Cell ID: 63

Date: 2014/07/04

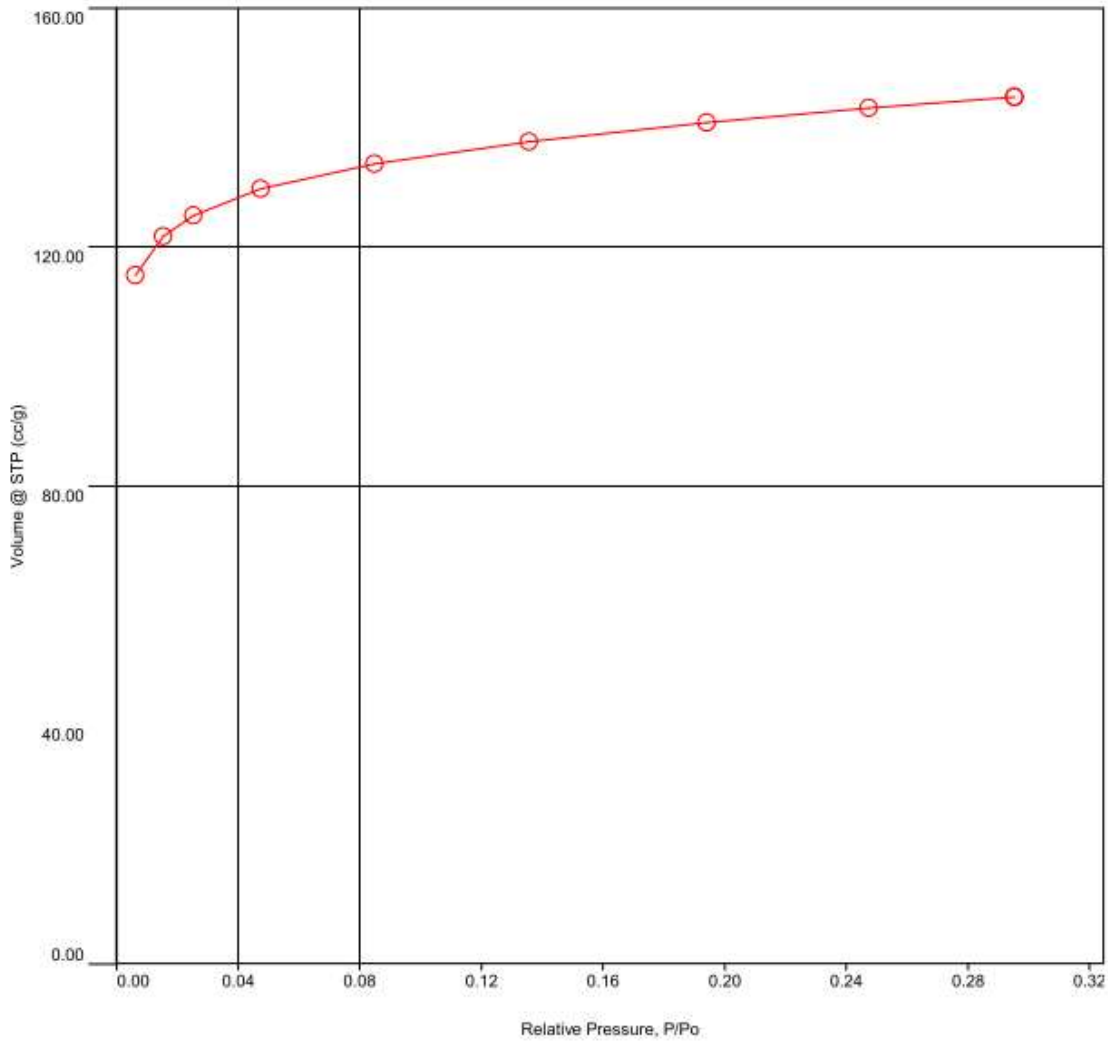
Filename: T:\mujtabal\Physical Activation AC 4.qps
Comment: Physical Activation AC 4
Sample Volume: 0 cc
Outgas Temp: 140.0 C
Bath Temp: 77.3 K
Equil time: 120/120 sec (ads/des)
End of run: 2014/07/04 14:07:16

Report

Operator: Torben
Date: 7/10/2014
Equil timeout: 240/240 sec (ads/des)
Instrument: Nova Station D
FW version: 0.00

Isotherm * Linear

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350K
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²
		Liquid Density:	0.808 g/cc



Appendix Figure 6: N₂ adsorption report for BET surface area 545 m²/g

Analysis

Operator: ES
Sample ID: Standart
Sample Desc:
Sample weight: 0.1249 g
Outgas Time: 24.0 hrs
Analysis gas: Nitrogen
Press. Tolerance: 0.100/0.100 (ads/des)
Analysis Time: 228.6 min
Cell ID: 70

Date: 2014/07/04

Filename: T:\mujtaba\Physical Activation AC 3.qps
Comment: Physical Activation AC 3
Sample Volume: 0 cc
Outgas Temp: 140.0 C
Bath Temp: 77.3 K
Equil time: 120/120 sec (ads/des)
End of run: 2014/07/04 14:02:55

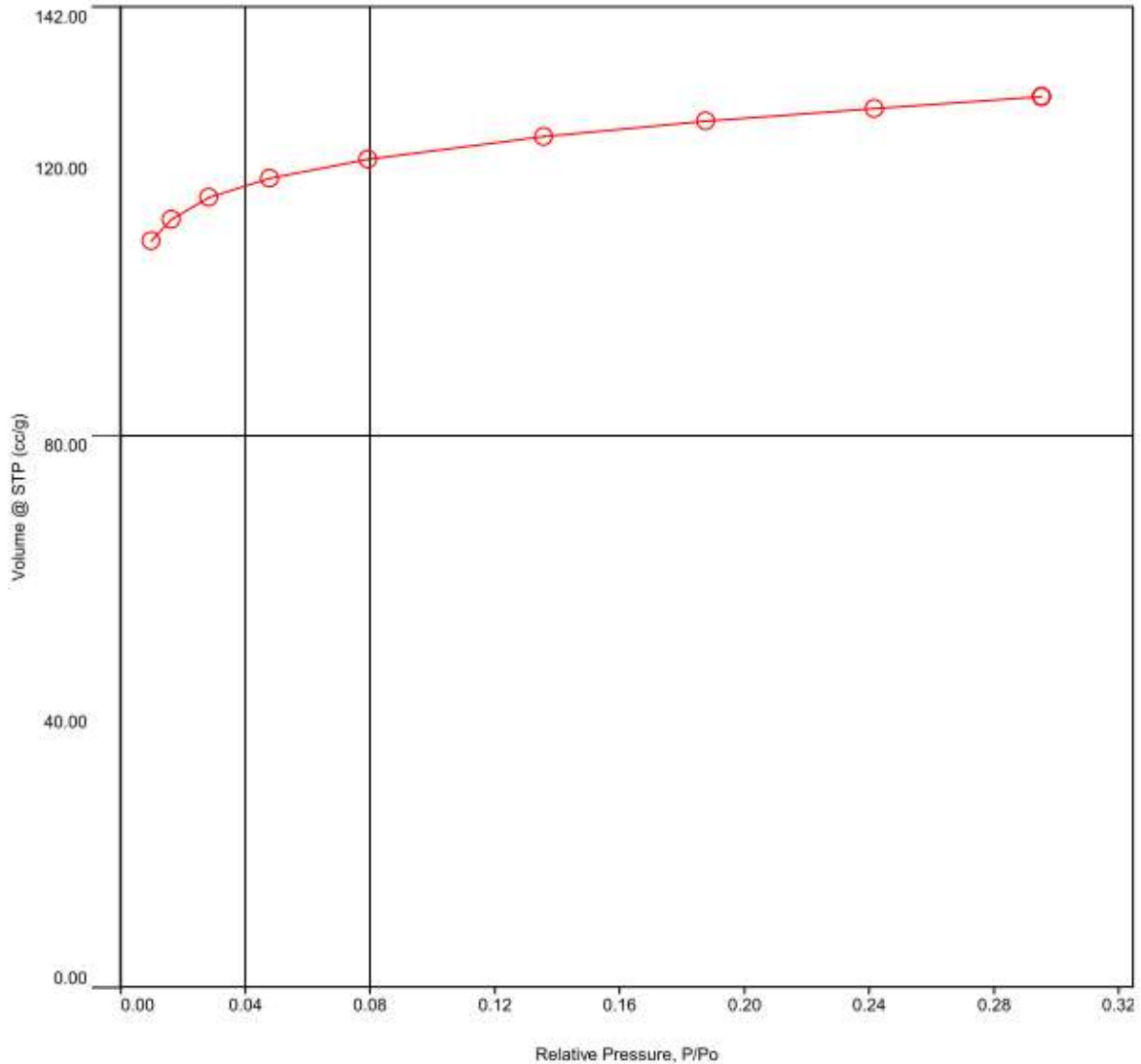
Report

Operator: Torben
Date: 7/10/2014
Equil timeout: 240/240 sec (ads/des)
Instrument: Nova Station C
FW version: 0.00

Isotherm * Linear

Data Reduction Parameters

Adsorbate	Nitrogen	Temperature	77.350K	Liquid Density:	0.808 g/cc
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²		



Appendix Figure 7: N₂ adsorption report for BET surface area 490 m²/g

Analysis

Operator: ES
Sample ID: Standart
Sample Desc:
Sample weight: 0.1336 g
Outgas Time: 20.0 hrs
Analysis gas: Nitrogen
Press. Tolerance: 0.100/0.100 (ads/des)
Analysis Time: 224.4 min
Cell ID: 69

Date: 2014/07/04

Filename: T:\mujtaba\Physical Activation AC 2.qps
Comment: Physical Activation AC 2
Sample Volume: 0 cc
Outgas Temp: 140.0 C
Bath Temp: 77.3 K
Equil time: 120/120 sec (ads/des)
End of run: 2014/07/04 13:58:42

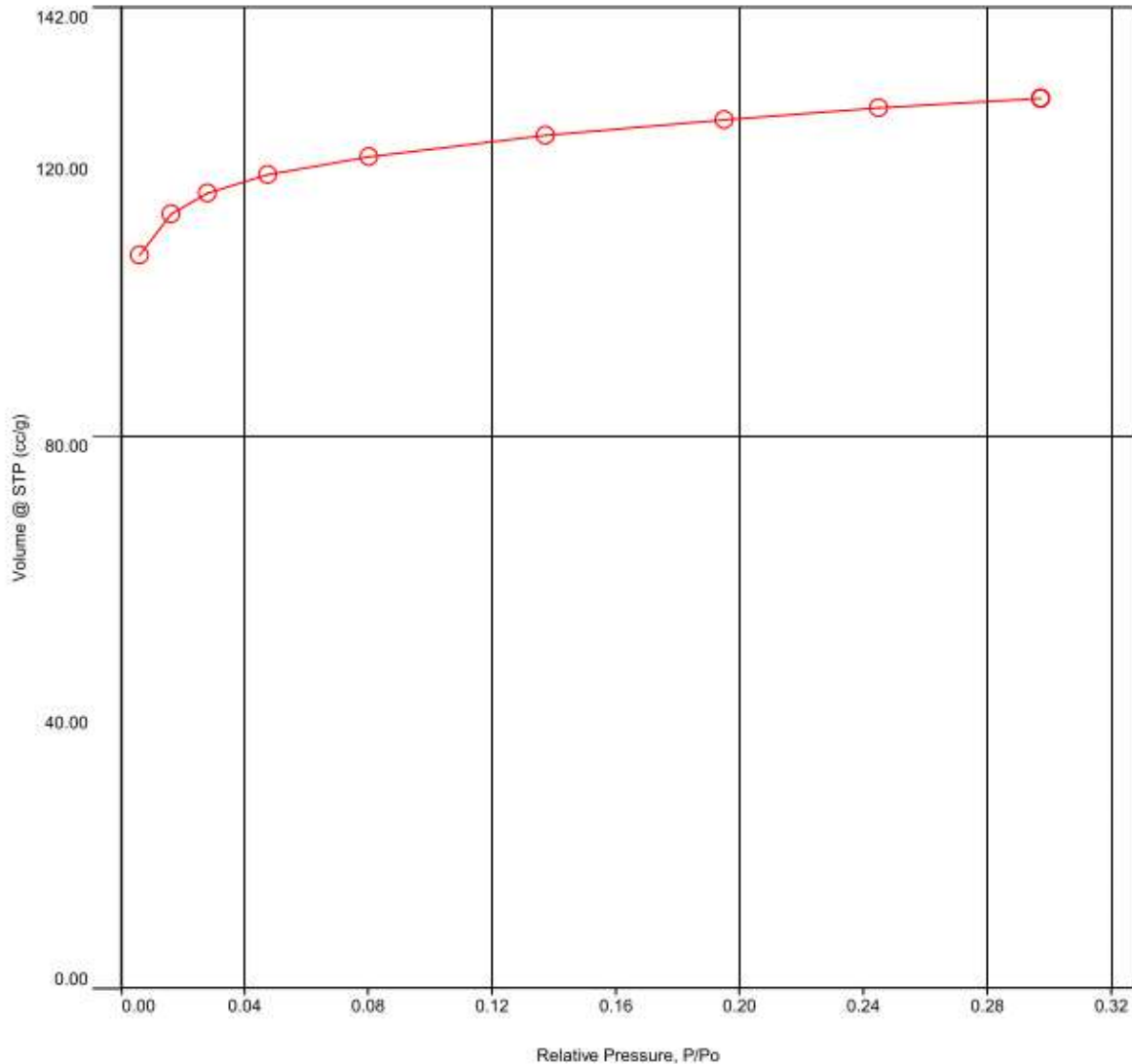
Report

Operator: Torben
Date: 7/10/2014
Equil timeout: 240/240 sec (ads/des)
Instrument: Nova Station B
F/W version: 0.00

Isotherm * Linear

Data Reduction Parameters

Adsorbate	Nitrogen	Temperature	77.350K	Liquid Density:	0.808 g/cc
	Molec. Wt.: 28.013 g	Cross Section:	16.200 Å ²		



Appendix Figure 8: N₂ adsorption report for BET surface area 492 m²/g

Appendix Table 5: The values of BET surface area and Yield of physical activated carbon prepared at T = 750 °C, steam flow rate 300 mg/min, time = 1 h and binder ratio (char / bio oil) = 1:0.65, db (dry basis)

	PA 1	PA 2	PA 3
BET Surface Area (m ² /g)	493 ± 26.97	491 ± 26.97	545 ± 26.97
Yield (wt. %) (db)	48 ± 0.362%	48.3± 0.362%	47.6 ± 0.362%

Appendix C

Standard Test Method for Determination of Iodine Number of Activated Carbon (D4607-94)



Standard Test Method for Determination of Iodine Number of Activated Carbon¹

This standard is issued under the fixed designation D4607; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the relative activation level of unused or reactivated carbons by adsorption of iodine from aqueous solution. The amount of iodine absorbed (in milligrams) by 1 g of carbon using test conditions listed herein is called the iodine number.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*²

C819 Test Method for Specific Surface Area of Carbon or Graphite (Withdrawn 1987)³

D1193 Specification for Reagent Water

D2652 Terminology Relating to Activated Carbon

D2867 Test Methods for Moisture in Activated Carbon

D3860 Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E287 Specification for Laboratory Glass Graduated Burets

E288 Specification for Laboratory Glass Volumetric Flasks

E300 Practice for Sampling Industrial Chemicals

¹ This test method is under the jurisdiction of ASTM Committee D28 on Activated Carbon and is the direct responsibility of Subcommittee D28.02 on Liquid Phase Evaluation.

Current edition approved March 1, 2011. Published May 2011. Originally approved in 1986. Last previous edition approved in 2006 as D4607 – 94 (2006). DOI: 10.1520/D4607-94R11.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

2.2 *NIST Publication:*

Circular 602—Testing of Glass Volumetric Apparatus⁴

3. Summary of Test Method

3.1 This test method is based upon a three-point adsorption isotherm (see Practices D3860). A standard iodine solution is treated with three different weights of activated carbon under specified conditions. The carbon treated solutions are filtered to separate the carbon from the treated iodine solution (filtrate). Iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of carbon is determined for each carbon dosage and the resulting data used to plot an adsorption isotherm. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.02 N is reported as the iodine number.

3.2 Iodine concentration in the standard solution affects the capacity of an activated carbon for iodine adsorption. Therefore, the normality of the standard iodine solution must be maintained at a constant value ($0.100 \pm 0.001 N$) for all iodine number measurements.

3.3 The apparatus required consists of various laboratory glassware used to prepare solutions and contact carbon with the standard iodine solution. Filtration and titration equipment are also required.

4. Significance and Use

4.1 The iodine number is a relative indicator of porosity in an activated carbon. It does not necessarily provide a measure of the carbon's ability to absorb other species. Iodine number may be used as an approximation of surface area for some types of activated carbons (see Test Method C819). However, it must be realized that any relationship between surface area and iodine number cannot be generalized. It varies with changes in carbon raw material, processing conditions, and pore volume distribution (see Definitions D2652).

4.2 The presence of adsorbed volatiles, sulfur, and water extractables may affect the measured iodine number of an activated carbon.

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

5. Apparatus

NOTE 1—All volumetric measuring equipment should meet or exceed the requirements of NIST Circular 602. Volumetric glassware meeting these specifications is generally designated as “Class A”. See also Specifications E287 and E288.

- 5.1 *Analytical Balance*, accuracy ± 0.0001 g.
- 5.2 *Buret*, 10-mL capacity or 5-mL precision buret.
- 5.3 *Flasks*, Erlenmeyer 250-mL capacity with ground glass stoppers.
- 5.4 *Flask*, Erlenmeyer wide-mouthed, 250-mL capacity.
- 5.5 *Beakers*, assorted sizes.
- 5.6 *Bottles*, amber, for storage of iodine and thiosulfate solutions.
- 5.7 *Funnels*, 100-mm top inside diameter.
- 5.8 *Filter Paper*, 18.5-cm prefolded paper, Whatman No. 2V or equivalent.
- 5.9 *Pipets*, volumetric type, 5.0, 10.0, 25.0, 50.0, and 100.0-mL capacity.
- 5.10 *Volumetric Flasks*, 1 L.
- 5.11 *Graduated Cylinders*, 100 mL and 500 mL.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—References to water shall be understood to mean reagent water conforming to Specification D1193 for Type II reagent water.

- 6.3 *Hydrochloric Acid*, concentrated.
- 6.4 *Sodium Thiosulfate*, ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$).
- 6.5 *Iodine*, United States Pharmacopeia, resublimed crystals.
- 6.6 *Potassium Iodide*.
- 6.7 *Potassium Iodate*, primary standard.
- 6.8 *Starch*, soluble potato or arrowroot.
- 6.9 *Sodium Carbonate*.

7. Hazards

7.1 Several potential hazards are associated with conducting this test procedure. It is not the purpose of this standard to address all potential health and safety hazards encountered with its use. The user is responsible for establishing appropriate

health and safety practices before use of this test procedure. Determine the applicability of federal and state regulations before attempting to use this test method.

7.2 Personnel conducting the iodine number procedure should be aware of potential safety and health hazards associated with the chemicals used in this procedure. The “Material Safety Data Sheet” (MSDS) for each reagent listed in Section 6 should be read and understood. Special precautions to be taken during use of each reagent are included on the “Material Safety Data Sheet” (MSDS). First aid procedures for contact with a chemical are also listed on its “MSDS.” A “Material Safety Data Sheet” for each reagent may be obtained from the manufacturer. Other safety and health hazard information on reagents used in this procedure is available.^{6,7,8}

7.3 Careful handling and good laboratory technique should always be used when working with chemicals. Avoid contact with hydrochloric acid or acid vapor. Care should also be taken to prevent burns during heating of various solutions during this test procedure.

7.4 The user of this test method should comply with federal, state, and local regulations for safe disposal of all samples and reagents used.

8. Preparation of Solutions

8.1 *Hydrochloric Acid Solution (5 % by weight)*—Add 70 mL of concentrated hydrochloric acid to 550 mL of distilled water and mix well. A graduated cylinder may be used for measurement of volume.

8.2 *Sodium Thiosulfate (0.100 N)*—Dissolve 24.820 g of sodium thiosulfate in approximately 75 ± 25 mL of freshly boiled distilled water. Add 0.10 ± 0.01 g of sodium carbonate to minimize bacterial decomposition of the thiosulfate solution. Quantitatively transfer the mixture to a 1-L volumetric flask and dilute to the mark. Allow the solution to stand at least 4 days before standardizing. The solution should be stored in an amber bottle.

8.3 *Standard Iodine Solution (0.100 \pm 0.001 N)*—Weigh 12.700 g of iodine and 19.100 g of potassium iodide (KI) into a beaker. Mix the dry iodine and potassium iodide. Add 2 to 5 mL of water to the beaker and stir well. Continue adding small increments of water (approximately 5 mL each) while stirring until the total volume is 50 to 60 mL. Allow the solution to stand a minimum of 4 h to ensure that all crystals are thoroughly dissolved. Occasional stirring during this 4-h period will aid in the dissolution. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. It is important that the standard iodine solution has an iodide-to-iodine weight ratio of 1.5 to 1. Store the solution in an amber bottle.

⁵ “Reagent Chemicals, American Chemical Society Specifications,” Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see “Reagent Chemicals and Standards,” by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the “United States Pharmacopeia.”

⁶ The “Chemical Safety Data Sheet” for the subject chemical is available from the Manufacturing Chemists Association, Washington, DC.

⁷ Sax, N. I., *Dangerous Properties of Industrial Materials*, 4th edition, 1975, Van Nostrand Reinhold Company, New York, NY.

⁸ *NIOSH/OSHA Pocket Guide to Chemical Hazards*, 1978, U.S. Department of Labor, Occupational Safety and Health Administration, Washington, DC. Available from U.S. Government Printing Office, Washington, DC.

8.4 *Potassium Iodate Solution* (0.1000 *N*)—Dry 4 or more grams of primary standard grade potassium iodate (KIO₃) at 110 ± 5°C for 2 h and cool to room temperature in a desiccator. Dissolve 3.5667 ± 0.1 mg of the dry potassium iodate in about 100 mL of distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. Mix thoroughly and store in a glass-stoppered bottle.

8.5 *Starch Solution*—Mix 1.0 ± 0.5 g of starch with 5 to 10 mL of cold water to make a paste. Add an additional 25 ± 5 mL of water while stirring to the starch paste. Pour the mixture, while stirring, into 1 L of boiling water and boil for 4 to 5 min. This solution should be made fresh daily.

9. Standardization of Solutions

9.1 *Standardization of 0.100 N Sodium Thiosulfate* —Pipet 25.0 mL of potassium iodate (KIO₃) solution from 8.4 into a 250-mL titration (or wide-mouthed Erlenmeyer) flask. Add 2.00 ± 0.01 g of potassium iodide (KI) to the flask and shake the flask to dissolve the potassium iodide crystals. Pipet 5.0 mL of concentrated hydrochloric acid into the flask. Titrate the free iodine with sodium thiosulfate solution until a light yellow color is observed in the flask. Add a few drops of starch indicator (8.5) and continue the titration dropwise until one drop produces a colorless solution. Determine sodium thiosulfate normality as follows:

$$N_1 = (P \cdot R) / S \quad (1)$$

where:

- N_1 = sodium thiosulfate, *N*,
- P = potassium iodate, mL,
- R = potassium iodate, *N*, and
- S = sodium thiosulfate, mL.

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceeds 0.003 *N*.

9.2 *Standardization of 0.100 ± 0.001 N Iodine Solution*—Pipet 25.0 mL of iodine solution (8.3) into a 250-mL wide-mouthed Erlenmeyer flask. Titrate with standardized sodium thiosulfate (9.1) until the iodine solution is a light yellow color. Add a few drops of starch indicator and continue titration dropwise until one drop produces a colorless solution. Determine the iodine solution normality as follows:

$$N_2 = (S \cdot N_1) / I \quad (2)$$

where:

- N_2 = iodine, *N*,
- S = sodium thiosulfate, mL,
- N_1 = sodium thiosulfate, *N*, and
- I = iodine, mL.

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceeds 0.003 *N*. The iodine solution concentration must be 0.100 ± 0.001 *N*. If this requirement is not met, repeat 8.3 and 9.2.

10. Procedure

10.1 The procedure applies to either powdered or granular activated carbon. When granular carbon is to be tested, grind a representative sample (see Practice E300) of carbon until 60 wt % (or more will pass through a 325-mesh screen) and 95 wt % or more will pass through a 100-mesh screen (U.S. sieve series, see Specification E11). Carbon received in the powdered form may need additional grinding to meet the particle size requirement given above.

10.2 Dry the ground carbon from 10.1 in accordance with Test Method D2867. Cool the dry carbon to room temperature in a desiccator.

10.3 Determination of iodine number requires an estimation of three carbon dosages. Section 11.4 describes how to estimate the carbon dosages to be used. After estimating carbon dosages, weigh three appropriate amounts of dry carbon to the nearest milligram. Transfer each weighed sample of carbon to a clean, dry 250-mL Erlenmeyer flask equipped with a ground glass stopper.

10.4 Pipet 10.0 mL of 5 wt % hydrochloric acid solution into each flask containing carbon. Stopper each flask and swirl gently until the carbon is completely wetted. Loosen the stoppers to vent the flasks, place on a hot plate in a fume hood, and bring the contents to a boil. Allow to boil gently for 30 ± 2 s to remove any sulfur which may interfere with the test results. Remove the flasks from the hot plate and cool to room temperature.

10.5 Pipet 100.0 mL of 0.100 *N* iodine solution into each flask. Standardize the iodine solution just prior to use. Stagger the addition of iodine to the three flasks so that no delays are encountered in handling. Immediately stopper the flasks, and shake the contents vigorously for 30 ± 1 s. Quickly filter each mixture by gravity through one sheet of folded filter paper (Whatman No. 2V or equivalent) into a beaker. Filtration equipment must be prepared in advance so no delay is encountered in filtering the samples.

10.6 For each filtrate, use the first 20 to 30 mL to rinse a pipet. Discard the rinse portions. Use clean beakers to collect the remaining filtrates. Mix each filtrate by swirling the beaker and pipet 50.0 mL of each filtrate into a clean 250-mL Erlenmeyer flask. Titrate each filtrate with standardized 0.100 *N* sodium thiosulfate solution until the solution is a pale yellow. Add 2 mL of the starch indicator solution and continue the titration with sodium thiosulfate until one drop produces a colorless solution. Record the volume of sodium thiosulfate used.

11. Calculation

11.1 The capacity of a carbon for any adsorbate is dependent upon the concentration of the adsorbate in solution. The concentrations of the standard iodine solution and filtrates must be specified or known. This is necessary to determine an appropriate carbon weight to produce final concentrations agreeing with the definition of iodine number. The amount of carbon sample to be used in the determination is governed by the activity of the carbon. If filtrate normalities (*C*) are not

within the range of 0.008 *N* to 0.040 *N*, repeat the procedure using different carbon weights.

11.2 Two calculations are required for each carbon dosage, as *X/M* and *C*.

11.2.1 To calculate the value of *X/M*, first derive the following values:

$$A = (N_2) (12693.0) \tag{3}$$

where:

*N*₂ = iodine, *N* (from 9.2).

$$B = (N_1) (126.93) \tag{4}$$

where:

*N*₁ = sodium thiosulfate, *N* (from 9.1).

$$DF = (I+H)/F \tag{5}$$

where:

- DF* = dilution factor,
- I* = iodine, mL (from 9.2),
- H* = 5 % hydrochloric acid used, mL, and
- F* = filtrate, mL.

For example, if 10 mL of HCl and 50 mL of filtrate are used:
 $DF = (100 + 10)/50 = 2.2$.

11.2.1.1 Calculate the value of *X/M* as follows:

$$X/M = [A - (DF) (B) (S)]/M \tag{6}$$

where:

- X/M* = iodine absorbed per gram of carbon, mg/g,
- S* = sodium thiosulfate, mL, and
- M* = carbon used, g.

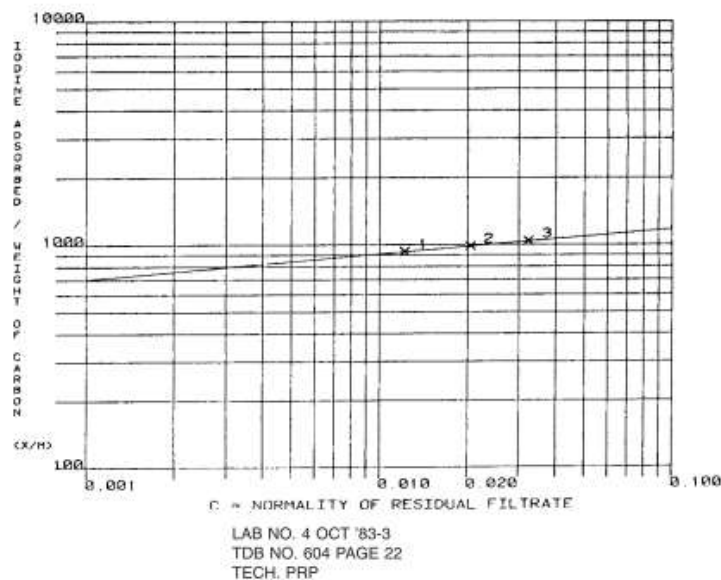
11.2.2 Calculate the value of *C* as follows:

$$C = (N_1 \cdot S)/F \tag{7}$$

where:

- C* = residual filtrate, *N*,
- N*₁ = sodium thiosulfate, *N*, and
- F* = filtrate, mL.

11.3 Using logarithmic paper, plot *X/M* (as the ordinate) versus *C* (as the abscissa) for each of the three carbon dosages (see Fig. 1). Calculate the least squares fit for the three points and plot. The iodine number is the *X/M* value at a residual



POINT 1		
X/M	-	932
C	-	0.012
POINT 2		
X/M	-	964
C	-	0.020
POINT 3		
X/M	-	1040
C	-	0.032
IODINE NO.	-	964
SLOPE	-	0.111
CORR. COEF.	-	0.999

FIG. 1 Activated Carbon Iodine Adsorption Isotherm

iodine concentration (C) of 0.02 N . The regression coefficient for the least squares fit should be greater than 0.995.

11.4 Carbon dosage may be estimated as follows:

$$M = [A - (DF)(C)(126.93)(50)]/E \quad (8)$$

where:

- M = carbon, g,
- A = (N_2) (12693.0),
- DF = dilution factor (see 11.2.1),
- C = residual iodine, and
- E = estimated iodine number of the carbon.

Three carbon dosages are calculated using three values of C (usually 0.01, 0.02, and 0.03).

12. Report

12.1 The reports should include the following:

12.1.1 Complete identification of the sample, including source, manufacturer's lot number, and carbon type.

12.1.2 The iodine number adsorption isotherm, the iodine value with a 95 % confidence limit for the determination.

13. Precision and Bias⁹

13.1 Interlaboratory precision for this test method was determined by a round robin in which six laboratories partici-

pated. Activated carbon made from five different raw materials was used in the round robin.

13.2 The following criteria should be used in determining the acceptability of the results:

13.2.1 *Repeatability (Within Laboratories)*—Precision of this test method in the determination of iodine number of activated carbons ranging from 600 to 1450 iodine number is ± 5.6 % of the average value measured in milligrams iodine absorbed per gram of carbon. This range corresponds to $2S$, or the 95 % confidence limits, as defined in Practice E177. If two results determined in the same laboratory differ by more than 5.6 %, they should be considered suspect.

13.2.2 *Reproducibility (Between Laboratories)*—The between laboratory precision of this test method in the determination of iodine number of activated carbons ranging from 600 to 1450 iodine number, is ± 10.2 % of the average value, as measured in milligrams of iodine absorbed per gram of carbon. This range corresponds to $2S$ or the 95 % confidence limits, as defined in Practice E177. Results obtained by two different laboratories which differ by more than 10.2 % should be considered suspect.

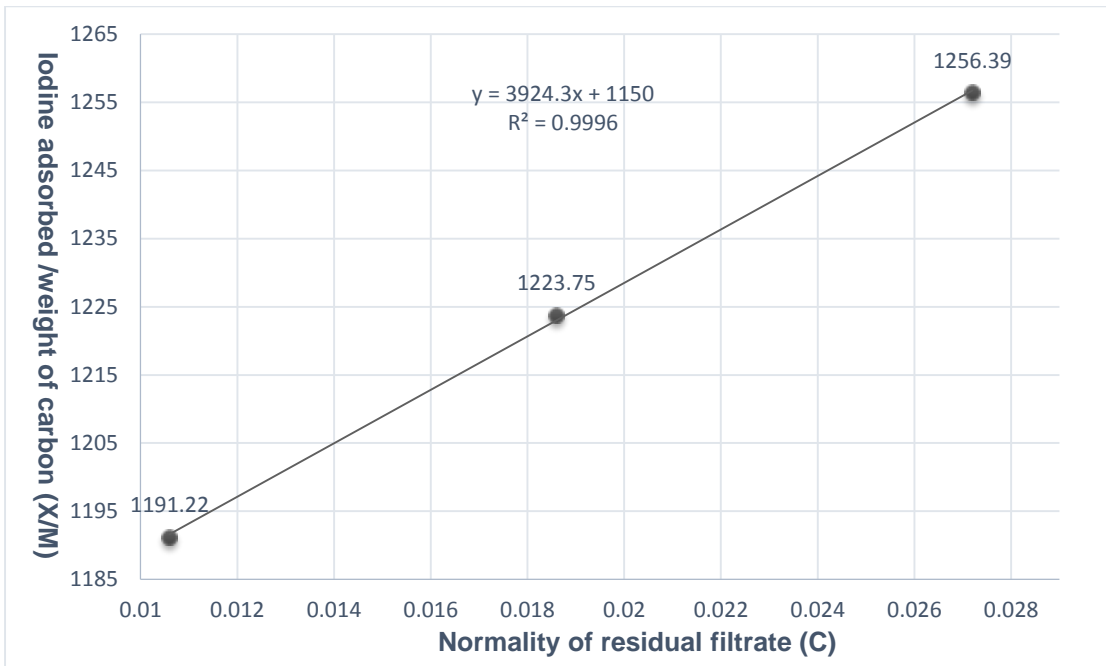
⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D28-1001.

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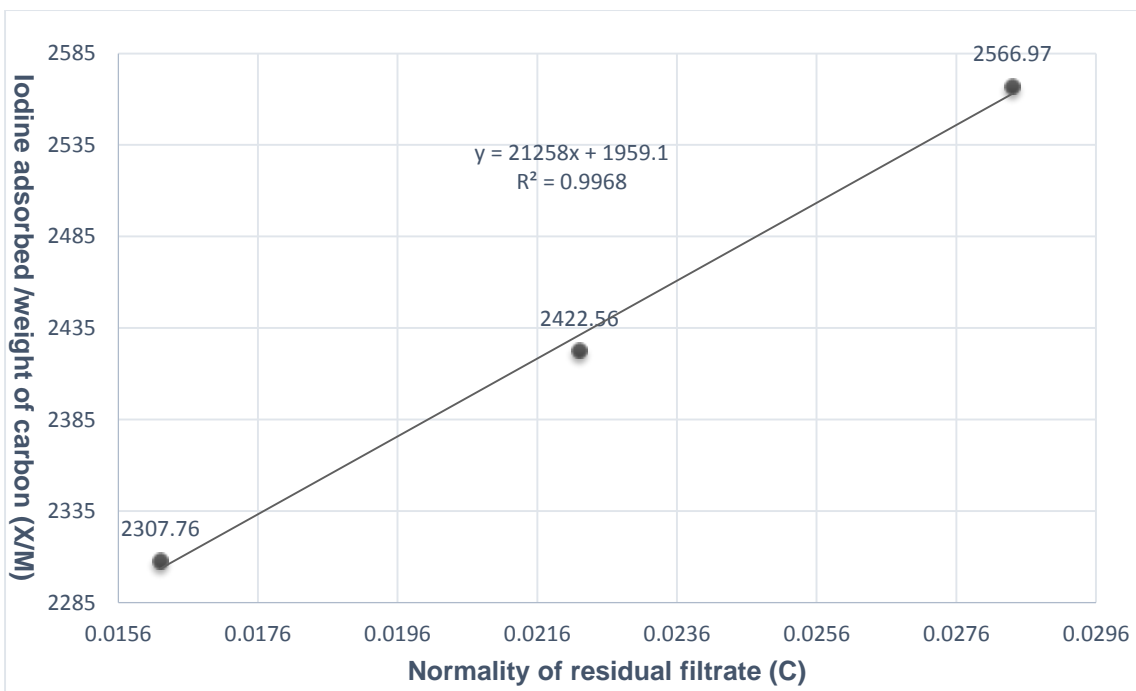
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Iodine adsorption test (Iodine number) results for chemical activated carbon



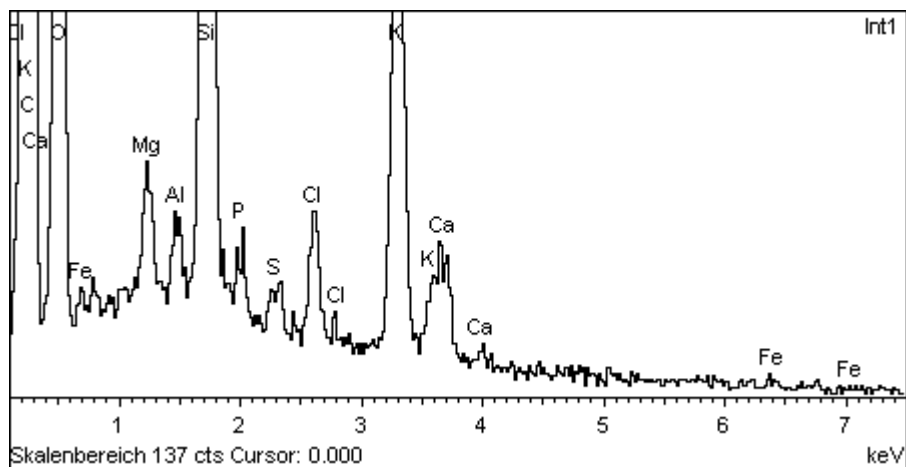
Appendix Figure 9: The regression coefficient value from Figure 3 is 0.9996 which is greater than 0.995 in WS 2 least squares fit plot. The Iodine number is 1224 ± 68.5 .



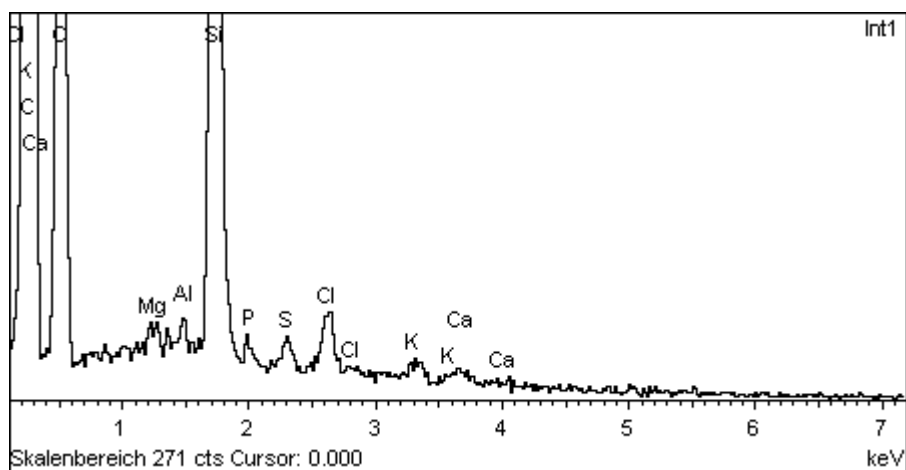
Appendix Figure 10: The regression coefficient in case of WS 3 is 0.9968 which fulfils the condition mentioned in D4607 standard. The iodine number is 2437 ± 129.6 .

Appendix D

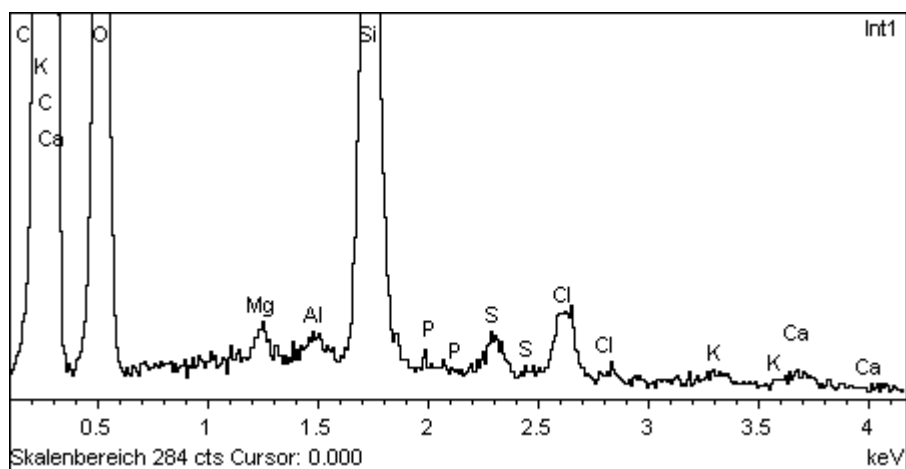
EDX measurement results from SEM analysis (Elemental analysis)



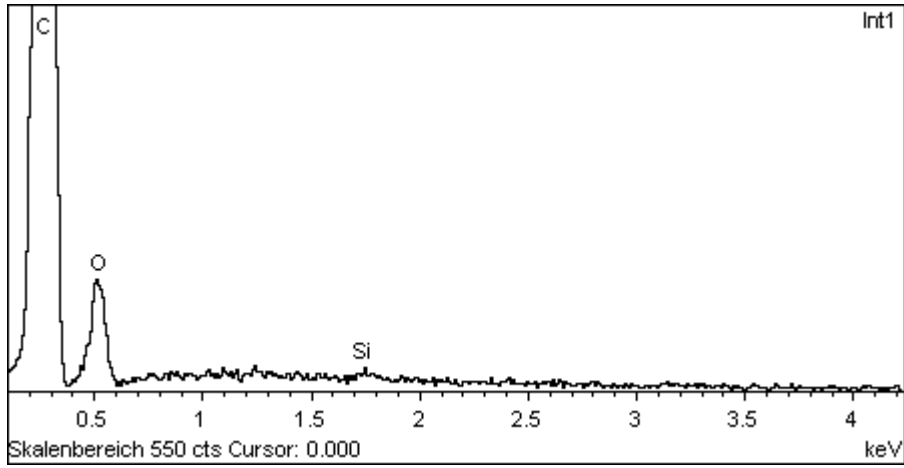
Appendix Figure 11: Elemental analysis for simple as received biochar



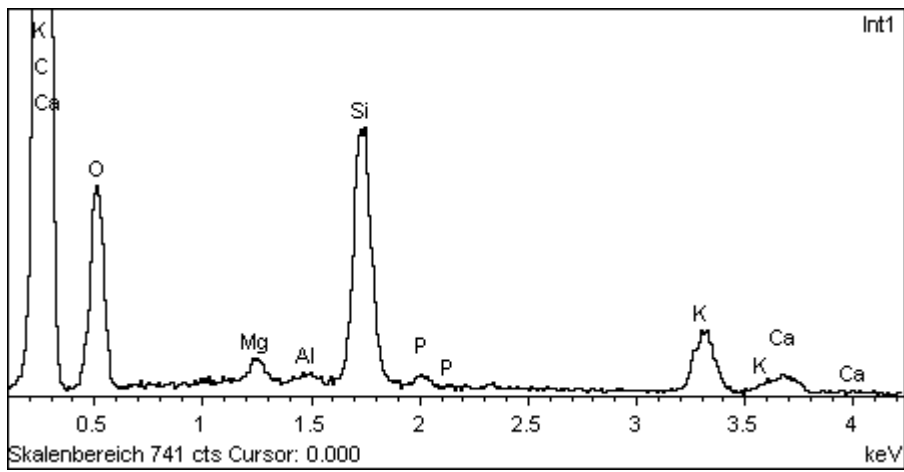
Appendix Figure 12: Elemental analysis for Demineralized biochar (1 N)



Appendix Figure 13: Elemental analysis of Demineralized biochar (2 N)



Appendix Figure 14: Elemental analysis for chemical activated carbon (2900 m²/g)



Appendix Figure 15: Elemental analysis for physical activated carbon (510 m²/g)