Hydrothermal carbonization and investigation of biochar using IR spectroscopy

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Abstract

Hydrothermal carbonization (HTC) is a thermal conversion of biomass to carbonaceous material called hydrochar, applicable in various sectors. Nevertheless, biomass's components highly affect the hydrochar yield and carbon content. IR spectroscopy techniques are essential for the study of hydrochar structures and the involved functional groups. A platform called library of spectra is essential to identify the associated functional groups and components.

In this study, the effect of HTC on biomass components and the effect of ammonium chloride (NH_4Cl), amino acids and KCl on solid yield, total carbon recovery and nitrogen contribution to the solid product were tested by adding these salts and amino acids on HTC of glucose solution. The investigation of hydrochar with IR spectroscopy was performed and a library of spectra was generated

HTC char mass increased when KCl was added whereas, NH_4Cl showed a slight decrease on mass and carbon recovery. On the other hand amino acid addition brought insignificant mass change however, a slight fluctuation on total carbon recovery was observed with temperature variation. The IR spectroscopy studies indicates that the hydrochar formed consists of a small cluster of complex structure which contains hydroxyl, carboxyl, carbonyl, aldehyde and ketone functional groups.

A maximum total carbon recovery of 90% can be achieved by adjusting the temperature, concentration of salts, amino acids and reaction time. The generated library of spectra can be applied in identification of the associated functional groups for further studies of substances.

Keywords:
HTC, Hydrochar, Functional group, Library of spectra, IR spectroscopy

Resumo

A carbonização hidrotérmica (*HTC*) é um tipo de conversão térmica de biomassa produzir um material chamado *hydrochar*, Os componentes da biomassa afectam consideravelmente a extracção de *hydrochar* e o conteúdo de carbono. A espectroscopia por infravermelhos essencial para o estudo das estruturas de *hydrochar* e os grupos funcionais envolvidos. Uma biblioteca de espedtros é essencial para identificar os componentes e grupos funcionais associados.

Neste estudo foram testados os efeitos nos componentes da biomassa de cloreto de amónio (NH_4Cl), aminoácidos e cloreto de potássio (KCl) na quantidade de sólidos produzida, recuperação total de carbono e contribuição de nitrogénio para o produto, através da adição dos sais e aminoácidos na solução de glucose por HTC. Analisou-se o hydrochar com espectroscopia por infravermelhos e gerou-se uma de espectros.

A mass de carbono aumentou quando KCl foi adicionado, enquanto a adição de NH_4Cl provocou uma ligeira redução de massa e carbono. A adição de aminoácidos não resultou numa variação de massa significantiva, no entanto foi observada uma ligeira alteração na recuperação total de carbono com a variação da temperatura. A análise da espectroscopia por infravermelhos indica que o *hydrochar* formado consiste num agregado de estruturas complexas contendo grupos funcionais de hidroxilo carboxilo, carbonilo, aldeido, e cetona.

Uma recuperação de carbono máxima de 90% foi obtida através do ajuste da temperatura, da concentração de sais, aminoácidos e do tempo de reacção. A biblioteca de espectros gerada pode ser aplicada na identificação de grupos funcionais para futuros estudos.

Palavras-chave:

Hydrothermal Carbonization, Hydrochar, grupos funcionais, biblioteca de espectros, espectroscopia por infravermelhos

Declaration

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List of Abbreviations

AA	Amino acids
AB	Absorption
AC	Ammonium chloride
AS	Average spectrum
ACP	Aqueous co-product
ATR	Attenuated total reflection
BR-E	Biogas residues experiment
CR	Correlation coefficient
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GS	Glucose solution
HTC	Hydrothermal carbonization
IC	Ion chromatograph
IR	Infrared
KIT	Karlsruhe Institute of technology
MSW	Municipal solid waste
OC	Organic carbon
QM	Quick compare methods
SEM	Scanning electron microscopy
Sp	Solid product
TC	Total carbon
Temp	Temperature
TIC	Total Inorganic carbon
TNb	Total nitrogen balance
TOC	Total organic carbon
TR	Transmission

1 Introduction

1.1 Background

The carbon dioxide concentration is expected to increase in the next five decades at an unprecedented rate owing to the burning of fossil fuels. These fossil fuels are known to cause rapid increase in the global temperature which already has created a lot of climatic changes and will no doubt worsen the condition with time. However to avoid these anthropogenic effects, efforts have been growing in almost all over the world. Kyoto Protocol is one such attempt where the signatories have committed to reduce the carbon dioxide emission from the present sources. For instance European Union (EU) had committed to increase their energy production from renewable sources from 6% to12% by 2010 [1]. The EU signatories have set their target to achieve 20% of the overall energy consumption by renewable energy sources and a 10% share for renewable energy in the transport sector (Directive 2009/28/EC) by 2020. To fulfil this target approximately 34% of electric city and 18% of direct heating and cooling have to be delivered by renewable energy sources. Apart from the concern of global warming, the rapid decline of fossil fuels in their quantity and reducing the dependency of EU on foreign sources for energy supply is a critical issue now a day.

To reduce the greenhouse gas emissions alternative renewable and sustainable sources of energy like wind energy, biomass energy have to be considered, but serious objections arose with limitation of regular supply of wind as an effective alternative. Hence, the challenge in current energy demand, energy supply, sustainability, limited fossil fuel resources and their environmental impacts intensifies interest in the use of biomass. Biomass is an alternative, renewable and sustainable energy sources with a large potential to mitigate the energy crisis as well as the environmental challenge caused by the use of fossil fuels.

The reduction of CO_2 can be accomplished by generating liquid fuels and electricity from renewable sources and the large contribution has been given by CO_2 - neutral energy crops [2]. Most of today's biofuels produced from crop grown on agricultural land. Nevertheless, when agricultural or pasture land previously destined for the food, feed and fibers markets is diverted to the production of biofuels the non fuels demand will still need to be satisfied. Hence other non feed alternatives have to be consider as substitute feedstocks for energy production via various biomass treatment technologies. A variety of themochemical or biological process can be used to convert biomass in to value added products which can be essential in several applications sector. Gas or liquid products predominate in biochemical transformations, while solids (biochar) are the main commercial products of thermochemical conversion.

In addition, the forecast of energy deficiency and the realities of recent increases in fuel cost have brought the world to the immediate need to conserve energy and to expand its domestic energy bases and change the direction to renewable and sustainable energy supply. The acceptable view has been

hydrothermal carbonization of wet biomass. The motivation behind the development and use of HTC is primarily from the desire to create sustainable carbon rich and stable material, the need for efficient biomass technologies and its advantage over others thermal conversion processes. HTC can be used for wide variety feedstocks that need less pre-treatment unlike other conversions technologies. However, types of biomass, their composition and reaction conditions highly affects the yield and properties of HTC char produced. Therefore, to have a better yield of energy efficient solid with maximum carbon recovery, suitable concentration of each component of biomass needed to be adjusted for example by blending various kinds of feedstocks together during the feed to HTC process. To accomplish this task, the concentration of each component of biomass was determined by conducting a study on the effects caused by individual component on the properties and value of HTC char produced. In this thesis the effects of biomass components on THC product is studied. Biomass, particularly glucose (hydrolysis product of cellulose) solution was carbonized with and without some inorganic salt such as ammonium chloride (NH_4Cl), potassium chloride (KCl) and organic compounds like amino acids (AA) added to examine their effect on the yield of HTC process. The contribution of individual element such as nitrogen, potassium to the solid product was also computed since the elemental composition of HTC char determine its energy value. Although HTC is one of the most promising technology for recovering energy from wastes little information is known on the characteristics of the HTC char and the functional group associated to it. To my knowledge so far no detailed investigation of HTC char with IR spectroscopy and examination of the presence or absence of specific functional groups was carried out. The properties of the hydro char need to be investigated by identifying the functional group linked to the molecules. IR spectroscopy is one of the most important tools to identify substances and very often employed in analysis to compare samples suspected of being identical. There are some studies already done on the investigation of biochar using their spectra. However, there is no any platform or a reference developed for comparing the biochar products for further works. Therefore, a reference library of spectra, which will be used in structural analysis and substances identification needed to be generated and applied for further studies.

1.2 Objectives

1.2.1 General objectives

The object of this work is to test and compare the hydrothermal carbonization effect on biomass components and investigation of HTC char with infrared spectroscopy, and the effects of inorganic salts and nitrogen containing organic compounds on HTC yield as well as contribution of nitrogen to the solid product.

1.2.2 Specific objective

- Conducting HTC on wet biomass and estimating the carbon distribution among the possible phases of products
- Calculating the total solid and carbon recovery in the solid, carbon efficiency of solid and evaluate the effects of the added salts and acids on the solid and carbon recovery as well as its carbon efficiency.
- Computing the contribution of nitrogen, potassium and chlorine in the three phase of products.
- IR spectroscopy and scanning electron microscopy (SEM) study of HTC char and identification of functional groups associated with it.
- Generating a library of spectra for HTC char produced at different temperatures and from different feedstocks.

1.3 Structure of Thesis

In the beginning, the basic science of HTC process and its characteristics that make it more significant than other thermal processes are studied theoretically. The objective is to know how the HTC process works and what are the operating conditions and parameters for controlling the process, and the possible advantages it has over the other thermal treatment of biomass. This is carried out by literature survey and contacting researchers and engineers.

Based on this knowledge, HTC experiment is conducted on glucose solution (model substance) at first followed by carbonization of the same substance with NH_4Cl, KCl and amino acid (AA) added. The optimum conditions that give a maximum yield of the required product are first investigated. The effect of additives on the solid recovery and the carbon distribution among the three phases of the products as well as the effect of additives on the condition of maximum yield are estimated by computed the mass balance and carbon recovery with solid (CRS).

After the hydrochars' properties, surface structure and composition are examined using chemical analysis methods, the changes on the features of the hydrochar caused by adding inorganic and organic additives are analysed by using spectroscopy techniques. Finally a library of spectra for the hydrochar produced at different conditions and with different additives is generated.

2 Literature Review

2.1 Hydrothermal Carbonization

The gradual transformation of organic matter for several millions of years via decaying process produces organic sedimentary rock which is known as coal. This was used as the dominant source of energy of the first half of the twentieth century. Moreover, it was processed further via pyrolysis, hydro carbonization, catalytic liquefaction and direct liquefaction for the improved utilization and application in a way not to have a large impact upon the environment. Now a day's several treatment of organic matters can produce coal resembling valuable products within shorter period of time.[3].

A short method of producing coal like materials know as bio-coal or biochar, from organic plant matters in an aqueous phase at moderate temperatures, called hydrothermal carbonization was first invented at the beginning of the 20th century by Friedrich Bergius (1913). This focused on the carbonization of biomass in-to bio-coal within a few hours using a pressure chamber at moderate temperature. The long lasting process known from nature was replaced in the laboratory with relatively higher temperature process, thereby accelerating the kinetics of the chemical reactions. More systematic investigation were performed by Berl and Schmidt in (1931), who varied the biomass source and treated the different samples in the presence of water and tried to summarize in a series of papers. Later Schuhmacher et al analysed the influence of pH in the outcome of the HTC reaction and found significant differences in the decomposition schemes as identified by the elemental composition of the product.[4]

Hydrothermal carbonization (HTC) is a thermo chemical process for the conversion of biomass at moderate temperature and pressure in the presence of water. Because of the need for efficient biomass conversion technology and convenient way of transforming various feedstocks, HTC gets considerable interest in these days. The resulting products are gas and a coal - water slurry with different chemical and physical properties from the original feedstocks. The produced carbonaceous materials are characterized by their extraordinary large specific surface area, well developed porosity and tuneable surface-containing functional groups as a result they can be used for several applications. HTC of biomass give a significant increase in energy density. A study by Ramke et al. (2009) compared the energy content of the input and output material using the gross calorific values. Figure 1 shows the carbon content vs. calorific value diagram of the resulting vectors connecting input material to output materials and directed from lower left to upper right thus displaying the increasing carbon content and calorific value. From energy content comparison of the input and output material using the gross calorific value, it could be determined that 60 - 90% of the gross calorific value of input solids are available in the solid char. The remaining energy is released as heat during the exothermic process of carbonization or is chemically bonded in carbon compounds dissolved in the liquid phase.

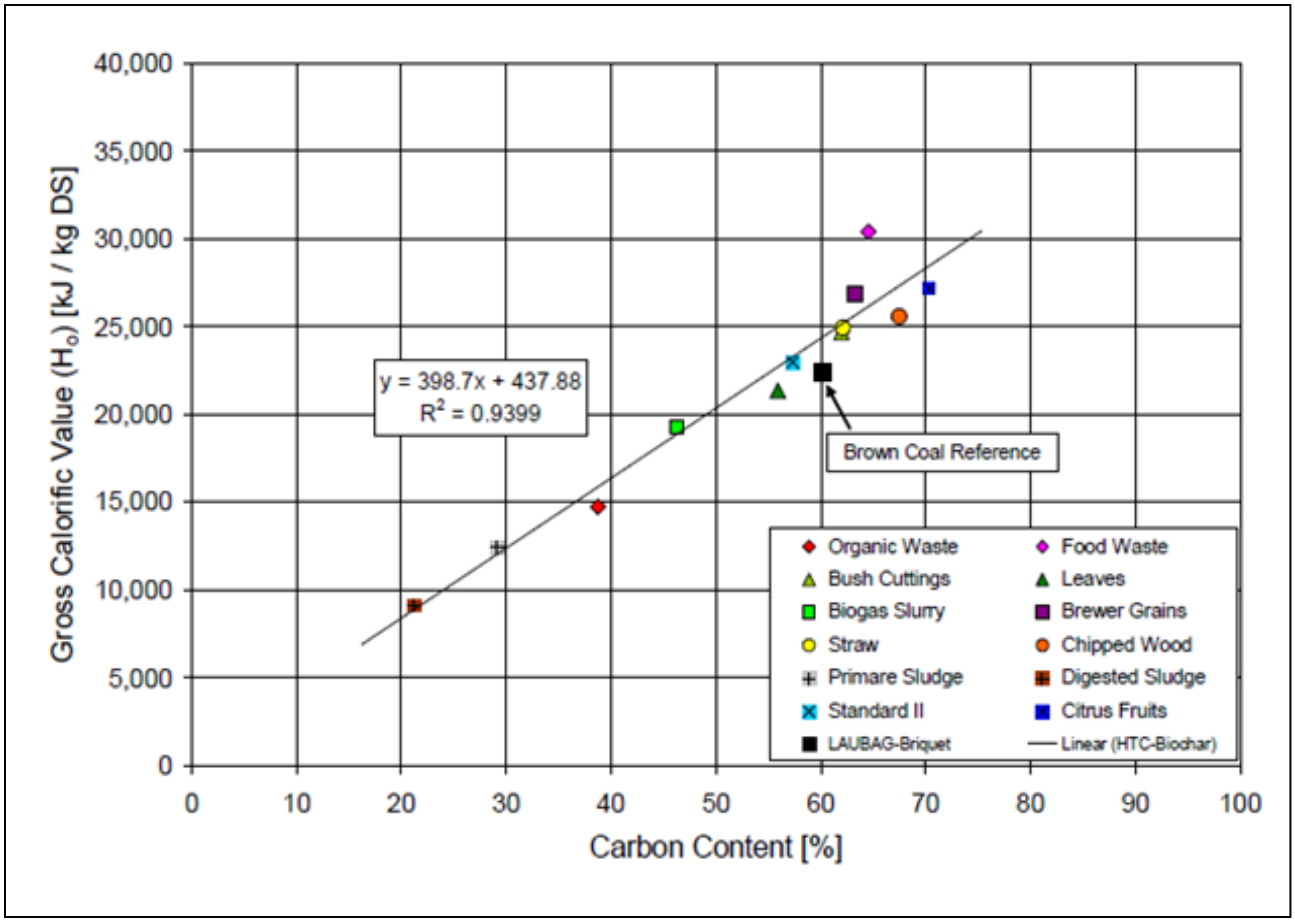


Figure 1. Carbon content - caloric value diagram

The simple chemical reaction for HTC process is a removal of water and volatile matter, thus reducing oxygen and hydrogen content (described by oxygen to carbon (O/C) and hydrogen to carbon (H/C) atomic ratio) in the biomass. [1], [5], [6]. The reaction mechanism like others conversion processes involves dehydration, decarboxylation, hydrolysis, condensation, polymerization and aromatization. Dehydration, decarboxylation and hydrolysis involve decomposing and removing compounds like water, carboxylic acid and carbon dioxide while others (shown in the right of Figure 2) built the solid products by changing the physical states and agglomerating the particles produced during the reaction.

$$\underset{\text{Carbohydrate}}{C_6H_{12}O_6} \xrightarrow{HTC} \underset{\text{HTC char}}{C_xH_yO_zP_n} + \underset{\text{water}}{bH_2O} + \underset{\text{Heat}}{\sim 950 kJ/mol}$$

where x, y, z , n and b are real number showing the balanced chemical equation while P represent other elements found to be in the HTC char such as nitrogen sulphur etc. depending on the composition of the raw feedstock as well as its physical and chemical properties.

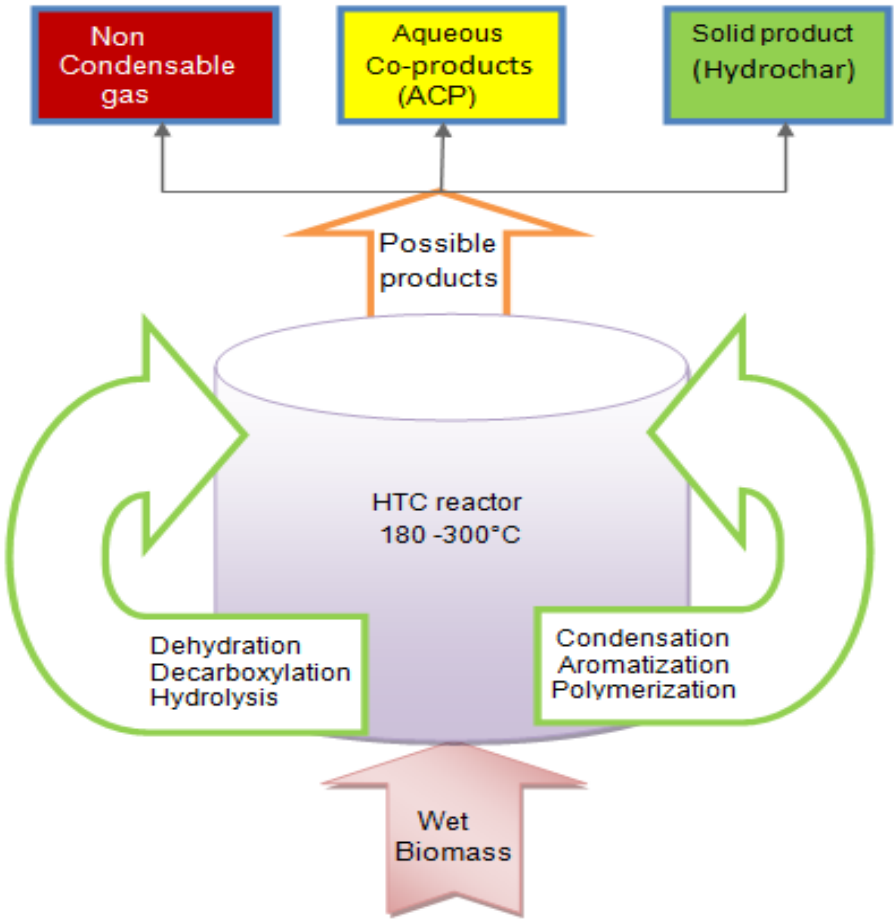


Figure 2: HTC reaction mechanism and possible products

2.2 Advantages of HTC Process

Several methods such as gasification pyrolysis and combustion, can be adopted for the thermal treatment of biomass. But each of these options have important limitations due to the properties and nature of the biomass types. By HTC process, wet biomass with moisture content (>70%) can be processed without the use of energy intensive drying in contrary to other thermal treatment methods. It has intensified as the amount of unused organic waste from urban areas and industrial processes is increasing with the raise of population and consumption of natural resources. The huge CO_2 and methane emissions from unused biomass like municipal waste, vegetable wastes and sewage sludge every day results in the production of innumerable tons of CO_2, which is continuously making its way into the atmosphere. HTC process transforms these organic wastes to carbon rich solid thereby reduce the CO_2 and methane emission from naturally decomposition of organic wastes at the same time, produces value added products and unlocks most efficiently the energetic potential in organic wastes: the waste to energy technology. During HTC

reaction, water, carbon dioxide and other volatile matters are cleaved, associated with the decline in the bulk density of biomass as well as the rise in the energy density. Thereby, the heating value of biomass increases significantly. Gaseous products like carbon dioxide and carbon monoxides are limited during HTC process because exposure to oxygen is limited to its initial presence in the reactor (autoclave) headspace. Hydrothermal carbonization of biogenic materials result in a high carbon efficient biochar compared to other biomass treatment emerged as a potential alternative strategy to produce renewable solid fuel source. HTC is also a higher carbon efficient process (above 90% can be attained) compared to the other biomass treatment technologies. Depending on the biomass used, 60-90% of carbon can be recovered with solid products. According to the study by Hans - Günter Ramke,75 -80& of carbon input is found in the solid phase; while 15 - 20% is dissolved in the liquid phase, and the remaining 5% are converted to gas mainly carbon dioxide from HTC of organic wastes.[1]

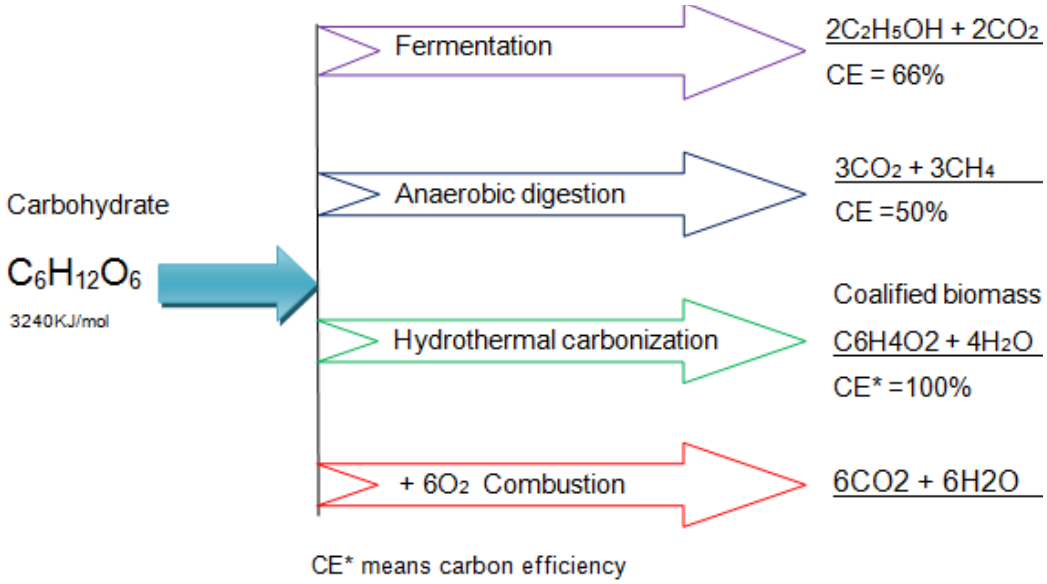


Figure 3. Comparison of different biomass conversion pathways in carbon transfer scheme

Now a day, awareness has been focused on the use of biomass to produce functional carbonaceous material, encompassing economic, environmental and social issues. HTC is competent technology for the conversion of wet biomass into valuable products with attractive structure and functionalization patterns for a wide range of applications some of which are described at the figure below.

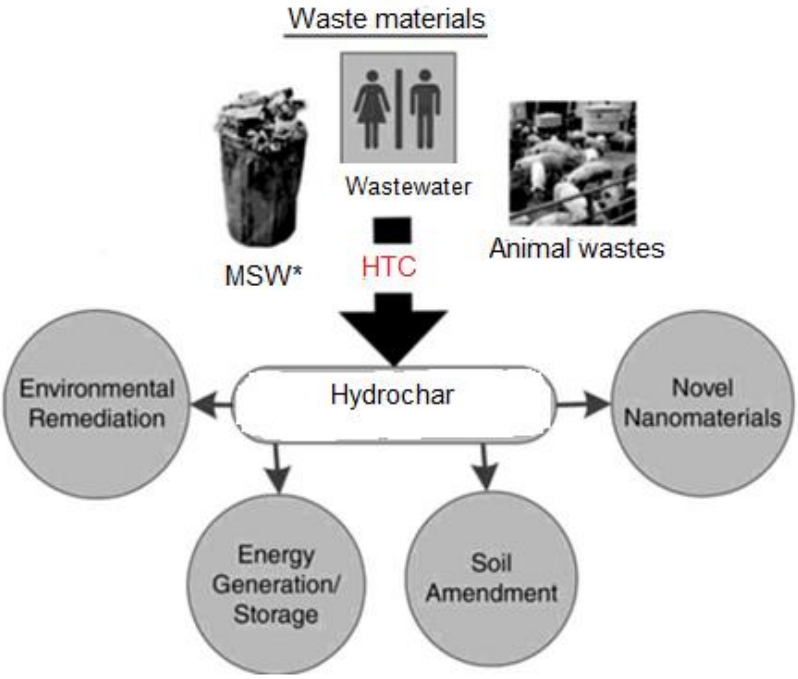


Figure 4. Application areas of HTC char

2.3 Factors Affecting Hydrothermal Carbonization

The quality and quantity of HTC products as well as the distribution of the organic carbon among the three phases (gas, liquid and solid) depend highly on temperature, residence time, type of feedstock, and on its composition and physical and chemical properties. At high temperatures decreasing solid mass yield with increasing heating value and high volume of gas production are observed. It was also determined that as the temperature increases, less carbon is recovered and more of carboxylic compounds are removed from the original biogenic material thus, mass of solid yield decrease. **D**ehydration of solid and solid carbon efficiency increases with both HTC temperature and reaction times. With very long reaction time, the conversion rate of biomass to high carbon content char apparently slows down due to side reaction occurring in the liquid phase. Thus, the characteristics of products and their energy value can be controlled by adjusting the composition of feedstocks, their properties and process parameters. Table 1 below shows the variation of hydrochar yields from grape seed as a function of temperature and time. As observed in the table, going down or right in the table indicates reduction of mass yield.

Table 1: Hydrochar yield from grape seed as a function of reaction temperature and reaction time[7]

	Residence time (h)		
Temperature (°C)	1	3	8
180	80.3 %	78.7 %	77.0 %
220	73.8 %	68.9%	67.7 %
250	67.2 %	63.9 %	62.3 %

2.3.1 Effects of organic and inorganic compounds on HTC of biomass

According to the study made by Joan G. Lynam, and M. Toufiq Reza some inorganic salts such as calcium propionate, calcium accetate, and acids might alter the mass yield (mass of char produced per mass of dry feedstock), total carbon retained in solid, carbon and energy efficiency of solid. For example, addition of acetic acid and/or lithium chloride (LiCl) to hydrothermal carbonization contribute to an increased HHV and reduced mass yield of the solid product. If 1g of LiCl and 0.4g of acetic acid were added per gram of biomass to the initial reaction solution, a 30% increased in HHV was found compared to treatment with no additives, along with greater mass reduction [8]. In HTC of glucose, the yield of carbonaceous materials in the presence of sulphuric acid was found to be1.6 times higher than that without sulphuric acid added. The surface O/C ratio of the formed carbon was 20% when sulphuric acid was added while it was 24% without sulphuric acid addition [9]. Moreover adding some inorganic salts to HTC of lignocellulose biomass shows a mass reduction while others give a slight mass increase compared to no salt added control (Table 2).

Table 2. Effect of some inorganic salts on HTC of lignocellulose biomass [8]

Types of salt added	Mass yield [mass unit]
No salt	0.5843
Ca propionate	0.6284
Ca accetate	0.5831
Mg acetate	0.5168
Ca Lactate	0.5005
LiCl	0.4535
$CaCl_2$	0.6241
Ca Formate	0.7275

2.3.2 Potential feedstock and compositions

HTC has huge potential feedstocks composed of various components and extractives which can have significant influences on the yield and properties of products. The composition of extractives varies depending on wood and straw-based biomass between triglycerides, amino acids, sterol and sterol

esters. The same goes for inorganic salts mainly consisting of alkali salt compounds. Wet biomass has cellulose, hemicelluloses, lignin, and inorganic salts, such as ammonium chloride, potassium chloride, potassium hydrogen phosphates, sodium nitrate, sodium nitrite and others at different proportion. Different contents of these components and their concentrations may affect its derived hydrothermal carbonization products caused by certain interactions under these subcritical conditions. The variation in solid yield and surface O/C ratio of the solid with types of feedstock used as examples is shown below in Table 3. As seen in the table the surface carbon to oxygen ratio as well as the bio-coal yield decrease with both residence time and temperature due to the removal of oxygen as carboxylic acid and other compounds. Besides that, it varies with types of feedstocks used.

Table 3. Effects of biomass types and process parameters on HTC coal yield [10]

Feed	Temperature[°C]	Residence time [h]	Coal yield [%]	O/C ratio
Cellulose				**0.83**
	225	3	63	**0.83**
	200	50	49	**0.61**
Peat Bog				**0.65**
	200	10	45	**0.29**
	250	0.3	36	**0.23**
Wood				**0.58**
	200	72	66	**0.25**
	250	72	56	**0.17**

Based on the study made by Hans -Güter Ramke and Dennis Böhse, the recovery value of organic carbon with solid product of HTC process is 95% and more. The distribution of the carbon fraction in the solid, liquid and gaseous phase is dependent on the various types of biomass used

Table 4: Distribution tendencies of the carbon fraction in the HTC product phases[1]

Substance	C- solid phase [%]	C- in liquid phase [%]	C- in gas phase [%]
Organic waste	74.9	19	6.1
Green cuttings	75.3	19.7	5.0
Bio gas slurry	72.2	22.1	5.7
Straw	75.4	19.7	4.9
Chipped wood	82.9	14.1	3.0

So far, only a few papers were focused on the comparison of the characteristics of hydro chars obtained from different biomass with different components and providing detailed information on biomass component interactions. In this work the composition of biogas residue from a mesophilic digestion (input material: 40% maize silage, 30% grass silage, 30% cattle manure) are used as a reference to make the biomass solution from D+ glucose monohydrate and make HTC process.

2.4 An Overview of Infrared Spectroscopic Techniques

In order to advance our understanding about the properties of hydrochar, comprehensive characterization of the chars produced from different substances under various conditions has to be carried out using infrared/FTIR spectroscopy. This is an essential step in the search to relate properties of substances to attempt in environmental application, and required a concerted effect of key players across disciplines, producers and users to choose the relevant characteristics that have to be measured and develop testing measure.

2.4.1 IR Spectroscopy

Spectroscopy is the study of matter and its interaction with electromagnetic radiation. All matters contain molecules which have bonds that are continually vibrating and moving around at a temperature above absolute zero. Bonds can vibrate with stretching motions or bending motions when they exposed to radiant energy of specific frequency and be at excited state. Bond will be promoted to excited state, when they exposed to radiant energy of same frequency as the energy differs between ground and excited states of the electrons within the molecules. Determining this frequency and relating them with the intensity of light absorbed by molecules allows finding out the bonds that exists in a molecule thus, the associated functional groups. These frequencies all lies within the infrared region of the electromagnetic spectrum.

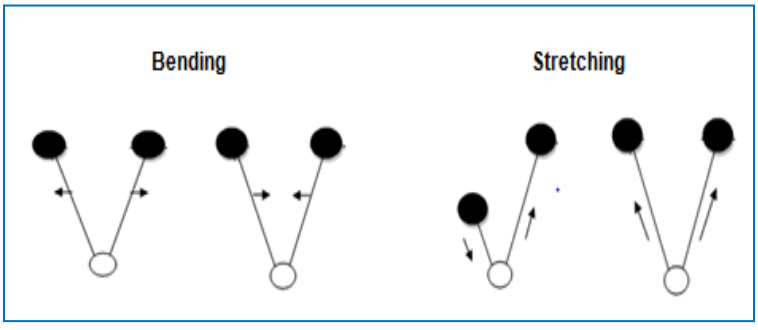


Figure 5: Some of the possible bond vibration of molecules

An IR spectrometer passes infrared radiation through sample and use detector to plot percent absorption or transmission of the radiation through the molecule versus the wavenumber of the radiation or transmission. A downward peak on the plot shown in Figure 6 represents transmission while an upward

peak in Figure 7 represent absorption as a function of wavenumber. In IR spectroscopy a unit of measurement called wave number (v), the number of waves to be found in a unite distance, is used since they are more manageable.

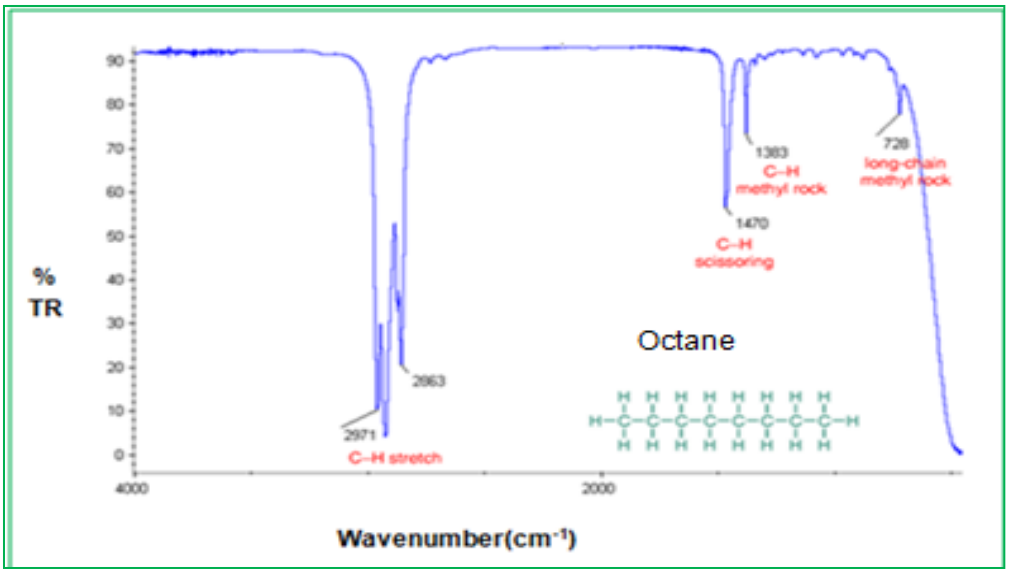


Figure 6**:** Transmission versus wavenumber measurement of IR spectra of octane

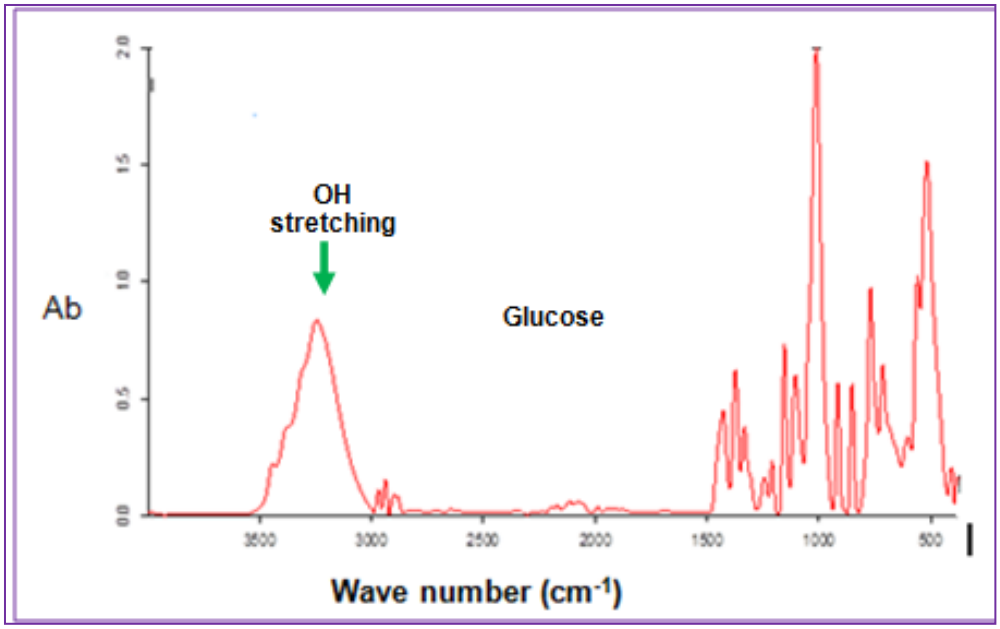


Figure 7**:** Absorption versus wavenumber measurement of IR spectra of glucose

An IR spectrometer is useful in determining chemical structure because energy that corresponds to specific values allows us to identify various functional groups within a molecule. A mid IR spectrum region usually extends from radiation around 4000cm^{-1} to 400cm^{-1} and can be split in to functional group region

(4000cm^{-1} -1600 cm^{-1}) and the figure print region (1600cm^{-1} - 400cm^{-1}). In nearly all spectroscopic studies of organic or inorganic materials, it is desirable to obtain laser-Raman spectra along with infrared spectra. The two methods are complementary sometimes and can provide considerable structural information. However, some substance which are active for IR spectrum might be Raman inactive; so care must be taken during IR and Raman spectrum application together.

2.4.2 Sample spectrum manipulation

Assigning a functional group at the observed band peaks before manipulating (modifying) the measured sample spectrum (row spectrum) may lead a wrong nomination to their absorption bands. Therefore, spectra post processing need to be performed to ensure that acceptable evaluation results for substance identification. For this aim OPUS software offers a number of manipulation commands primarily serve to increase the accuracy of the information about the sample and to reduce the amount of interferences reflected in the spectra. Some of these are described below:-

I. **Baseline correction**; is applied when the spectrum baseline is strongly deviates from the theoretical horizontal line which may be due to sample scattering losses.
II. **Atmospheric compensation**; this helps to avoid the effect of CO_2, H_2O and humidity from the ambient air and occur if there is a difference in the H_2O and /or CO_2 concentration between the moment of background measurement and the moment of sample measurement.
III. **Spectrum subtraction**; In the case of a binary mixture the observed spectrum can be viewed as the sum of the two pure component spectra M= [P_1] + [P_2], where M is spectrum of the mixture, P_1 and P_2 are the spectra of the components. Rearrangement of this equation in terms of the known spectra: [P_2] = [M] - [P_1] gives the spectrum of an unknown component. This analysis assumes that the concentration and path length of the known pure component are identical to those the mixture. It is very important to generally run a background spectrum first and then making spectrum subtraction in spectrum measurement of a pure substance. The background will often be the spectrum of empty cell.
IV. **Peak peaking**; allows determination of the exact spectrum peaks position .i.e. the exact wavenumber value (X-axis) at which maximum (in case of absorption spectrum) and minimum (in case of transmission spectrum) occurs.

For further detail studies and better comparison of the most relevant spectral information of the substance to analyzed as well as to produce accurate library of spectra, it is essential to make further pre-processing techniques such as first and second derivatives in addition to optimization [11]. A big difference is observed on the spectrum of substances before and after manipulation as shown in Figure 8 and Figure 9 below. The small waves in the wavenumber range 3500cm^{-1} - 3800Cm^{-}1 in the first figure are due to the absorption of water molecules case by moisture from ambient and might be wrongly assigned as amine functional groups if the spectrum is modified by manipulation techniques. The reveres peak near the 2200cm^{-1} - 2400cm^{-1} is caused by the effects of carbon dioxide from the atmosphere and removed by

atmospheric compensation. Furthermore, a very small wave forms are indicated in the finger print region of the spectrum which can be removed by performing spectrum smoothing.

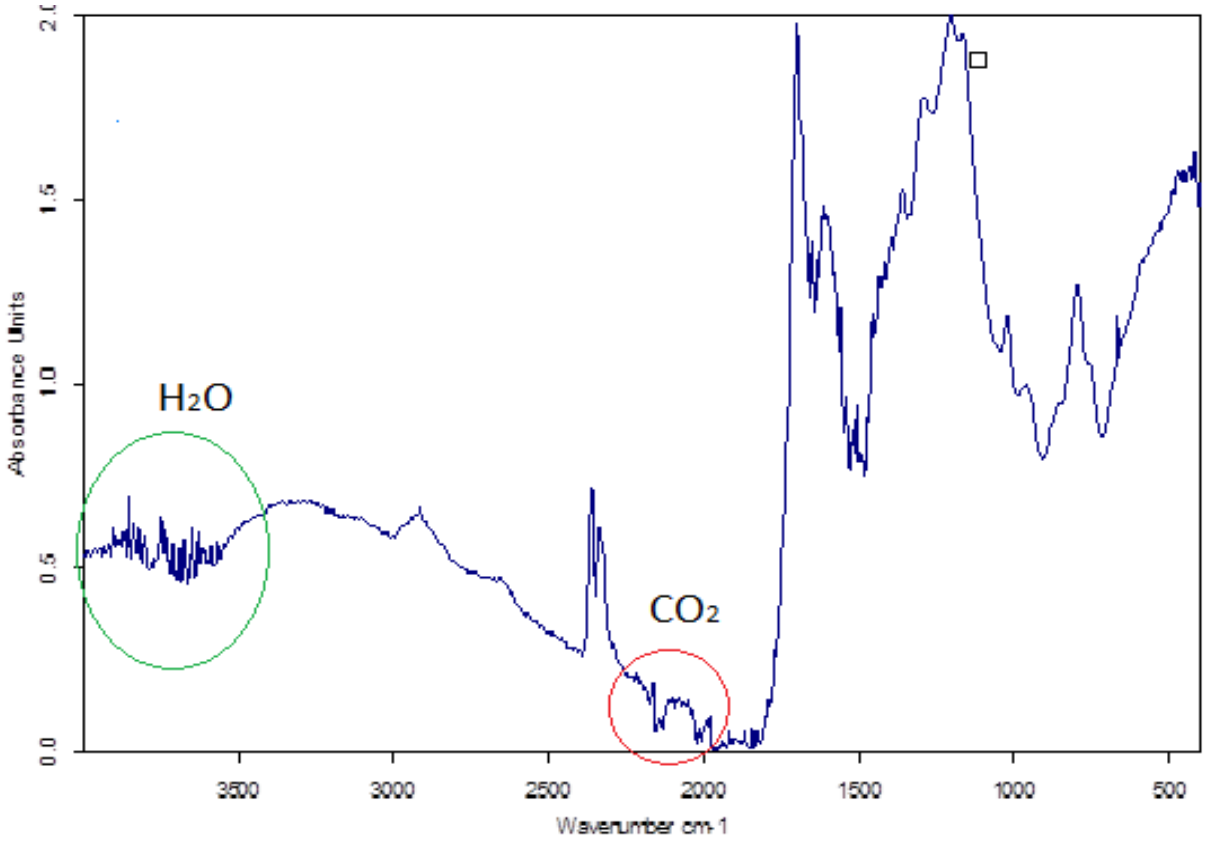


Figure 8: IR Spectrum of HTC char before manipulation

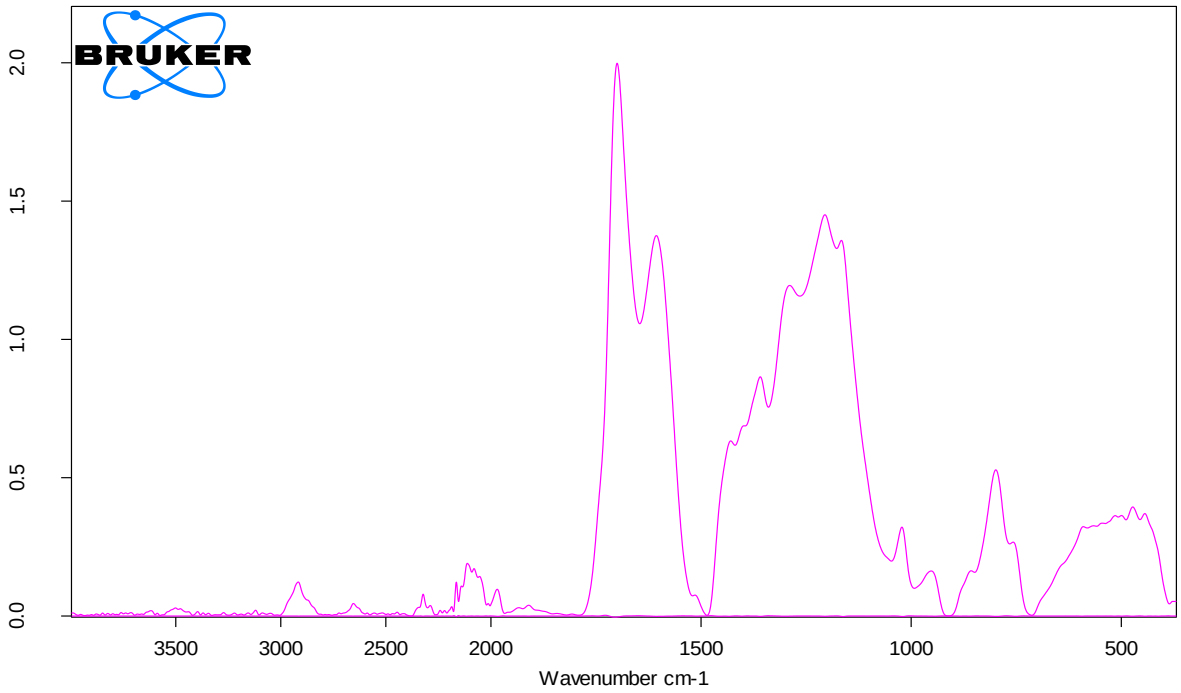


Figure 9. IR spectrum of HTC char after manipulation

2.4.3 Sample spectrum evaluation

Once the spectrum is processed, based on our analytical interest i.e. either quality control, substance identification or quantitative analysis, sample spectrum evaluation using the corresponding evaluation commands such as quick compare, spectral search and quantitative analysis are required and decide how to deal with the level of the spectra. The interest in this task is to identify the functional groups involved with HTC char by comparing their spectra with the existing spectra of library or with correlation tables from previous studies.

2.4.3.1 Quick compare methods (QM)

QM is one of the quality control techniques used to compare the spectrum of samples with one or several reference spectra file. The data sample and the reference samples have to have the same spectrum types, i.e. they both have to be either absorption (AB) or transmission spectrum (TR). A correlation coefficient, ranging from -1 (inverted spectra) and +1 (identical spectra), was calculated and compared with the threshold defined in the set up made for the reference spectrum [11]. The result of comparison is displayed showing both the spectrum of sample and reference with the corresponding correlation coefficient of the sample and the threshold of the reference as indicated in the figure below.

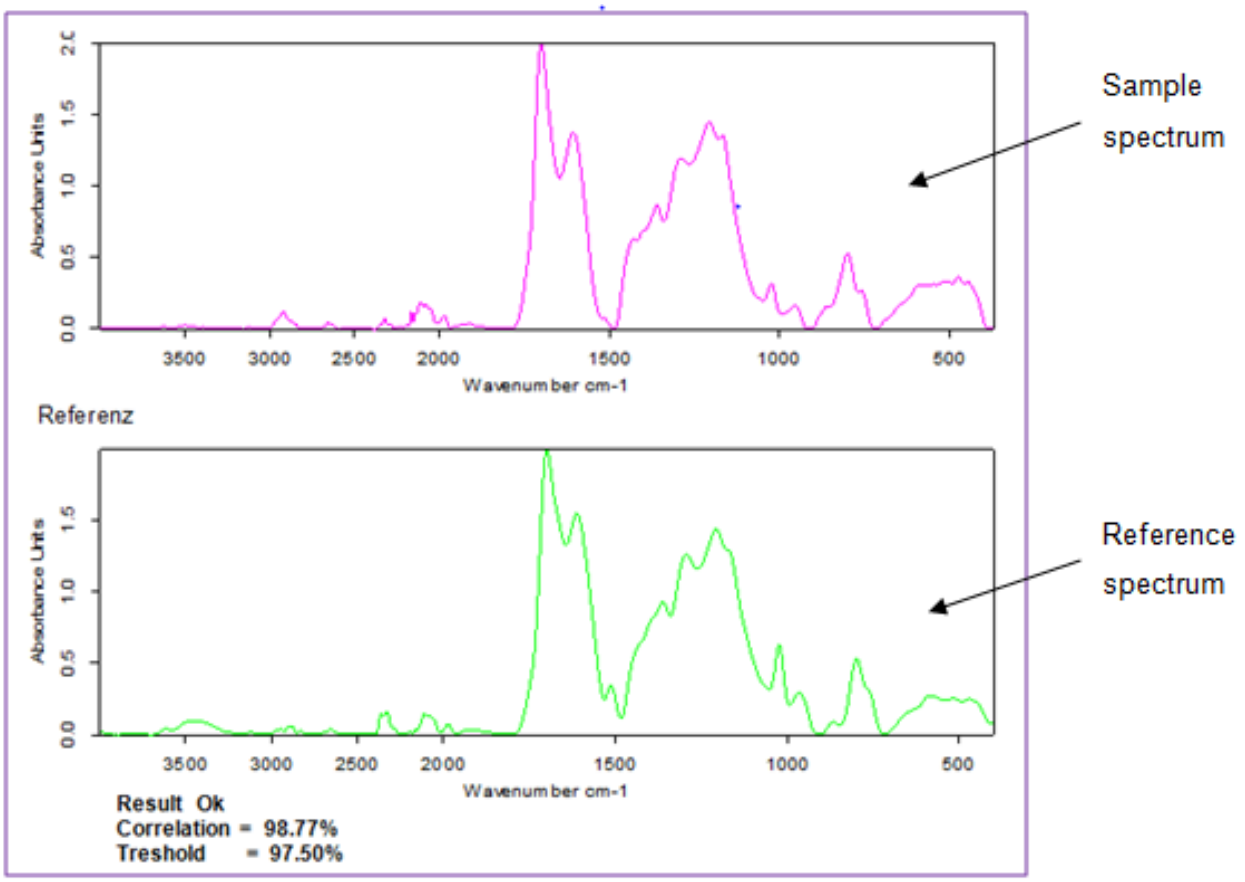


Figure 10: IR spectra comparison

2.4.3.2 Spectrum search

OPUS software package might have spectrum of known substance with defined structure and chemical formula as a library, thus used to identify an unknown compound or mixtures by comparing the spectrum of known substances from the library with the samples spectra. The spectrum search is used to perform this comparison and displays the spectrum of the known substances which have similar structure with the spectrum of unknown samples. The result of comparison will be presented in chemical structure, hit quality, molecular formula and spectra of samples and references together as shown in the figure below.

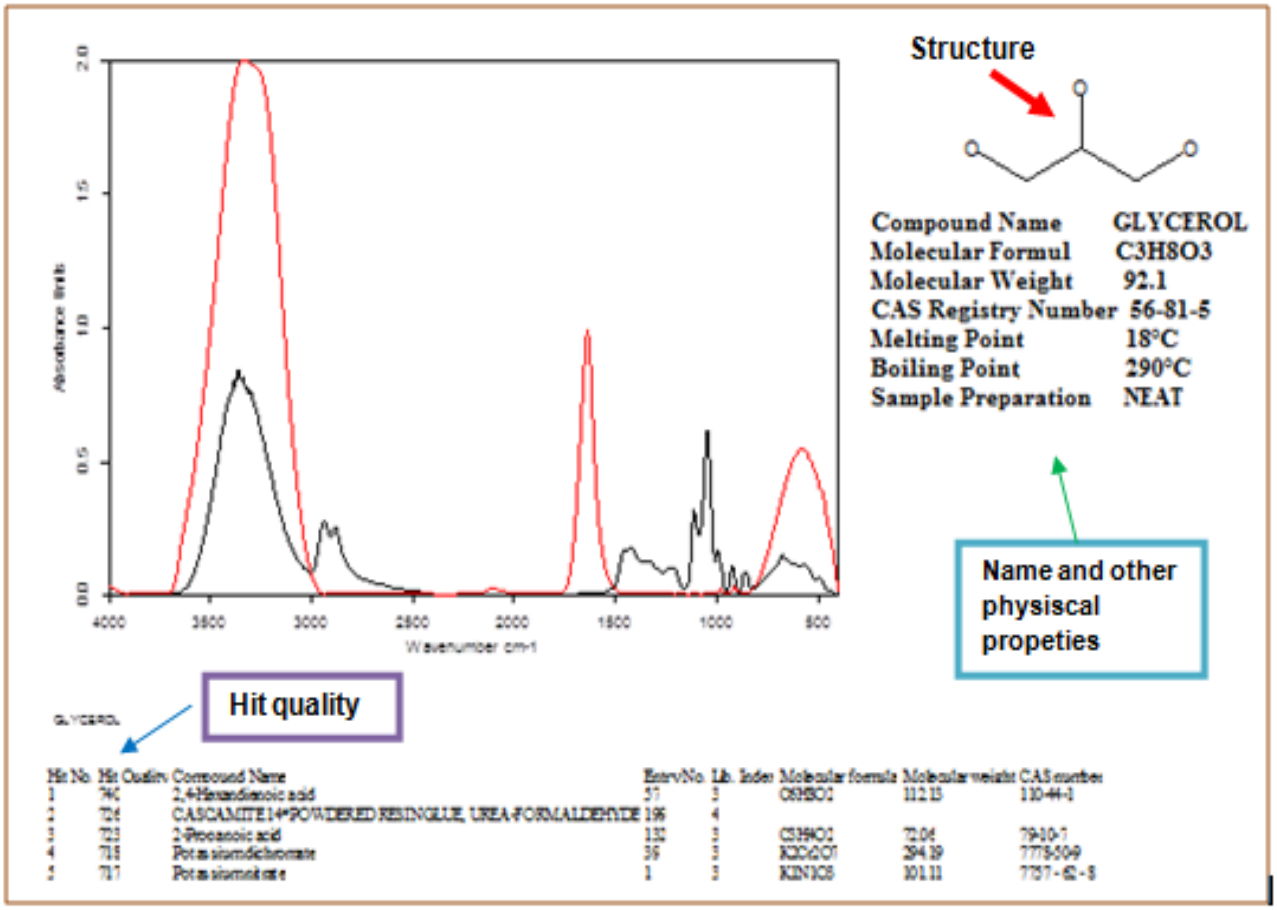


Figure 11: Spectrum comparison using spectrum search from the library

The search can be within any wavenumber ranges by excluding unwanted portion. For example as shown in Figure 11 above the sample spectrum (red), (spectrum of water) and the spectrum from the library (spectrum of glycerol) have approximately the same structure in the wave number range of 3700 cm^{-1} - 3300cm^{-1}, except variation in their intensity, indicating that the two substance might have the same functional group stretching in this region. But the overall structure similarity have a hit quality of 711 which is lower than the sample has with 2-4, hexandieanoic acid which has a hit quality of 740.

3 Materials and Methods

3.1 Material used

D+ glucose monohydrate ($C_6H_{12}O_6$, molecular weight1 80.17g/mol), supplied by Merck, KGaA, www.merck.de, was chosen from components of biomass to test HTC effects on biomass components. Ammonium chloride (NH_4Cl) and Potassium chloride (KCl), both produced from merck, three amino acids (phenylalanine, $C_9H_{11}NO_2$, with molecular of weight 165g/mol, Glutamic acid ($C_5H_9NO_4$, with molecular weight 147 g/vmol), glycine, $C_2H_5NO_2$, with molecular weight of 75g/ mol) are used as additives to examine contribution of nitrogen in solid. Other additives can be also found and need to be investigated, but due to time limitation only effects of these three additives are studied.

Glucose monohydrate contains one mole of water per mol of glucose. Thus mass of glucose needs to be considered in dry base. Therefore from ''m'' mass glucose monohydrate, the mass of glucose in dry base is computed.

Mass of glucose in dry base = m * {mass of dry glucose /mole}/ {mass of glucose monohydrate/ mole}....1

From this 99.9% is mass of glucose in dry base and the remaining 0.1% by mass is water. The concentration of inorganic and organic salts added was determined by using a 15% by mass solid component bio gas residue analyzed by university of Hohenheim and karlsruhe institute of technology (KIT).

Table 5**:** Concentration of nutrient in biogas residues [Sources Biogas analysis report in University of KIT]

		Ammonium	Nitrite	Nitrate	Phosphate	potassium	TOC
Units		mg/L	mg/L	mg/L	mg/L	µg/ml	
Liquid		1734	N.D*	N.D	52.05	3185	1774mg/L
Solid	BR-E-1	186.4	N.D	N.D	N.D	311	
	BR-E-2	171.6	N.D	N.D	N.D	317	10.77

N.D*: not detected

3.1.1 Sample preparation

The aim is to produce glucose-water solution with same total organic carbon (TOC) as a 15% by mass solid components of biogas residues from a mesophilic digestion (input material: 40% maize silage, 30% grass silage, 30% cattle manure). In order to determine the amount of glucose and additives used in the feedstocks, a simple calculation was computed for each experiment. Because it only

provides the organic carbon, carbon from glucose will be considered in this calculation The calculation steps are indicated at the appendix and the result is given in Table 6 just below.

Table 6: Amount of samples and additives used

Utilities	Glucose solution	NH_4Cl solution	KCl solution	Amino acids solution (AA)		
				Phenylalanine	Glutamic acids	Glycine
Mass of additives [g]	0.0	0.0373	$6.2*10^{-7}$	0.2502	0.6555	0.2919
Mass of water[g]	157.2990	157.313	157.229	157.2921		
Mass of glucose [g]	67.1240	67.1168	67.1124	67.6133		
M_{total}[g]	224.4230	224.4671	224.332	226.103		
V_{total}[ml]	200					

3.2 Experimental set up

A number of thermal and electrical equipments are used in order to carry out HTC process as well as to study the characteristics of the products. Some of these equipments are listed below. Autoclave is the most important one in which the reaction, thus conversation of biomass carried out. Many kinds of autoclave with different design are available. The one which is used in this test is shown in Figure 12. It has 10ml capacity of which 30% has left as a dead zone so that only 7ml of sample can be carbonized in one autoclave per batch. The autoclave tubes are made from stainless steel and should be as strong as possible to resist the raise in pressure during the reaction.

Figure 12: The reactor autoclaves

Spectroscopy is a technique which is used to obtain an infrared spectra of substances and relate the absorption, emission, photoconductivity and Raman scattering of liquid, solid and gas eous samples. The IR spectroscopy involves collecting absorption information and analysing the information in the form of a spectrum. The frequencies at which there are absorptions of IR radiation can be correlated directly to bonds within the compound in question thus strength the structural identification of functional groups like for instance C = O, C - O or N - H. IR spectrometer simultaneously collects a spectrum data in a wide spectral range and display the measurements in terms of absorption or transmission versus wavenumber on the connected computer interface. An IR spectrometer (tensor 27, from Bruker), which allows measuring all types of samples whether they are solid or liquid, is used to investigate the HTC char in this experiments. The spectrometer works on the principle of attenuated total reflection (ATR) and has an advantage of the possibility to measure a wide variety of solid and liquid sample without any complex sample preparation. The measurement is carried out by simply placing the sample on the platinum surface attenuated total reflection (ATR). Radiation from the IR sources interacts with the sample after passing through the IR objective. Reflected light from the sample is collected on the IR objective, and then guided to the IR detector by additional optical components.

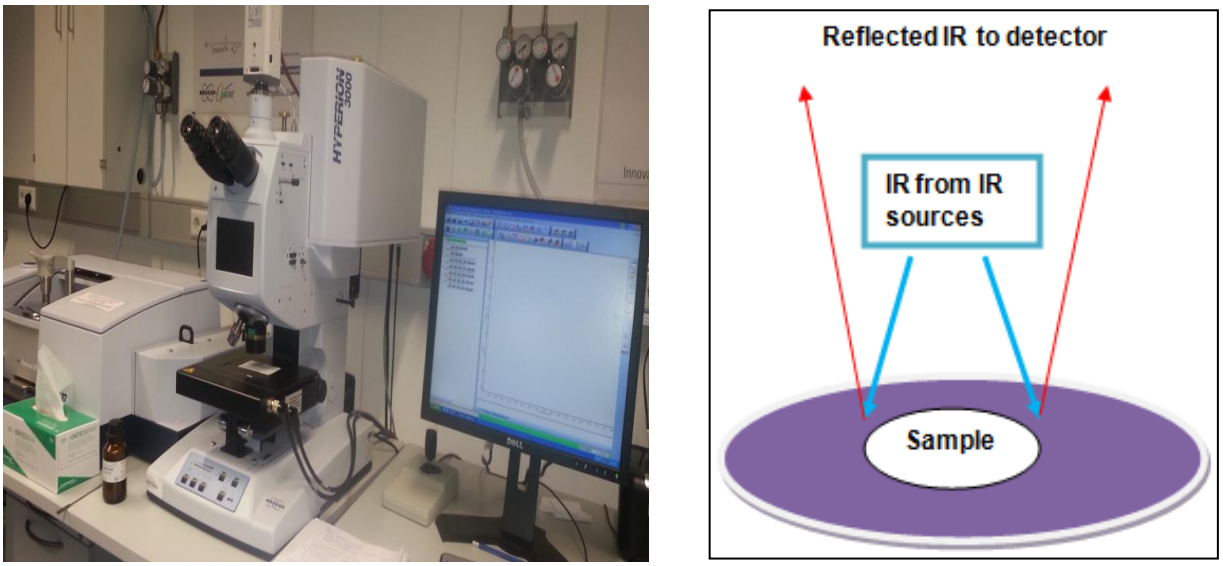


Figure 13: BRUKER TENSOR 27, FT-IR, BRUKER OPTICS (left); scheme of light reflected from sample surface (right)

The gas chromatography (GC) is helpful for separation, identification and quantification of components of gaseous mixtures, and consists of several components such as injector, column oven and detector. The sample is injected using a micro syringe onto the head of the chromatographic column at the injector port and transported through the column by the flow of inert carrier gas. For optimum column efficiency, the sample should not be too large. As the sample is eluted from the column and passed through the detector (TCD and/ or TID detector), one of the detector wire is exposed to a mixture of carrier gas plus sample,

and the other wire is exposed only to the reference stream of carrier gas. Then the difference between the two gas streams cause a difference in the electrical conductivity of the wires and this difference is automatically recorded and the result is displaced in the computer interface.

A gas chromatograph (HP6890, 2 column, hyesep Q and Molsieve 5A) with inert helium as a carrier gas and manual sample injection type is used in this experiment. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component.100 micro litter of sample with at least 95% of injection efficiency was accepted for accurate analysis of the sample.

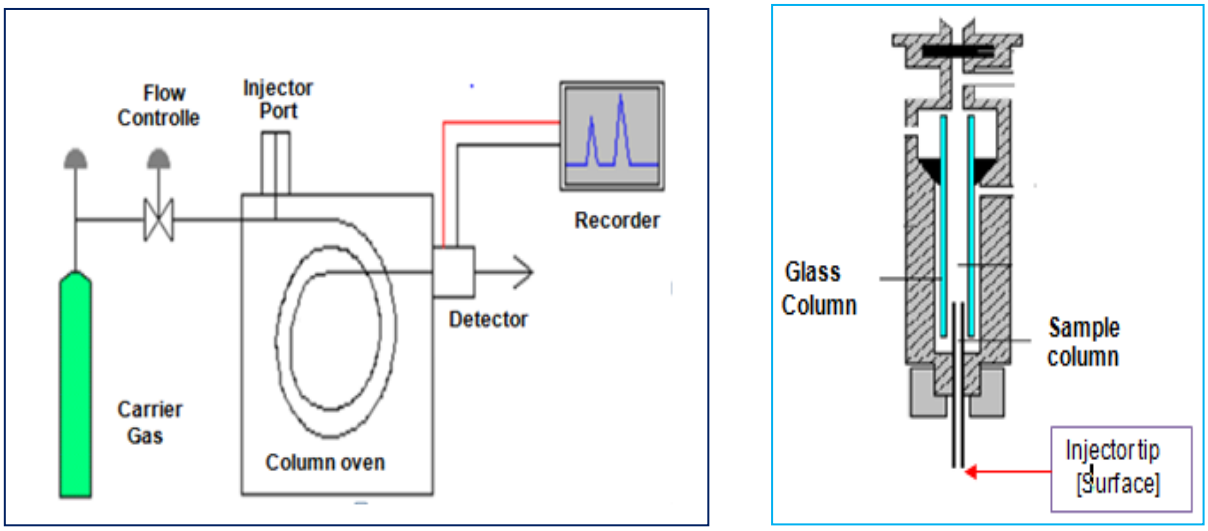


Figure 14: Schematic diagram of gas chromatography and the injection syringe

Besides this other equipment such as scanning electron microscope (DSM 982 Gemini. Carl Zeiss Ltd.), Ion chromatography for determination of anion concentration and the deferent procedure for TOC (Dimatoc 2000) determination in the liquid product, elemental analyzer (Vario El CUBE, from elemental analysis system GHbH, elementar.de), electronic balance, nylon membrane filter with sieve diameter of 0.45µm are some of the equipments applied for chemical analysis methods. Moreover, an OPUS7.2.139.1294 software is used for analysis, modification, manipulation and evaluation of the measured spectra of HTC char samples.

3.3 Experimental Procedure

In this study four experiments were performed. HTC of glucose solution, HTC of glucose solution with NH_4Cl, KCl and a mixture of three amino acid added to HTC of glucose solution experiments. Each experiment was performed two to three times. It must be emphasized that the experiments were all conducted under suitably controlled conditions and only very slight loss which cannot be avoided were observed, and the smaller quantities in the initial onset of the samples used make the calculation on the balance of each element difficult. Thus the elemental analysis and balance was only done for the most significant element carbon and nitrogen. In the first experiment a solution of glucose was prepared by

mixing with distilled water to a proportion in which the total organic carbon content is 10.77%, The TOC of a 15% by mass solid component of biogas residue. The mixture was shaken vigorously to create a homogeneous suspension. Then HTC is conducted in10ml stainless steel tubular autoclaves (Figure 12) loaded up to 70% with homogeneous glucose solution (≤1 mm in particle size) suspension. After the solution is loaded the autoclave is purged for one minute with argon or helium to remove oxygen, and the reaction is carried out at 180°C, 200°C, 220°C, 240°C, 260°C and 300°C for three hours including the heating time. Three hour reaction time is take because at three and above three reaction time it is possible to avoid the heating time. After that. the autoclave was allowed to cool down to 40°C before it was opened.

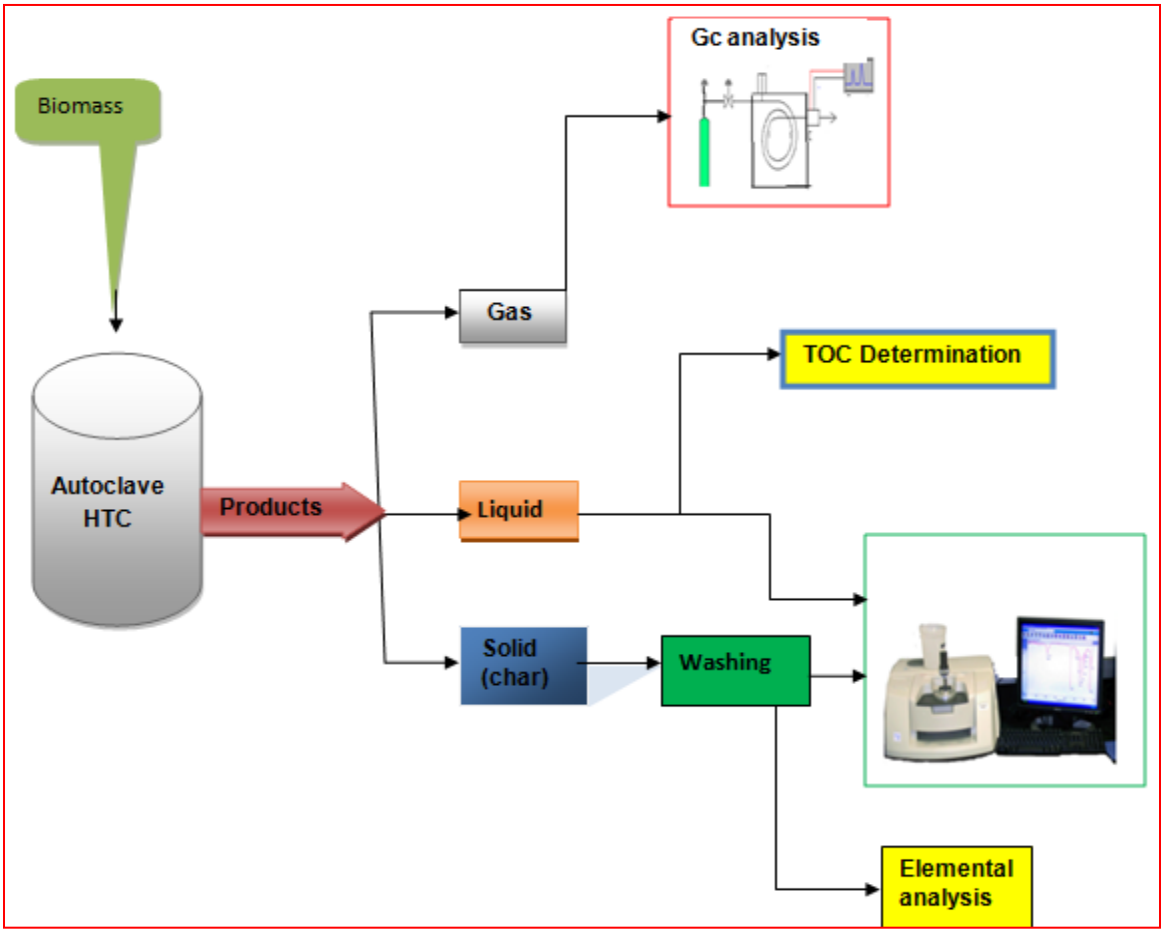


Figure 15: Schematic flow diagram of experimental procedure

After the gas is removed, the liquid portion and the wet solid were separated by either vacuum filtration (using 25mm nylon membrane filter with a sieve diameter of 0.45µm) or micro tube centrifugal separator. But the later was noted to have more loss compared to vacuum filtration, thus vacuum filter is used for all experiments to separate the liquid products from solid. The solid is measured after drying at 40°C at constant weight for 24 hours. The solid has to be washed either with a 0.0125% by mole or with distilled

water in a ratio 5ml to 0.5g for 1 hour. But the difference is not significant, thus in this work water was used for washing. The solid yield and total carbon recovery was calculated based on the mass of glucose and carbon initially present in the feed.

Total solid recovery (TSR) = {mass of dried char (m)}/ {mass of dry glucose in feed(m_g)} ……..…..2

Carbon recovery in solid (CRS) = {Mass of carbon in char}/ {mass of carbon in feed}……..…..…..3

According to the additives used, for example for amino acid, the solid is divided in-to two parts regarding the analytical methods. One part is dried at 40°C for 24 hours and the other taken to determination of protein content in wet base. The dried solid is grinded manually to a size of which it is acceptable for elemental analysis and IR measurement.

The IR spectra of liquid, dried solid and washing water is measured by using IR spectrometer. The measured spectra are modified and evaluated with various OPUS software evaluation techniques before designation of the functional group associated with a particular observed absorption bands. The bands assignments are after closer examining of the bands and comparing these values with those in the library as well as with the help of previously studied correlation tables which shows functional group and their ranges of corresponding frequency of absorption in wavenumber. The surface morphology and structure of the char were studied using scanning electron microscope (SEM) with respect to chemical structure.

4 Results and Discussion

3.4 Results

The experimental setups are dedicated on the solid recovery from the pure glucose solution using hydrothermal carbonization (HTC) and on the determination of determine the carbon efficiency of the resulting solid product. Furthermore, experiments were also conducted to investigate the contribution of nitrogen in solid when nitrogen containing inorganic salts and organic compounds are added to the solution. The optimum temperatures for maximum solid recovery and high carbon efficient solid production were estimated from the mass balance and elemental analysis and were found to be at 240°C and 300°C respectively.

3.4.1 Analysis of HTC product of glucose solution (GS)

HTC of pure glucose solution (GS) produces products in three phases, like hydrothermal carbonization of any other biomass. The carbon distribution by mass (m/m) among the three phases was calculated by determining the mass of carbon in each phase and comparing it with the dry starting mass. The product yields (m/m) range in 40 - 50% in between 200 - 300°C. The losses can be plausibly explained as wetting and spill or droplet losses and account for 1 - 5% in total mass balance. The liquid can only be separated from the solid at a temperature of 180, 200 and 210°C otherwise, liquid products were absorbed at the solid's surface and make the solid more moisten.

Table 7: Overall mass balances of HTC products of glucose.

Temp. (C)	Mass of solid [g]	Mass of liquid [g]	Mass of gas [g]	Liquid absorbed at solid surface [g]
180	0.061	5.931	0.004	1.500
200	2.32	0.527	0.234	3.747
210	2.34	0.14	0.456	3.534
220	2.021	0	0.326	4.367
240	1.082	0	0.379	5.837
260	1.045	0	0.443	5.975
300	0.949	0	0.273	5.939

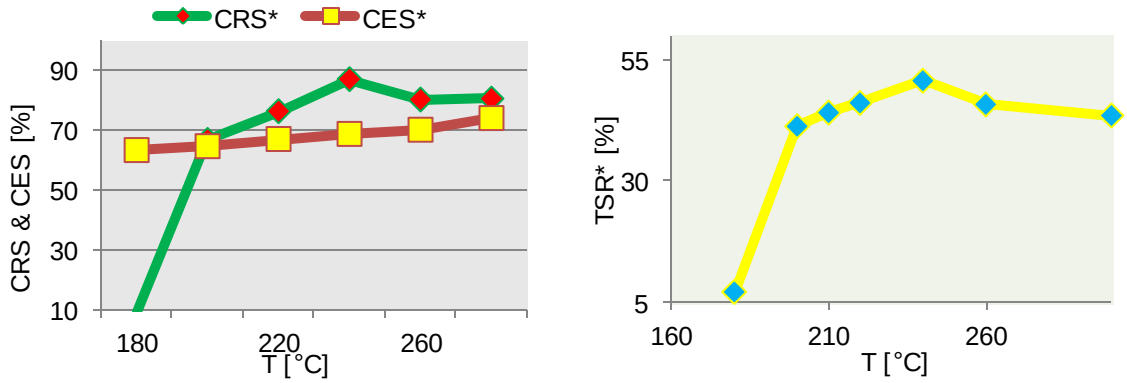
3.4.1.1 Carbon distribution among the three phases and carbon efficiency in solid

Carbon analysis in solid; From elemental analysis, it was found that the carbon retained in HTC char ranges from 66% at 200°C to 87% at 240°C while the remaining 5 -16% is in liquid and <5% is in gaseous products. The carbon composition for solid produced at 180°C is 62%. However, a very small amount of solid was recover compared to the solid produced at temperatures above 200°C. Nevertheless, the higher portion of carbon is retained in the solid phase as well as the carbon efficiency (CES) increases with

temperature as shown in Figure 16. The total carbon recovered in solid (CRS) at a given temperature is computed as;

$$CRS\ [\%] = \{ ([C] * m) / 0.8381g \} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where, CRS: carbon recovered in solid, [C]: concentration of carbon in solid, m: mass of solid, 0.8381: mass of carbon in the feed. The CRS at 200°C for example; CRS= (0.853 * 68%)/ 0.8381] * 100 = 69%. The carbon recovery and carbon efficiency as well as total solid recovery trends with temperature are shown at Figure 16.



CRS*: carbon recovery in solid, CES*: carbon efficiency of solid, TSR*: total solid recovery

Figure 16: Total solid recovery, carbon recovery and carbon efficiency of HTC char from pure GS

Carbon calculation in liquid; Some portions of carbons initially present in solid transferred to the liquid phase as dissolved organic carbon and highly observed at lower temperature, particularly at 180°C. This is because the residence time is short to carbonize the solution at this temperature. The oily colour of the liquid at Figure 17 also illustrates the more organic carbon content of liquid produced at this temperature. About 5.9ml of liquid was produce at 180°C while for the rest of temperatures approximately 2 - 4ml or less of liquid can be obtained. But as temperature rise, the TOC of liquid product is decreased. The decline of carbon content with rise in temperature suggests that organic compounds released into the process water are transforming to the solid products.

Table 8: Total organic carbon(TOC) of aqueous product

ACP @ Temp.	TIC* [mg/L]	TC* [mg/L]	TOC* [mg/L]	TNb* [mg/L]
180	n.f*	97748	97748	<100,00
200	n.f	37355	37355	<1000,00
210	n.f	14786	14786	<1000,00

n.f*: not found: TIC*: total inorganic carbon, TC*: total carbon, TOC*: total organic carbon, TNb: total nitrogen balance

The determination of carbon fraction in the liquid product was computed as;

$$TOC = [CL] * V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5$$

Where TOC: total organic carbon (g), [CL]: carbon concentration in liquid (mg/l) and V(ml): volume of liquid product. Thus at a temperature of 200°C, TOC = [37355mg/L] * 3.6ml = 0.1345g or 16% of carbon is released with liquid product. The same calculation was done at all other temperatures and all the result accounts less than 20% of the initial carbon present in the feedstock Table 9.

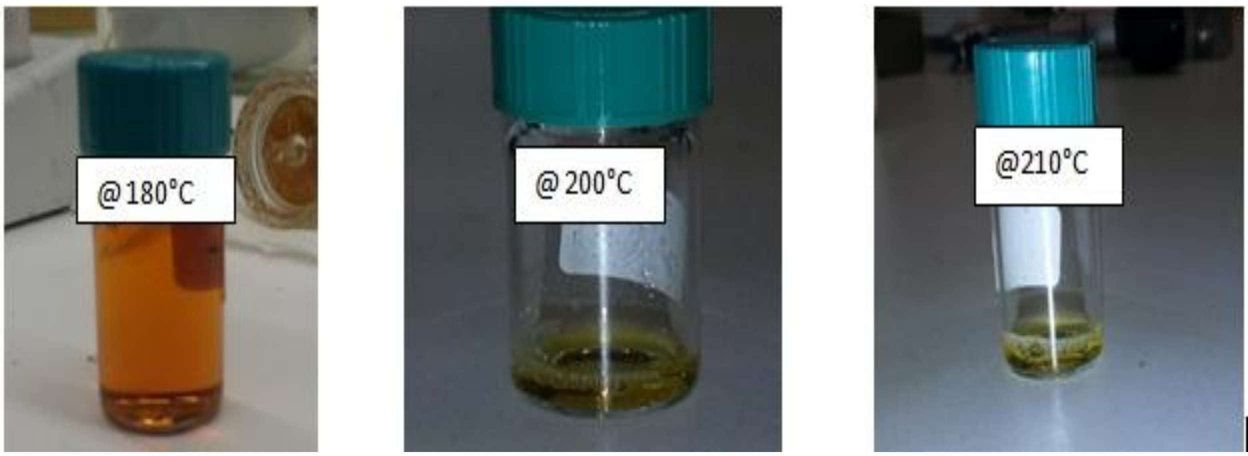


Figure 17: Aqueous products from HTC of glucose solution

3.4.1.2 Gas product analysis and carbon fraction in gas phase

The gas product, with higher content of CO_2 and small amount of CO, started to be produced at 200°C and increased in volume with the rise in temperature. As shown from the GC analysis, there are O_2 and N_2 with slight reduction with temperature in the product gas (Figure 18). Nevertheless, oxygen gas couldn't be produced from HTC of glucose solution. Also, the concentration of dissolved oxygen in the solution is insignificant since the autoclave was purged with argon before reaction. As indicated at Figure 18, the concentration of nitrogen in all experiment is nearly the same and the amount is also less than the detection limit of the analytical method. In such circumstance, the sources of nitrogen and oxygen is suggested to come from the ambient during injection. If that is the case, the concentration of oxygen in product gas has likely to be in proportion as it appears in the atmosphere, since oxygen alone couldn't leak selectively from the ambient air. Therefore, the higher fraction of oxygen in the product gas is due to the effect of argon gas (Ar) inside the gas chromatograph. The gas chromatograph identified the area under the Ar peak as oxygen since the GC is not calibrated for argon gas. The display of argon gas as oxygen in the GC might be due to the molar mass of the two gases are close to each other (32g/ mole for O_2 and 39.95g / mole for Ar.) and retain to show a peak in GC at approximately the same retention time. Thereby, the fraction of Ar was displayed as concentration of oxygen. Thus the amount of oxygen is found to be higher than nitrogen in the GC analysis. So the sources of both nitrogen and oxygen gas is

from the ambient and Ar. After removing nitrogen and oxygen the composition of gaseous products is only carbon dioxide and carbon monoxide as indicated by right picture of Figure 18.

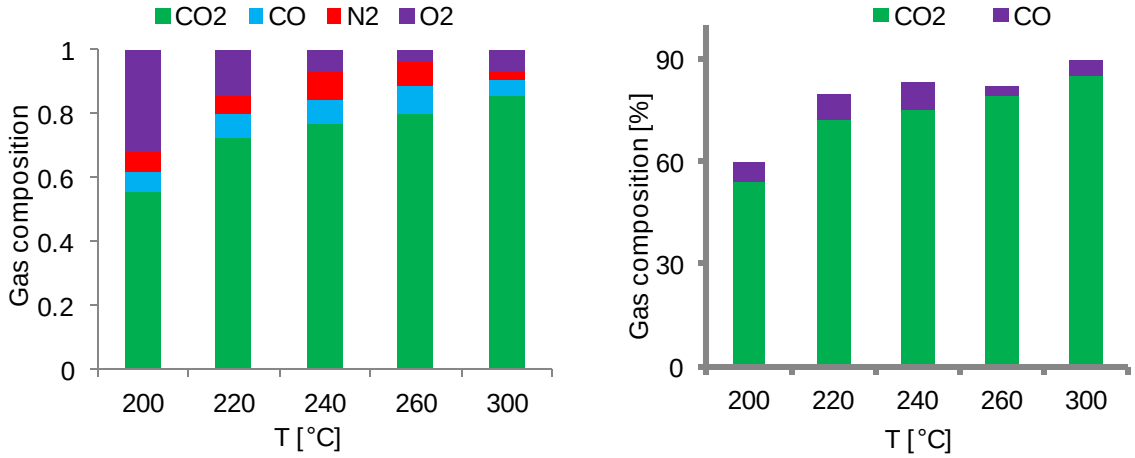


Figure 18: Gas products of HTC of glucose solution

The identification of argon as oxygen in the gas chromatograph is also checked by injecting pure Ar and helium (He) to the gas chromatograph. The analysis displayed that 99.8% of the result was considered as oxygen peak in case of argon injection while, only nitrogen and oxygen exactly at a ratio as the two gases appear in the atmosphere are obtained in case of He injection **(**Figure 19)

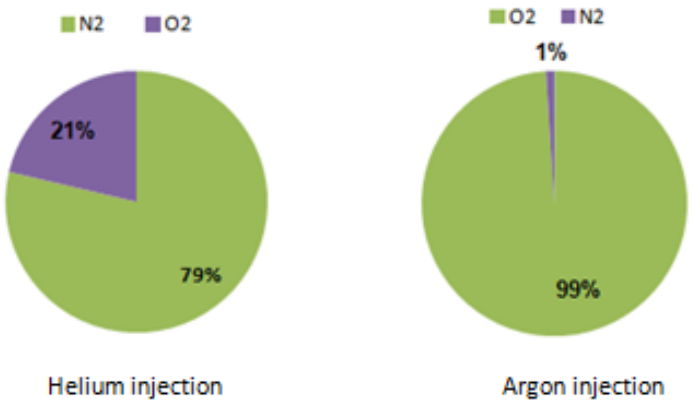


Figure 19: Gas chromatograph analysis of helium and argon

Carbon calculation in gas product; Carbon fraction in gaseous product is computed by using density of gases from literature (Density of CO_2 (ρ_{CO2}) =1.96 g/ L, density of CO ($\rho_{(CO)}$) = 1.15 g/ L at room temperature) and the gas composition from

Figure 20.

$$CFG = 0.273 * [CO_2] * \rho_{(CO2)} * V_g + 0.429 * [CO] * \rho_{(CO)} * V_g \quad \text{.....6}$$

where, CFG: carbon fraction in gas, [CO_2] : concentration of CO_2 in gas product,

V_g : volume of gas product, [CO] : concentration of CO in gas product.

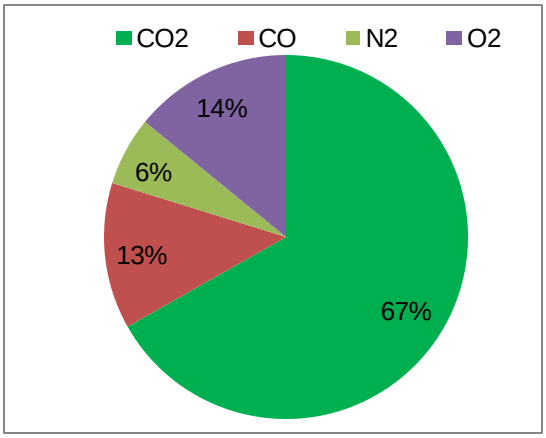


Figure 20**:** Composition of gas products at 240°C

The average mass of glucose and carbon in 7ml of sample solution respectively were found to be 2.0973g and 0.8381g. Therefore, the carbon fraction in gas product at 240°C as example was done below. The average volume of gas produced at 240°C is 35ml. By applying equation 6 above and taking the composition of gas from

Figure 20, the CFG for HTC process at 240°C is calculated to be 0.0126g. Thus, 0.0126g or {0.0126/0.8381g * 100 =1.5% which is <5 %} of carbon is released with the gaseous product. As indicated in Table 9 at the last column the carbon amount in the gas product is less than 5% at all temperatures.

Table 9: Solid recovery & carbon distribution among each phase of HTC products from GS.

Temperature [°C]	Carbon distribution among the three phase [%]		
	Solid	liquid	Gas
180	9.40	64.15	0
200	66.60	16.05	0.663
210	73.80	6.17	0.840
220	76.20	n.f*	1.173
240	86.90	n.f*	1.250
260	80.10	n.f*	3.000
300	80.40	n.f*	3.380

* n.f: not found

The overall carbon balance, expressed in percentage, was done by comparing the carbon in each phase of the product with the carbon original present in the feedstock. The result in this experiment shows an overall balance in between 80- 90 % while it is likely to be above 90%. The reason is that some fraction of

carbon was lost with washing water. To check this aspect the TOC analysis of washing water at few temperatures was conducted and the result is indicated in Table 10. The volume of washing water is taken in such a way that its PH value is above 4.5. In addition to the loss with washing water, there is also some losses in the wall of the reactor tube.

Table 10: Total organic carbon content of washing water.

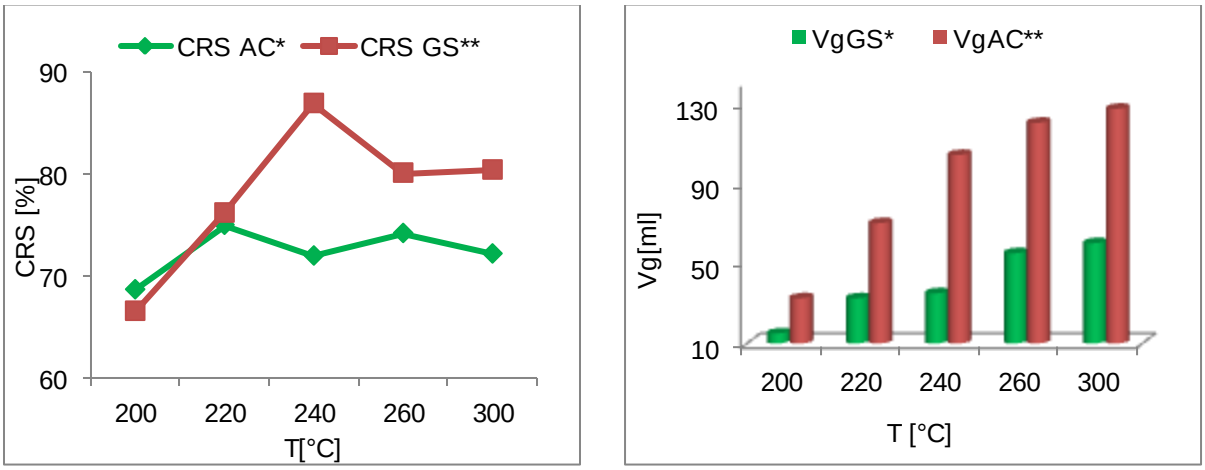
ACP* @ T.[°C]	TIC [mg/L]	TC [mg/L]	TOC [mg/L]	V_w* (ml))	TOC [%]
200	n.f*	1912	1912	25	5.7%
220	n.f*	3652	3652	12.5	5.45
240	n.f*	953	953	19.5	2.22
260	n.f*	1265	1265	17.5	2.64

n.f* : not found, V_w * : volume of washing water, ACP* : aqueous product, TOC*: total organic carbon

3.4.2 Effect of inorganic salts and amino acids on the yield and structure of HTC char

3.4.2.1 Effect of inorganic salts.

It is expected that nutrient and inorganic salt addition to hydrothermal carbonization (HTC) of pure glucose solution (GS) would affect product yield and surface structure of the char. In this experiment the effects of NH_4Cl (AC) on HTC of GS was examined. The solid mass recovered for HTC of GS with NH_4Cl added (AC) was computed and compared with the mass yield from HTC of GS. The maximum solid recovery was found to be 45%, which occurs at 220°C, while 50% solid at 240°C was attained in HTC of GS. The total carbon recovery in solid (CRS) is slightly less compared to the CRS from HTC of GS as indicated by Figure 21 (left). But the solid has nearly similar carbon efficiency (CES) with increasing trend with temperature like in the CES of solid produced from GS (Figure 16). Likewise the volume of the gas, predominantly CO_2 with trace amount of CO, is higher at the same temperature and thus the fraction of carbon explored with gas is to some extent increased (6%) in HTC of GS with AC added. Nevertheless, for all experiment, the carbon content of the liquid phase decreased with increase temperature and the majority of carbon remains still in the solid phase.

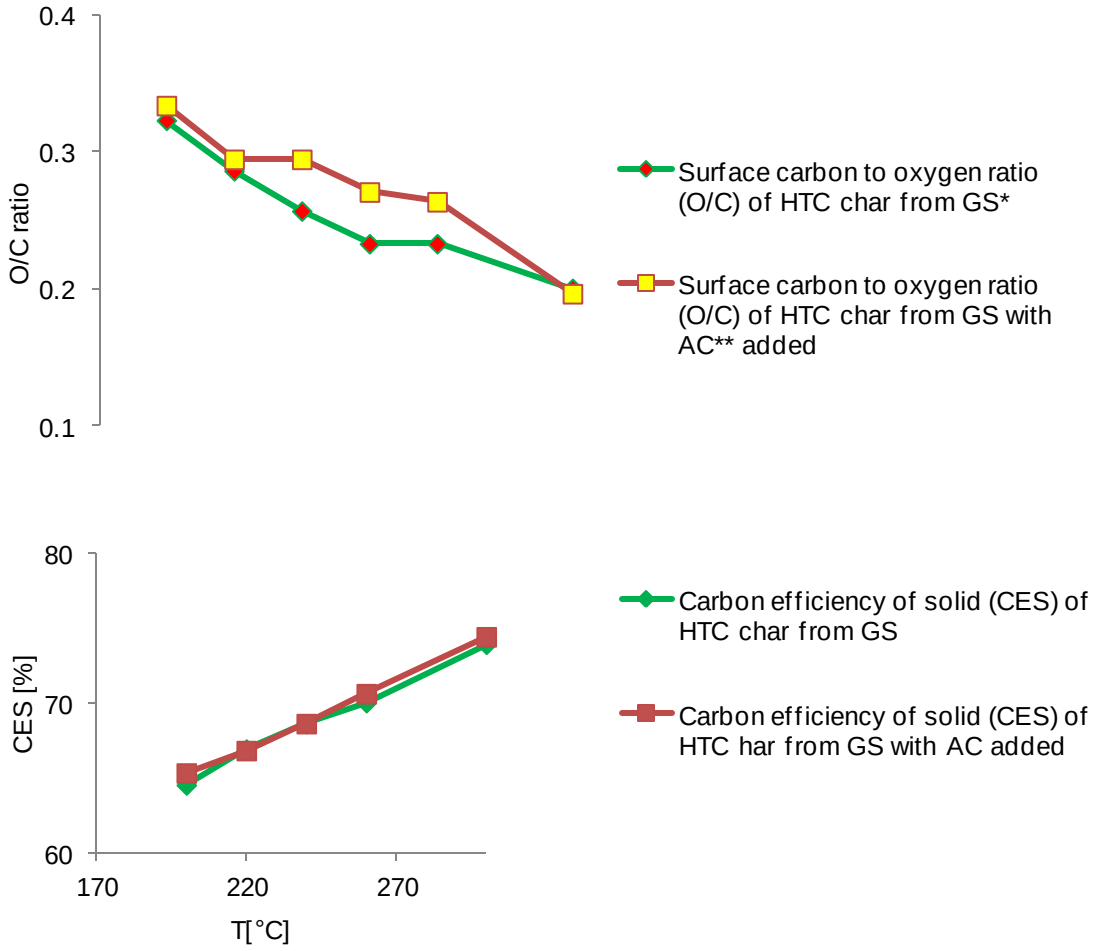


CRS AC*: carbon recovery in solid with AC added, CRS GS**: carbon recovery in solid from HTC of GS, VgAC**: gas volume from HTC of GS with AC added, VgGS**: gas volume from HTC of GS

Figure 21: Carbon recovery in solid and volume of gas products from HTC of GS with NH_4Cl (AC) added

The surface carbon to oxygen ratio (O/C), surface morphology, crystalline structure and orientation of molecules make up the HTC char as examined by scanning electron microscope (SEM) can be another evidence for the effect of ammonium chloride on the HTC of GS. The concentration of other elements in solid such as H_2, N_2, Cl_2 are lower compared to carbon and oxygen. The surface O/C ratio of HTC char produced from GS with AC added is higher compared to the surface O/C ratio of HTC char produced from GS (Figure 22).The reason is due to more carbon is cleaved with gaseous product (last column of Table

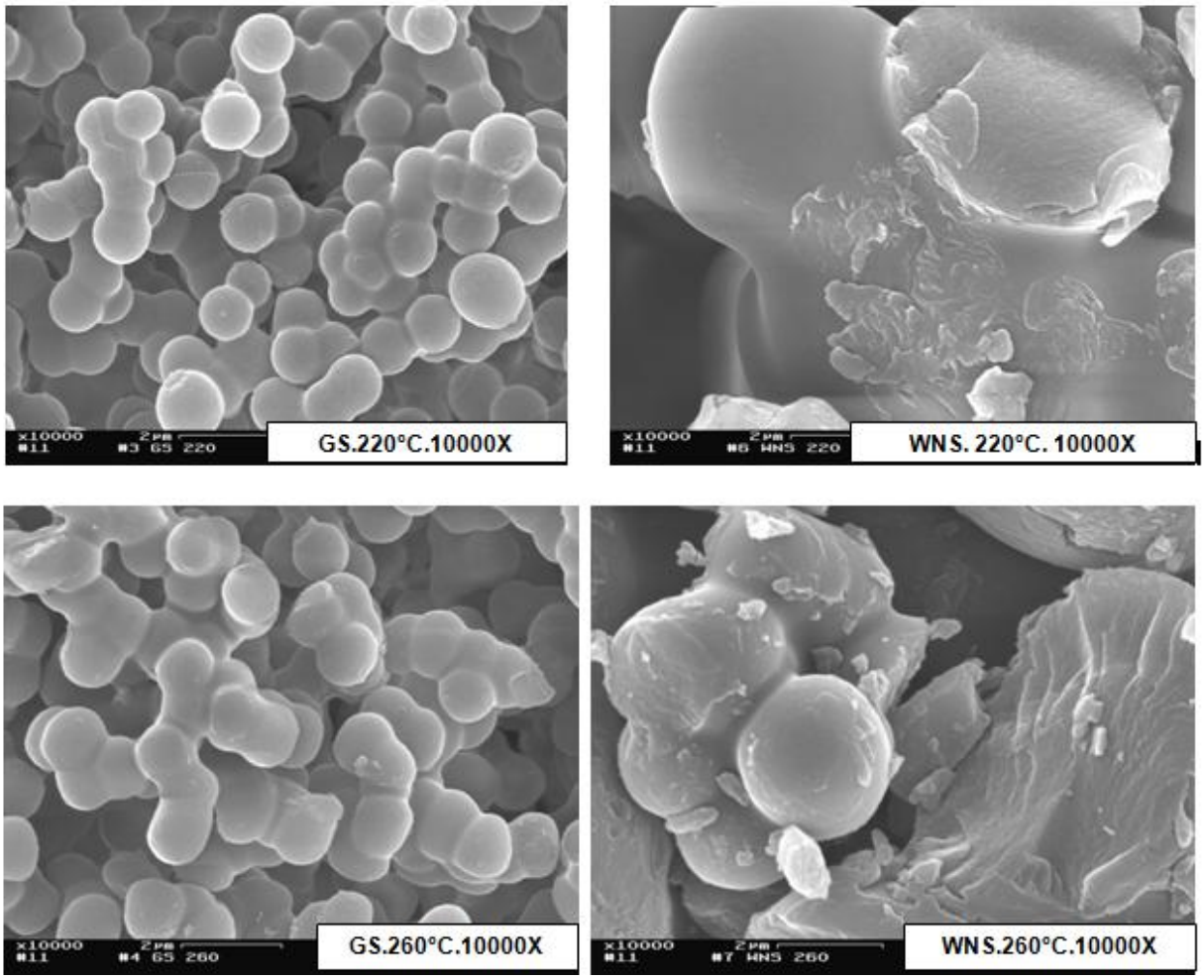
11) and also more of carboxylic groups might be exposed to the surface of the char due to the catalytic effects of ammonium chloride.



GS*: glucose solution, AC**: ammonium chloride

Figure 22: Effect of NH_4Cl on CES and surface O/C ratio of HTC char

The SEM image of the solid char indicates that the materials so formed are composed of agglomerates of carbonaceous microspheres, evidenced by Figure 23.



GS: Glucose solution. WNS: glucose solution with NH_4Cl added

Figure 23: SEM Image of HTC char

The physical nature of HTC char, as shown in Figure 24 indicates that HTC char from pure glucose solution has brown colour. On the other hand, HTC char produced at the same temperature, from glucose solution with AC added is black.

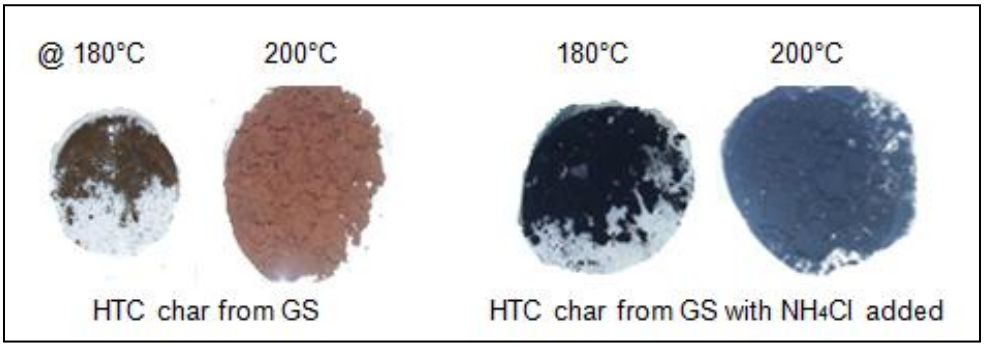


Figure 24: Physical appearance of HTC char produced from GS without and with NH_4Cl added

3.4.2.2 Carbon distribution among the three phase products

With same calculation done for HTC product of glucose solution at 4.1.1 and 4.1.2, the solid balance and carbon distribution among the three phases of HTC products from GS with NH_4Cl (AC) added were computed. Carbon retained within the solid varies from 68% to 75% within 200°C - 300°C temperature ranges.

Table 11: Carbon distribution tendencies among the three phases product of HTC of GS with AC added

Temperature [°C]	Carbon distribution among the three phases [%]		
	solid	Liquid	Gas
200	68.70	18.3	0.94
220	75.00	8.3	2.90
240	72.00	6.8	5.40
260	74.20	5.5	5.04
300	72.20	3.3	6.30

Similar to the total carbon balance on HTC of glucose solution Table 10, the sum total of carbon from each phase of the products is expected to be above 90%. But the result goes down to 85%. This is due to the liquid products of HTC, which contains some organic carbon adsorbed at solid's surface were removed with washing water as well as the loss with the reactor tube wall.

3.4.2.3 Nitrogen contribution

The amount of nitrogen contributed by ammonium chloride in the feed is very small, see material and method section (**Error! Reference source not found.**) in the sample solution. Due to this, nitrogen nalysis result in all phases of products indicated below the detection limit of the analytical methods, thus the nitrogen determination is impossible on each phase of products.

3.4.2.4 Chlorine contribution

Elution of chlorine (Cl) from the solid product indicates a small presence at 200 and 220°C only and found to be 0.152% and 0.12% respectively. Thus the total amount of Cl recovered with solid is computed from

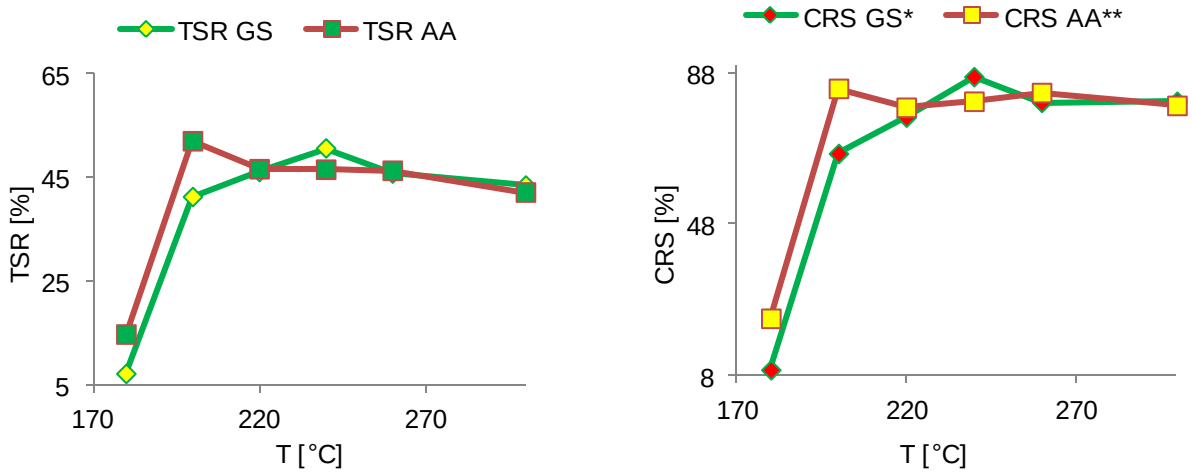
$$ClS = [Cl] * m \quad \ldots\ldots 7$$

where CIS: total chlorine retained in solid [%], [Cl: chlorine concentration of solid and m: mass of solid product. Therefore, the result gives 5.41% and 4.56% respectively.

3.4.3 Effects of Amino Acids

3.4.3.1 Solid recovery and carbon efficiency

Adding amino acids in HTC of glucose solution (GS) shows maximum solid recovery at lower temperature (200°C) compared to the maximum solid recovery from HTC of pure GS (240°C). The initial value of glucose and carbon composition are similar with the value used in calculation 0 (i.e. 2.0973g and 0.8381g respectively). The same computation was done for total solid mass recover (TSR) and total carbon retained (CRS) in the solid as well as the carbon distribution among the three phases. The result is shown in Figure 25 and Table 12 respectively. The total carbon balance from all phases for HTC of GS at 180°C is 73%. This is because more losses were experienced during solid liquid separation since solid product at this temperature is too small and was difficult to handle.



CRS GS*: carbon recovery in solid from HTC of GS, CRS AA**: carbon recovery in solid from HTC of GS with AA added

Figure 25. TSR and CRS in HTC char produced from GS with AA added

Table 12. Carbon distribution among the three phase from HTC of GS with amino acid (AA) added

Temp [°C]	Carbon distribution among the three phase[%]		
	solid	Liquid	Gas
180	23.00	50.00	0.014
200	83.80	10.10	1.4
220	78.80	3.84	3.50
240	80.40	2.06	4.33
260	82.70		5.13
300	79.30		6.42

Figure 26 is the SEM images of HTC char produced from pure GS, at the first figure, and HTC produced from GS with AA added, the second figure, with the same magnification power of 100X. As observed from

the image, carbon microsphere composed of small primary agglomerated particles with great variation of shape among themselves are observed on the HTC char produced from GS with (AA) added. Moreover, the particles observed on the surface are clearer for HTC char with AA added when compared to the particles of HTC char produced from GS when investigated at the same magnification power.

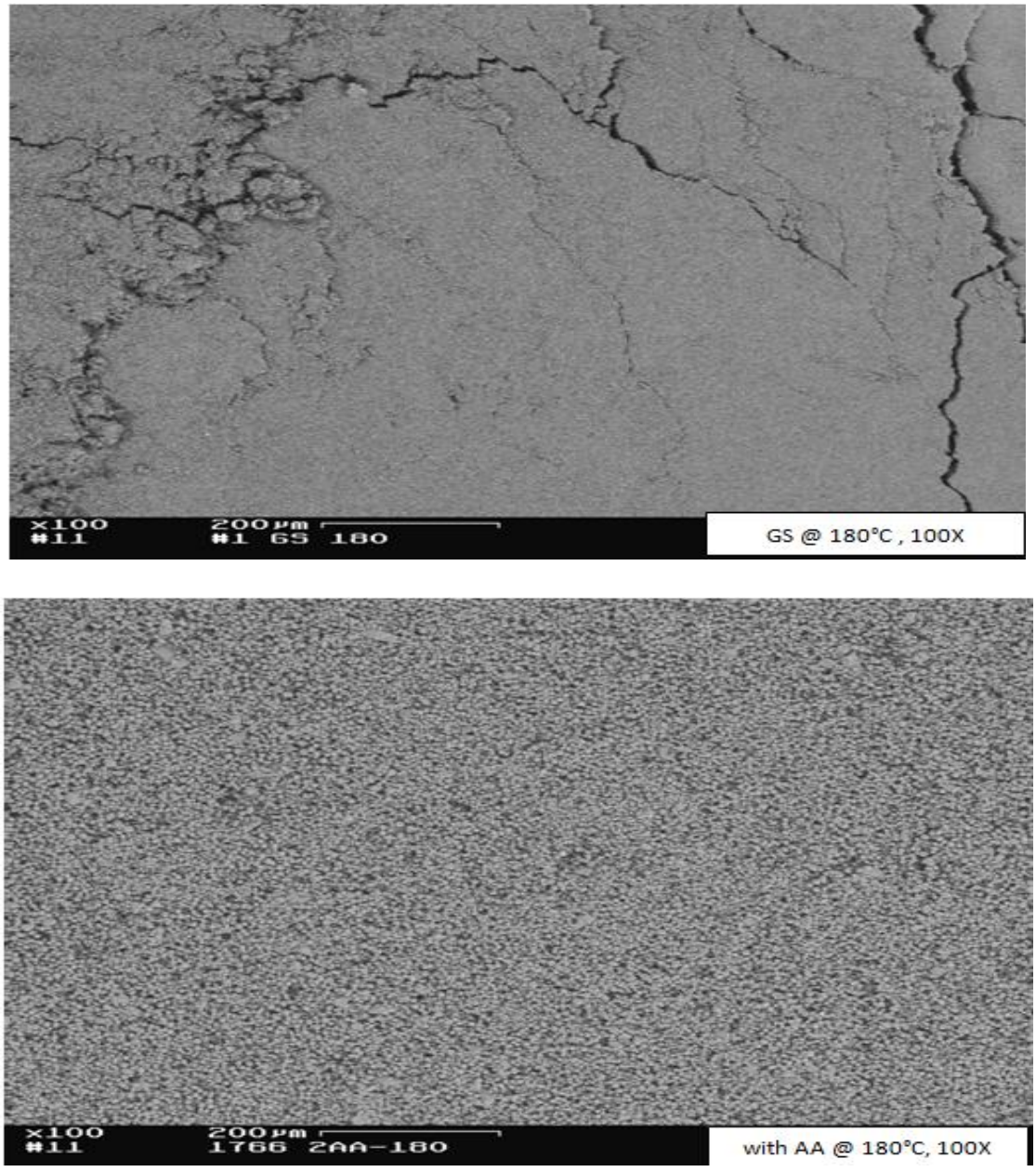


Figure 26: SEM image of HTC char without and with AA added at a magnification power of 100X

The comparison at different magnification power, (that mean 2000X for AA added and 3000X for GS) also indicates that, the different is clearly observed as HTC char produced with AA added are agglomeration

of particles having different size and shape Figure 26, while almost all of the particles of HTC char from GS have same size and look like regularly oriented.

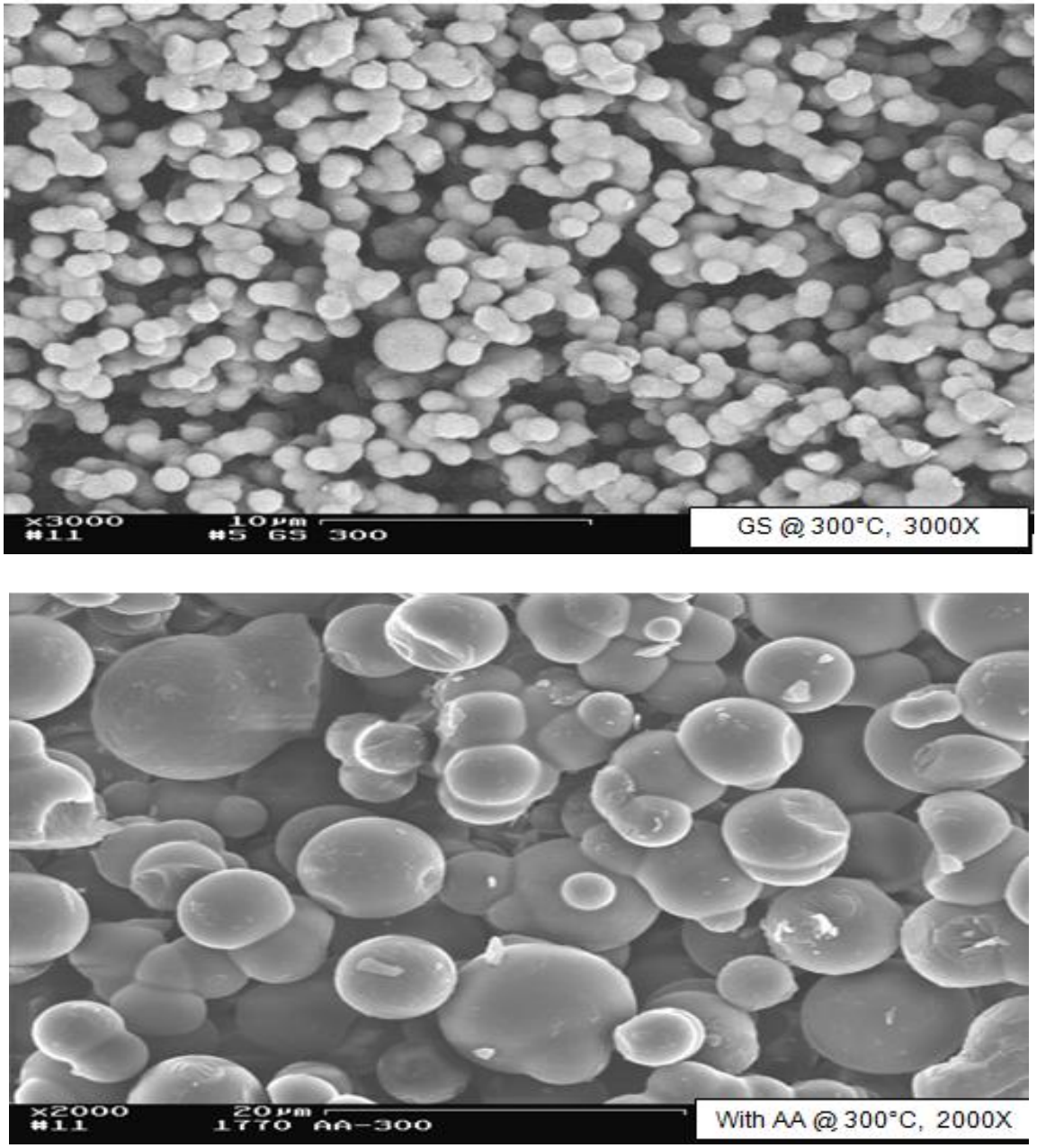


Figure 27: SEM image of HTC char from GS With and Without AA added at different magnification power

The surface oxygen to carbon ratio of HTC char produced from GS with AA added is higher in comparison to surface oxygen to carbon ratio of HTC char produced from GS (Figure 28). However the carbon efficiency shows a slightly higher at a temperate above 240°C.

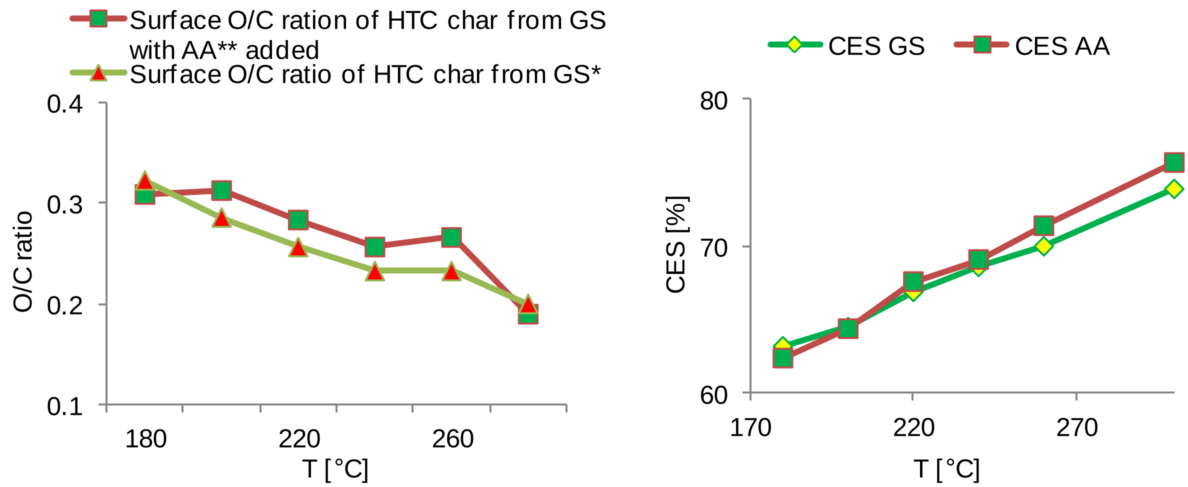


Figure 28. Surface O/C ratio and CES of HTC char produced from GS with and without AA added.

3.4.3.2 Estimation of nitrogen

Estimation of nitrogen in solid; the elemental analysis indicated substantial amount of nitrogen in solid product with amino acids (AA) added compared to NH_4Cl added. This is due to the presence of more nitrogen, contributed by AA in the onset. The concentration of each acids in the solution is given in mass percentage at section (**Error! Reference source not found.**) from which amount of nitrogen within the olution is found to be 0.6911g/l.

TNS = $[N_2]s$ * m ……………………………………………………………….8

Where TNS: total nitrogen in solid (mg), $[N_2]s$: nitrogen concentration of solid (%), m: mass of solid. Thereby, nitrogen involved with the solid is computed and compared with the initial in the feed. The result is shown in Table 13.

Table 13: Nitrogen contribution in solid products

T[°C]	$[N_2]s$[%]	[C]s[%]	N_2 recovery [%]
180	1.66	62.4	105
200	0.5	64.4	47.94
220	0.753	67.6	51.12
240	0.803	69.1	51.12
260	0.803	71.4	54.69
300	0.859	75.7	

At 180°C, the nitrogen amount is higher than the initial feed indicating that since the base of calculation is in milligram a small contamination effects case a high fluctuation of the calculation result. Beside that a + /

- 5% error should be considered. Thus, approximately 50% of nitrogen is likely to contribute in the solid products at a temperature of reaction above 200°C.

Estimation of nitrogen in liquid products; Nitrogen and nitrogen contending ions produced with liquid and gaseous products are below the detection limit of the analytical methods, let the computation difficult in these phases. Total organic carbon analysis of the liquid product (The same goes for chlorine ions determination in each phases.

Table 14) indicates that the concentration of nitrogen containing ions are small similarly to in the case of HTC of GS with NH_4Cl added. The same goes for chlorine ions determination in each phases.

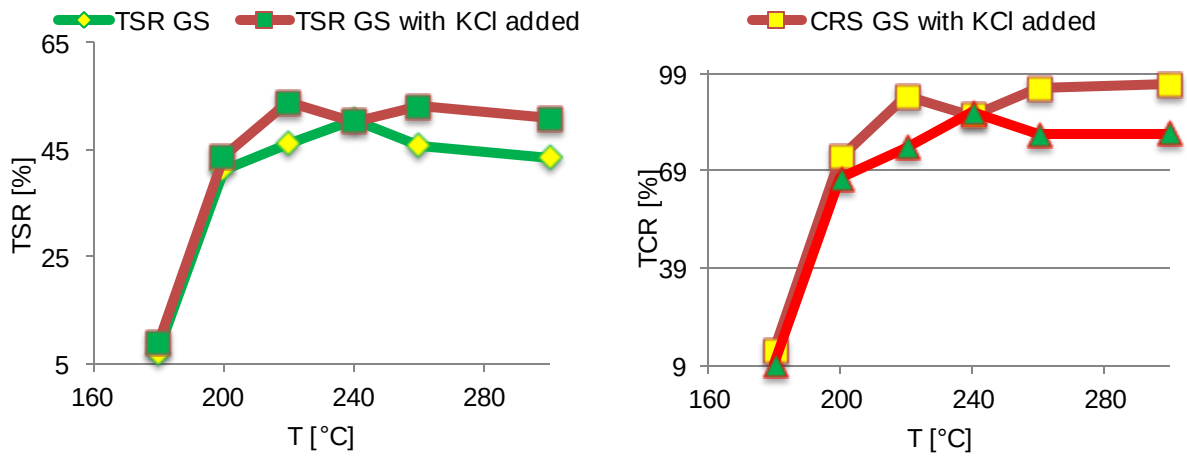
Table 14: Liquid product analysis of HTC of GS with AA added

ACP @ T [°C]	V_L[ml]	NH_4^- [mg/l]	NO_2^- [mg/L]	NO_3^- [mg/l]	TC [mg/l]	TOC [mg/l]	TNb
180	5ml	<100	n.d	<10	80769	80769	<1000
200	3.2	<100	n.d	<10	23157	23157	<1000
220	2.4	<100	n.d	<10	13407	13407	<1000
240	2.4	<100	n.d	<10	7205	7205	<1000

n.d: not determined, ACP: aqueous products

3.4.4 Effect of Potassium chloride

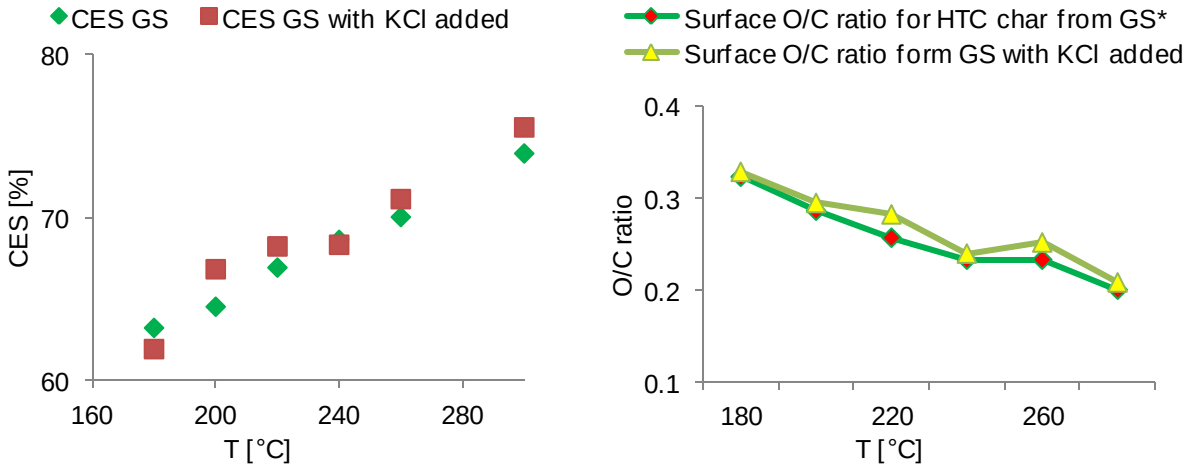
By adding KCl to HTC of glucose solution, the solid mass yield gives a slight increase compared to HTC of pure glucose solution as well as with NH_4Cl and amino acid added. The total mass of solid and total carbon recovered within the solid is calculated with the same procedure as 3.4.1.1 and the results are shown on the graph in Figure 29. The maximum solid recovery (53%) occurs at 220°C while in case of HTC of pure glucose solution maximum solid recovery of 50% (m/m) was found at 240°C. However, there is a small fluctuation of solid recovery above 220°C in case of KCl added HTC of glucose solution. But at all temperature the mass yield is higher. The added salt might catalyzed the condensation reactions which cause the formation of products that can precipitated in the HTC char, result in an increase in mass of solid.



TSR GS : total solid recovery from HTC of GS, CRS GS : carbon recovery in solid from GS

Figure 29: Total solid recovery (TSR) and carbon recovery in solid (CRS) of HTC of GS with KCl added

From the elemental analysis and examination of HTC char with SEM, the carbon efficiency (carbon component) and surface carbon to oxygen ratio of HTC char from glucose solution and from glucose solution with KCl added are nearly the same Figure 30.



CES GS: carbon efficiency of solid produced from glucose solution, O/C: surface oxygen to carbon ratio, GS*: glucose solution

Figure 30. Carbon efficiency and surface O/C ratio of HTC char produced from GS with KCl added

Unlike the image of HTC char produced from GS, the SEM image of HTC char produced with KCl added have particles having different size and distributed regularly.

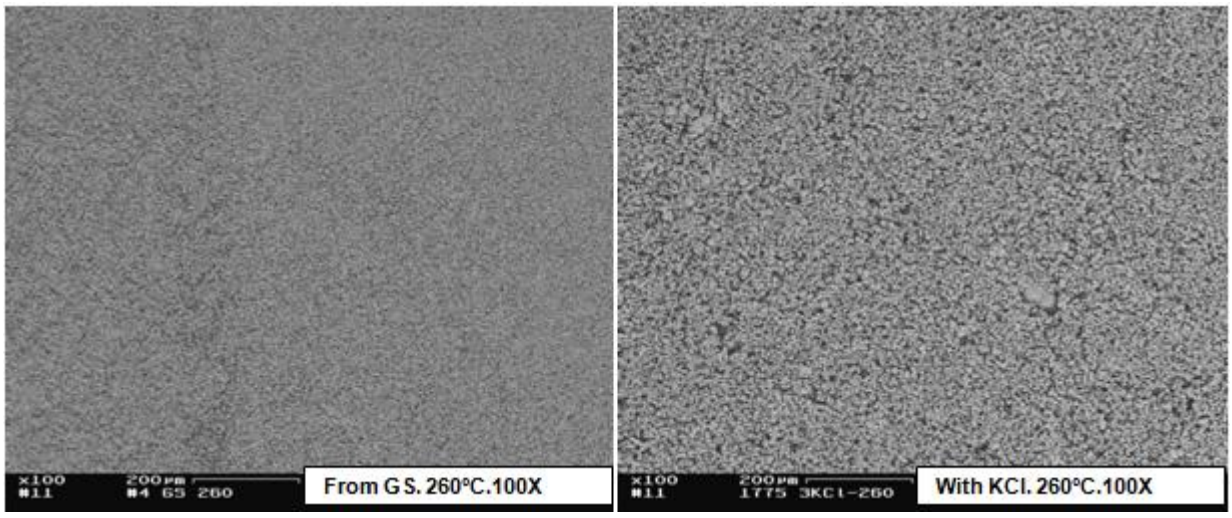


Figure 31. SEM image of hydrochar produced from GS without and with KCl added

The particle's size difference also observed when compared at different magnification power (i.e. using low magnification power for the HTC produced with KCl added and high magnification power for HTC produced from GS).

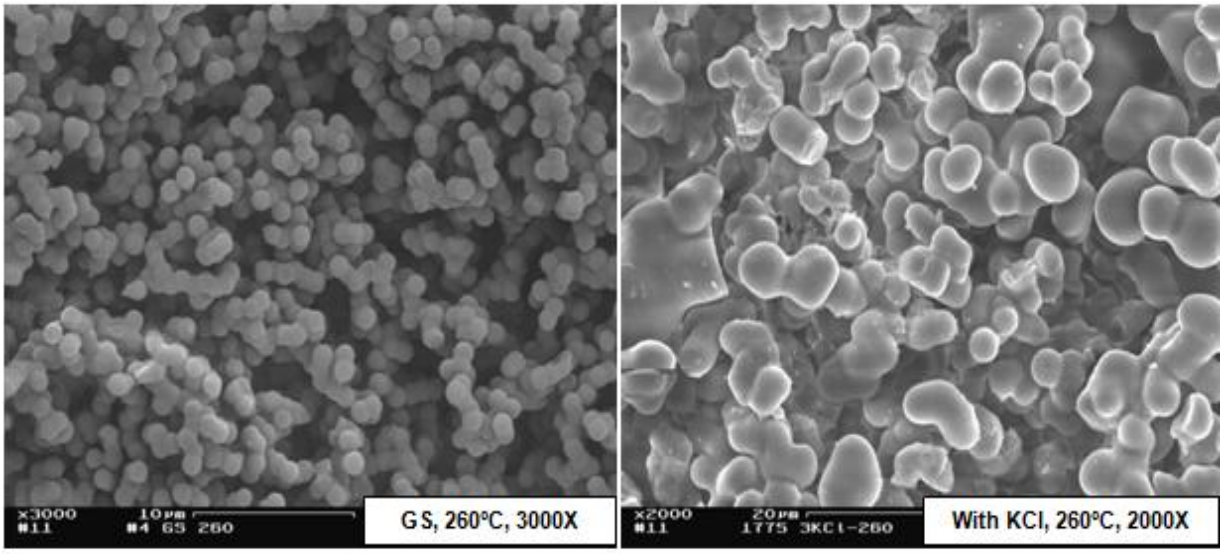


Figure 32. SEM image of HTC char from GS without and with KCl added at different magnification power

In the HTC of glucose solution with KCl additive, aqueous products are only produced (can be separated from solid) at 180 and 200°C. At temperatures above 200°C the liquid products are adsorbed on the solid's surface. Since the initial amount of (KCl) used in the feed is very small (see **Error! Reference ource not found.**), (K^+) and (Cl^-) ions are impossible to be determined. The HPLC of liquid product indicates that the presence of other organic components dominate the peak which should be observed on the expected retention time of Cl^- ion due to its small presence.

3.4.5 Investigation of hydrochar with IR spectroscopy and identification of functional groups

By applying some of the manipulation and evaluation techniques from OPUS software packages, the spectra of the hadrochar (HTC char) produced from pure glucose solution (GS) and with NH_4Cl(AC), amino acid (AA) and KCl added were compared with the spectra from the demo library within the software as well as among themselves in order to distinguish the associated functional groups. The average spectrum (AS) of the HTC char produced from GS at all temperatures was computed and used as reference at a threshold of 97.5. Each spectrum produced at individual temperatures was first compared with the average spectrum. The comparison showed a little to no change as indicated by the correlation coefficient (CR) >99% Table 15. Only small variation for the char produced at180°C is observed near 3600 - 3000cm^{-1}, where the OH functional group is found to exist. Another variation might exist in the finger print region due to the difference in number of carbon atoms single and double bonds as well as different in isomeric structure.

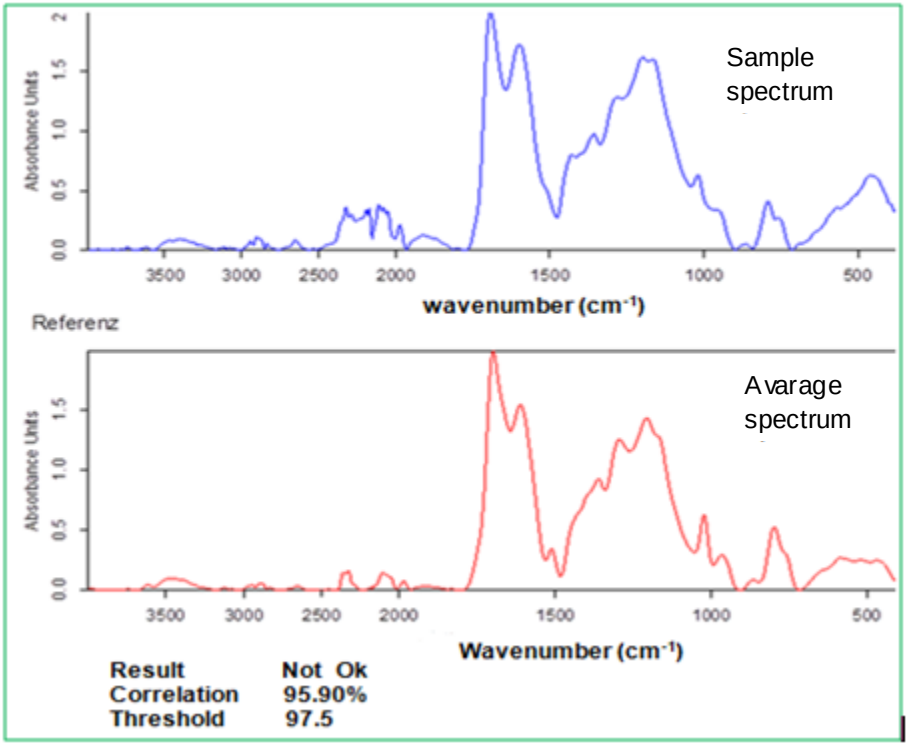


Figure 33: Comparison of HTC char produced with AA additive and average spectrum (AS)

A small variation on the correlation coefficient is observed when HTC char produced with AC, AA and KCl added were compared with AS indicated by the CR Table 15. The effect is mainly observed with AA and AC added where the amine functional group is found to exist.

Table 15: Correlation coefficient of HTC char produced from GS with AC, AA and KCl added compared with AS

Temperature [°C]	Char from Glucose	With NH_4Cl additives	With amino acid additives	With KCl additives
180	97.6	Nm*	96.81	99.5
200	99.94	97.52	96.61	98.48
220	99.97	98.23	96.73	98.38
240	99.80	96.21	95.71	98.02
260	99.60	97.5	97.34	98.44
300	99.40	97.91	97.79	98.46

Nm*: Not measured

Another spectrum evaluation technique applied in this investigation is spectrum search which shows substances having known functional groups and similar structure with HTC char. Closer looking the spectra and the structural bonds of both the sample and reference spectra from the library, HTC char found to have 994 hit quality with phenazine and suggested having aromatic ring with complex molecules.

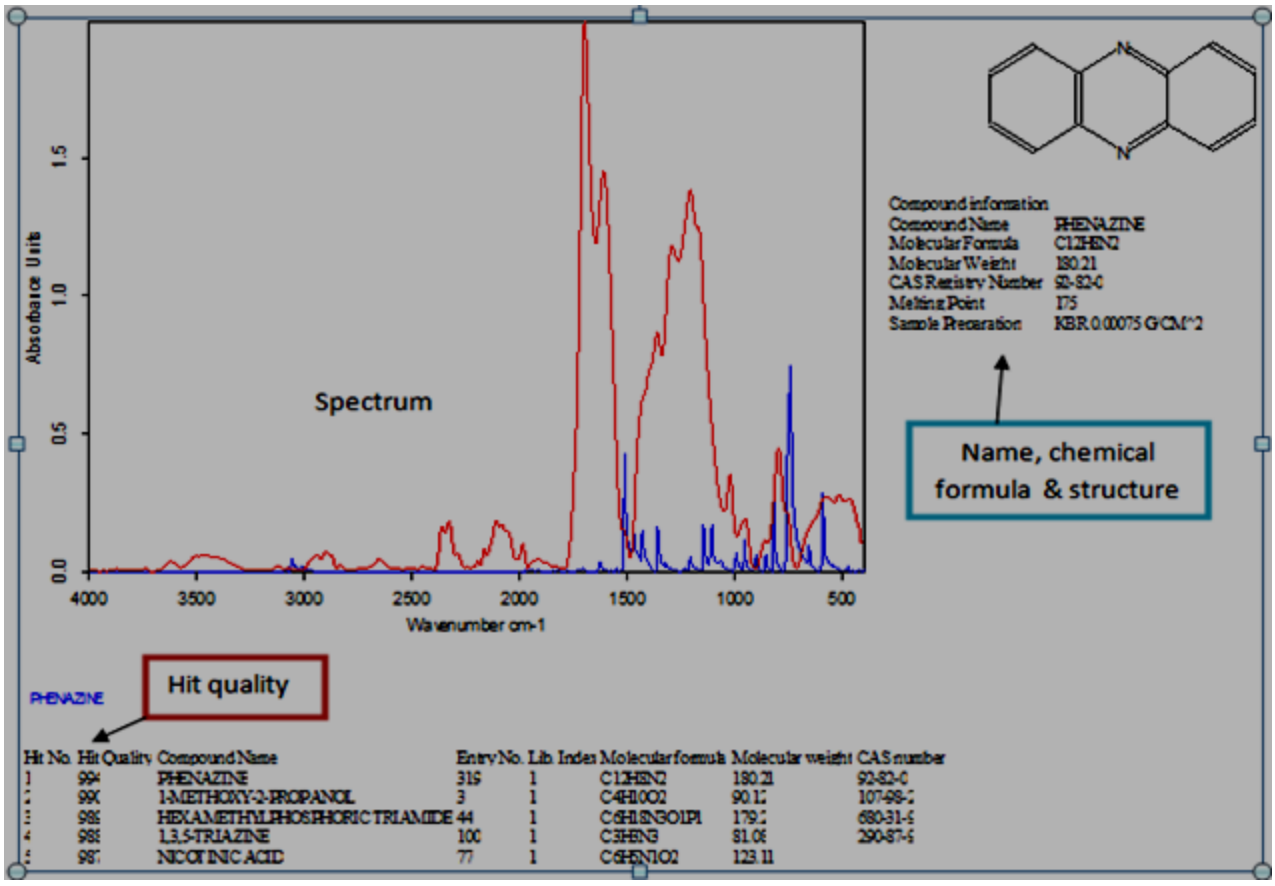


Figure 34: Spectrum search result of HTC char from the existing library of spectra

The spectrum searches for the char at 180°C in the range of 3700cm^{-1}–3000cm^{-1} lists spectra of all substances which have a functional group possessing stretching vibration in this region such as OH, amine and amide functional groups. As indicated in Figure 35, the reference (green) and sample spectrum (red) have the same shape in the wave number range specified. So the substance with the highest hit quality likely to have the same structure with the sample, thus exhibit the similar functional groups. The broad band for 4-hydroxy 4-methyl-2- pentanone at this region is due to the presence of OH functional group as shown in the structure. Thus, HTC char at the same region also have OH functional group.

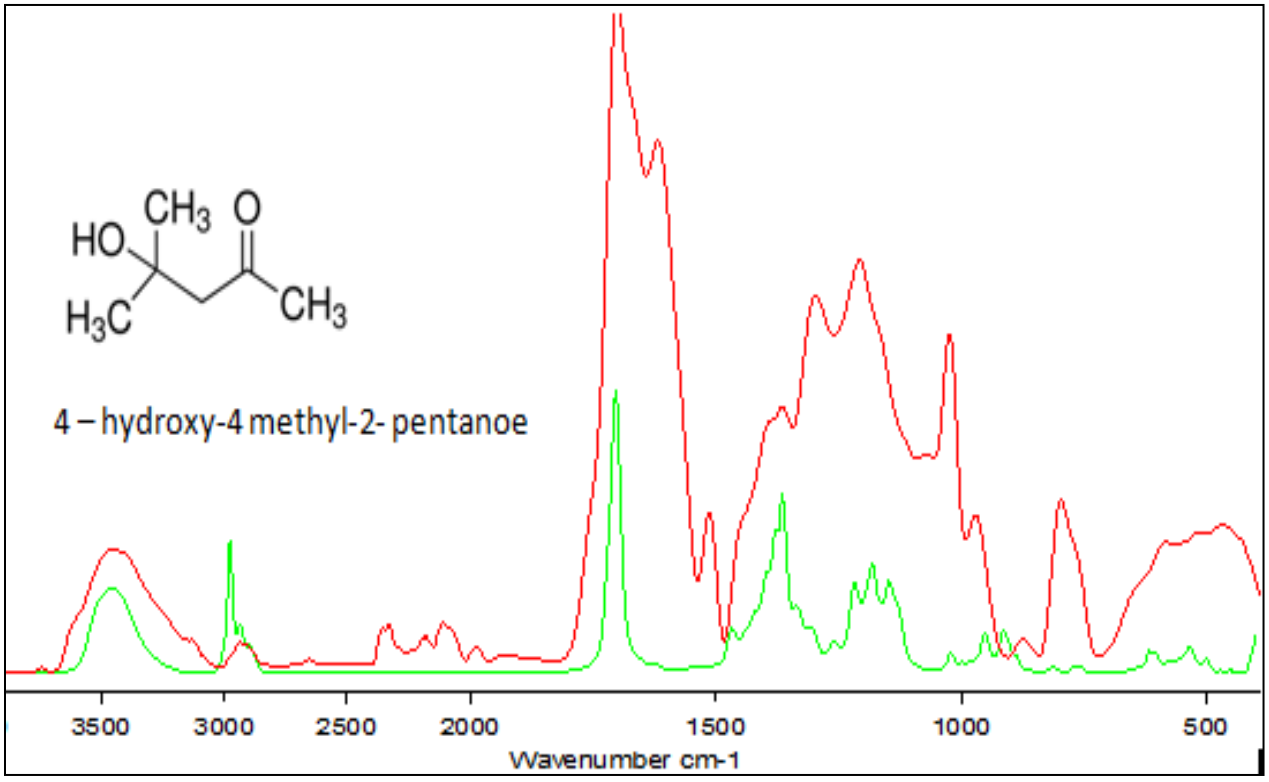


Figure 35: Spectrum searching in a specific wavenumber range (3700cm^{-1} - 3100cm^{-1})

The spectra comparison was also done for some own measured samples in order to suggest the possible functional groups similar to the known samples

3.4.5.1 Identification of functional groups of hydrochar

By applying the above spectra interpretations, the spectra of hydrochar were examined and the main functional groups are identified. The IR spectroscopy study of the produced char indicates that, the entire spectra looks like the same. But a closer look in to the spectra shows a small difference in the intensity and width of the bands. This is due to the variation in the number of carbon - carbon single and double bond as well as the corresponding stretching bond strength. Often, only a few of the bands corresponding to particular functional groups are interpreted whereas the rest are used for detail molecular comparisons.

The bands in the fingerprint region originated from interacting vibration modes resulting in a complex absorption pattern. Usually this region is quite complex and often difficult to interpret one by one. The HTC char produced in these experiments shows three major absorption bands in the functional group region of IR spectrum. The region in between 3200cm^{-1} – 3600cm^{-1} shows a broad band which indicates the presence of OH functional group. This band is more usual at lower reaction temperatures, since more of oxygen atom is remained in the solid. However, over 3424cm^{-1} a broad bands were also suggested to be an overtone of C=O bands which accompany carbonyl or a ketone functional group at 1698cm^{-}1. But at a higher temperature the bands in this region disappeared showing that it is due to the OH functional group instead of overtone. The CH_3 stretching absorption has a very week band at around 2922cm^{-1}. A weak absorption bands near a wavenumber of 2200cm^{-1}, is simply due to the absorption of the diamond crystal during measurements. A wide band with two maximum peaks can be noticed in between 1700cm^{-1} – 1500cm^{-1} and shows the presence of C = O in a ketone or carboxyl functional groups. Absorption bands below 1600cm^{-1} to 400cm-1 contains vibration of mixed origin and termed as a figure print of the molecule; contains many overtone and combination bands that are distinct for individual compounds. In the infrared spectrum of certain substances, there are weak but characteristic bands that are known to be due to overtone or combination bands. So, the weak peak band near 2927cm^{-1} is probably of the overtone of the peak near 1463cm^{-1}, which is the asymmetric bending of CH_3.

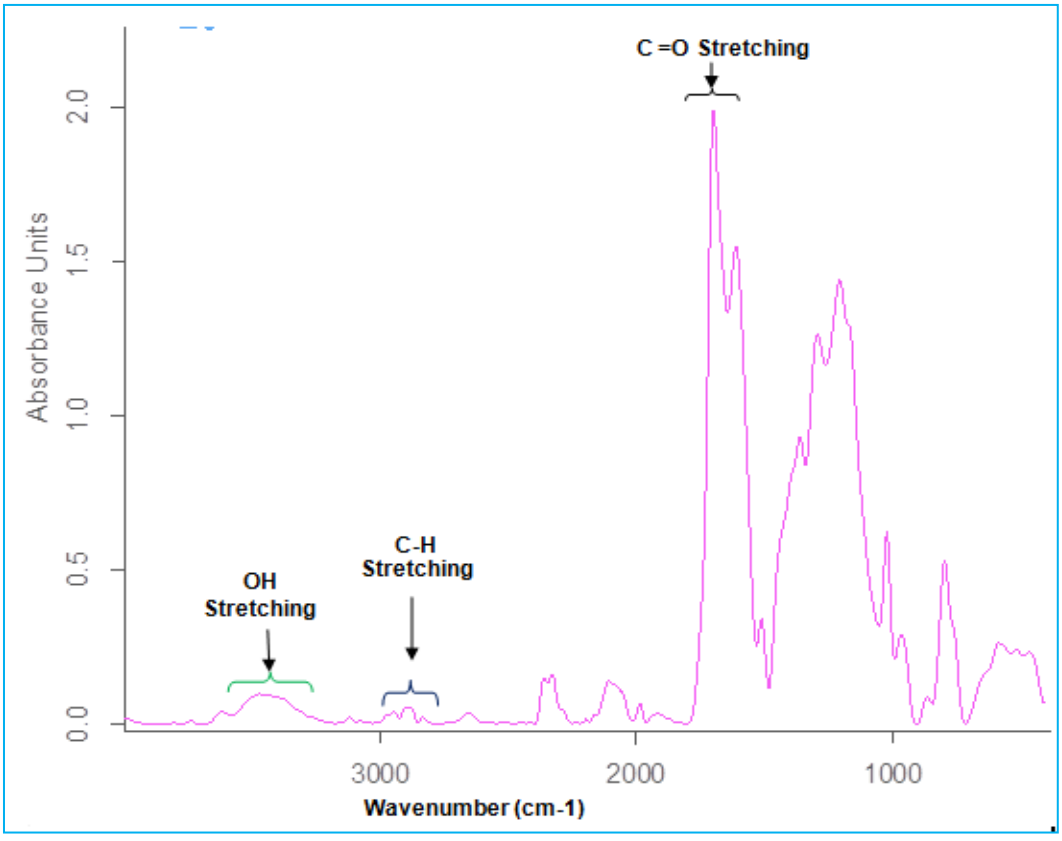


Figure 36: Fundamental Functional group associated with HTC char

3.4.5.2 Effects of temperature and additives on the IR spectrum of HTC char

The spectra variation is also observed for the char which are produced at highly different ranges of temperature. As indicated in the wave number range of 3600cm^{-1} – 3200cm^{-1} (Figure 37) a broad band caused by the presence of hydroxyl functional group is highly observed at lower temperature. Moreover, the double peaks near 1745 – 1545 cm^{-1} is found to be more intense and become equal as temperature of HTC reaction is increase.

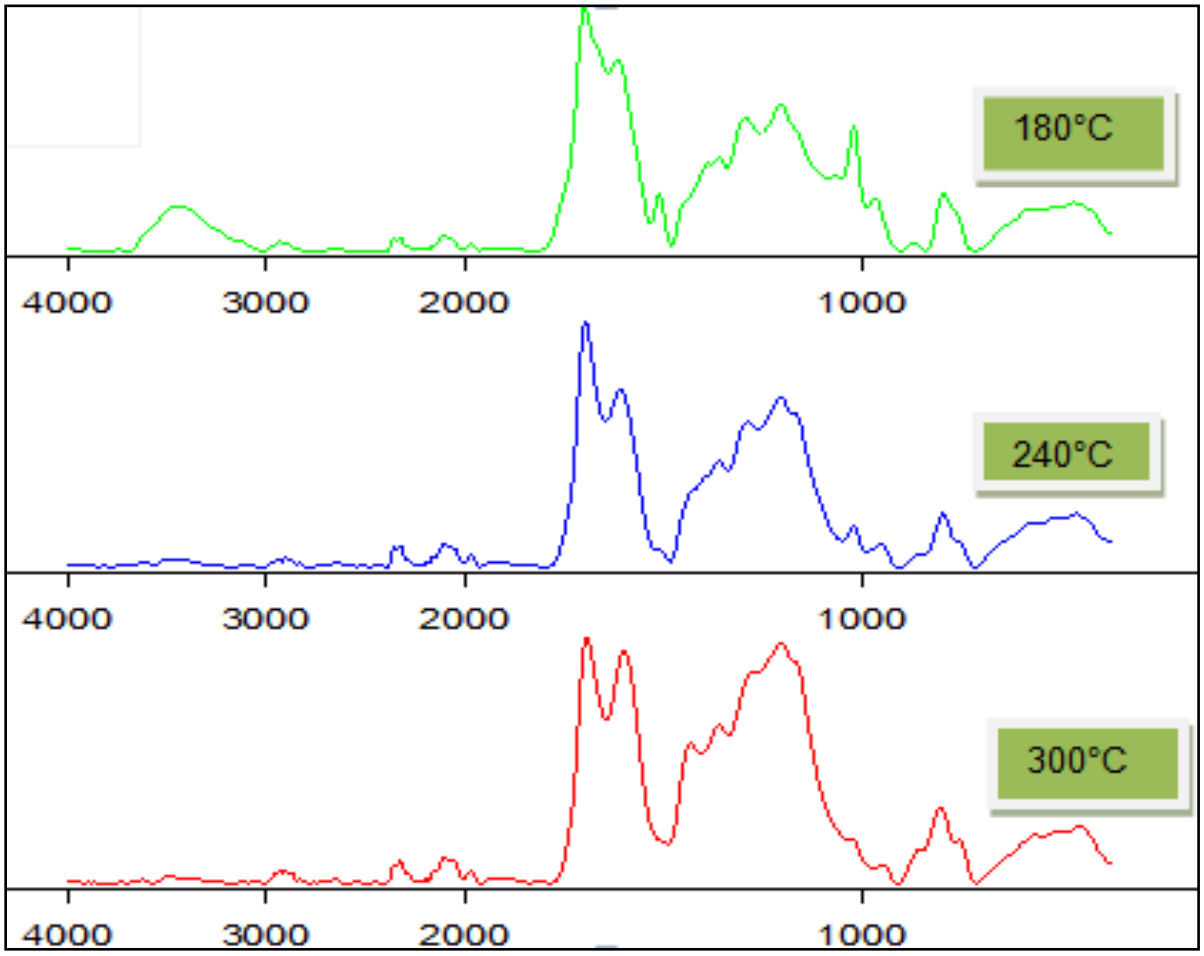


Figure 37: IR spectra variation with temperature of reaction

All the spectra of the char produced in the range of the given condition with and without additives looks like the same as demonstrated by the correlation coefficient Table 15 from the spectra quick compare to each other and with the average of the products at all conditions. However, a closer look at a specified wavenumber reveals the presence of a minor variation particularly below 1600cm^{-1} and in the 3600 – 3000cm^{-1}.

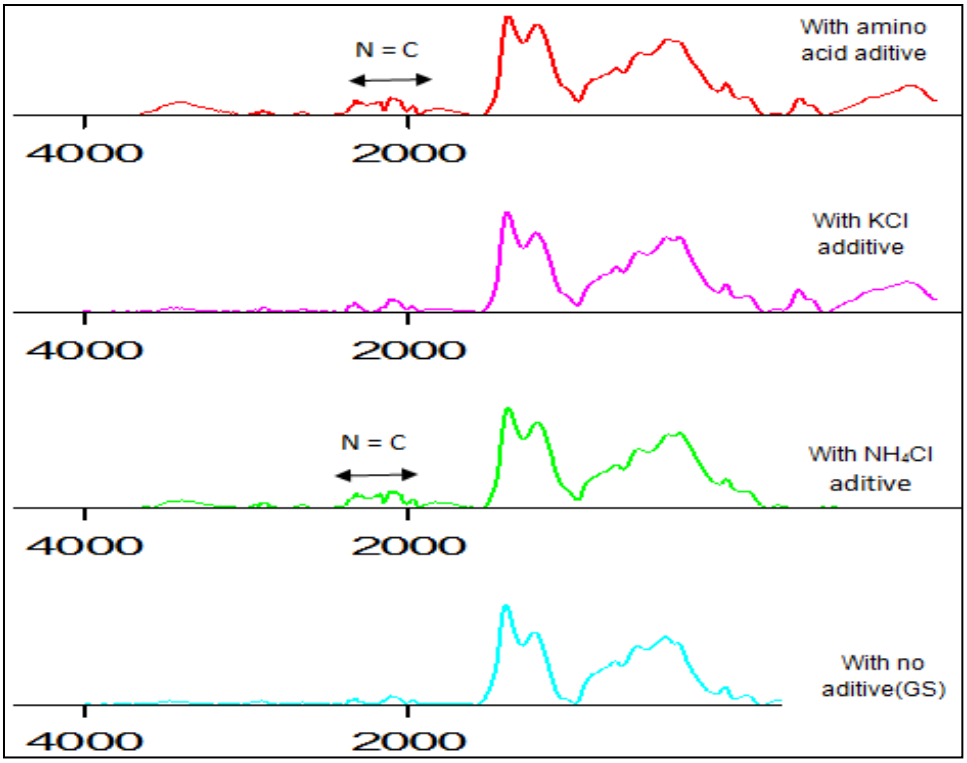


Figure 38: Effects of additives on IR spectrum of HTC char

The effects of additives on the IR spectrum of HTC char are essentially observed for the products with NH_4Cl and amino acids as indicated in Figure 38. The presence of amine functional group shows a small wave near 2250cm^{-1} due to asymmetric stretching of N=C bonds, which is not observed in the case of no additive and KCl additives char spectra. Amine functional groups are also fundamentally noticed in the wave number range below 1600cm^{-1}. However, identifying the exact absorption bands in this region is doubtful, since it involves several absorption bands.

3.4.5.3 Library of spectra

A Library of spectra is a collection of spectra of different known substances involving their chemical formula, spectrum, Lewis structure and physical properties as much as possible. This library used to relate some of the properties such as structure, spectrum shape, with unknown substance to identify what chemical bond and functional group are found within unknown substance. From the measured spectra of HTC char produced in the experiments above, the spectra of some of the feeds, as well as the chars from different feedstock, carbonized at different condition, a library of spectra called ''OPUS HTC CHAR LIBRARY 2014'' is generated. The spectrum search is tested from this library for different products. However, there is still some information which should be added in the a library of spectra such as molecular formula, at least one from the possible chemical structure (Lewis structure) and physical properties if possible as well as molecular mass.

3.5 Discussion

Hydrothermal carbonisation (HTC) of a 29% (m/m) pure glucose solution (GS) was performed at a temperature between 180°C - 300°C in a step of 20°C. The result shows that, a solid mass yield (mass of solid product per initial solid in the feed) ranging from 40 - 50%, with carbon efficiency varying from 63 - 75% were attained above 200°C. From past studies by M. Sevilla and A.B. Fuertes, 30-50% of mass yield with 40 -70% carbon efficiency was achieved by HTC of cellulose at 230- 250°C temperature ranges [12].

As tested by (Joan G. Lynam, M. Toufiq Reza, Victor R. Vasquez, Charles J. Coronella), addition of salts such as calcium chloride, calcium lactate, Lithium chloride, calcium formate and calcium acetate on HTC of hemicelluloses affect the mass yield. It was found that some salts such as calcium propionate, calcium chloride and calcium formate addition to HTC of hemicelluloses shows a slight increase in mass yields while others, like magnesium acetate, calcium lactate and lithium chloride shows mass yield lower than the no salt added control (see 2.3.1) due to the removal of high fraction of hemicelluloses and cellulose during the reaction [8]. Similarly, adding potassium chloride salt on HTC of GS shows an important effect in terms of solid mass yield while NH_4Cl has found positive impact on the degradation of the substances at lower temperature due to its acidic nature in solution. It is found that a 5% reduction in mass yield is observed for the run with NH_4Cl added, whereas 5% increase in mass yield is obtained in the HTC of GS with KCl added. This might be due to the catalytic effect of KCl to produces substances that precipitate in the solid.

According to Joan G. Lynam and Charles J. Coronella, acetic acid addition to hydrothermal treatment might increase, decrease or might not affect the mass yield and carbon efficiency of the solid products depending on the concentration of acid added as well as the applied reaction temperature.

It was also indicated by SEM study that the micropores and external surface structures as well as particles constituting the surface of HC char with AA, NH_4Cl and KCl added are considerably larger than that of HTC char produced from GS when investigated at the same magnification power. Different structures with deformed shape are observed when these additives are used in HTC process indicating the contribution of these compounds on the degradation of glucose.

IR spectroscopy study indicates that the char has complex aromatic structure mainly consists of carbon, thus found to have hydroxyl, carbonyl, carboxyl and aldehyde functional groups. Addition of nitrogen containing inorganic salts, such as NH_4Cl, and organic compounds such as amino acid shows a small wave near the $2200cm^{-1}$ wavenumber region of IR spectra of hydrochar.

Additives such as ammonium chloride shows a slight reduction of solid recovery while potassium chloride indicate an increase in solid yield. On the other hand addition of amino acid shows a slight fluctuation since types of acids and their concentration as well as temperature of reaction have, from no to higher, effects on the products of HTC process.

4 Conclusion and Recommendation

4.1 Conclusion

In this study, hydrothermal carbonisation (HTC) of 29% (m/m) pure glucose solution (GS) was carried out between180°C - 300°C for three hours reaction time. At all temperatures above 200°C higher than 40% of solid was recovered, while at180°C approximately10% of solid recovery was attained, due to the less residence time for carbonizing glucose at this temperature. A maximum solid recovery of 50% (m/m), with 68% carbon efficiency, was achieved at 240°C.

By adding NH_4Cl on HTC of GS, 3-6% of mass yield reduction is observed whereas, up to 5% mass yield increment is attained from KCl added HTC of GS. On the other hand a very small change on mass recovery as well as fluctuation of carbon efficiency is observed when amino acid (AA) is added in HTC of GS. 50% of initial nitrogen, contributed by AA is retained in the solid at all temperatures above 200°C while, less than 5% of chlorine atom is found in the HTC produced from GS with NH_4Cl added. However, the less presence of nitrogen and chlorine in ammonium chloride added solution and potassium and chlorine in potassium chloride added solution at the initial onset make the computation of these elements in each phase of products difficult. In general, amino acids addition on HTC of glucose solution shows more less effect on solid mass yield compared to ammonium chloride and potassium chloride salts additives. Thus addition of inorganic salts and nitrogen containing organic compounds have a great impact on the HTC of biomass.

SEM investigation indicates that, the hydrochar produced from glucose solution with NH_4Cl added has deformed shape like cracked rock while with KCl added the char has a smooth having micropores and layers on the surface. In case of amino acid additives HTC char was found to have agglomerates of particles having different shapes and sizes. Moreover, carbon to oxygen atomic ratios on the surface of HTC char produced using all additives (Figure 22, Figure 28 and Figure 30) has lower than the surface carbon to oxygen ratio of HTC char produced from pure glucose solution. IR spectroscopy study indicates that the char has complex aromatic structure mainly consists of carbon, thus found to have hydroxyl, carbonyl, carboxyl and aldehyde functional groups. Addition of nitrogen containing inorganic salts, example NH_4Cl, and organic compounds such as amino acid shows a small wave near the 2200cm^{-1} wavenumber region of IR spectra of HTC char.

In conclusion additives such as ammonium chloride shows a slight reduction of solid recovery while potassium chloride indicate an increase in solid yield. On the other hand addition of amino acid shows a slight fluctuation since types of acids and their concentration as well as temperature of reaction have, from no to higher, effects on the products of HTC. However in all cases HTC retains the majority of carbon in the solid product. Thus, it is a convenient way to produce a highly carbonized material which can be utilized in a broad spectrum of application. It has strong potential to become an environmentally,

energetically and resource - wise sound conversion process for wet biomass such as sewage sludge, algae biomass, biogas residues by sequestering the carbon with the solid char. Still much to be learned about chemistry of the process and structure of the products. Reported results from this experiment using glucose and inorganic salt additives shows a variation in yield and surface structure of the HTC char produced.

4.2 Recommendation.

For complete elemental analysis of the HTC products in each phase, the concentration of additives has to be higher than used here in this experiments. This can be carried out by increasing the size of reactor so that the sample would have to have enough concentration of each element in each phase, particularly in solid, of the product which can exceed the detection limits of the equipment used for analysis. The reaction time is one of the main factors affecting the yield and characteristics of the product, hence the experiment might be better if it is tried to perform changing the reaction time and find the optimum residence time for the maximum solid recovery and carbon efficiency.

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7 Appendix

Calculation for determination of amount of sample required

Some calculations were done to determine amount of all materials and utilities needed. In order to determine the amount of glucose used as well as water and additive needed to be added to keep the solution at total organic carbon concentration of 10.77%, the following simple calculations were done. An arbitrarily assumption of 200ml solution was taken to be prepared for all experiments. Parameters such as density of water(ρ_w) = 0.9975g/ml, density of glucose(ρ_g) = 1.581g/ml, molar mass of glucose 180.17g/mol, molar mass of water 18g/mol), taken at room temperature, were used in the calculation. Referring to the total organic carbon in glucose, from solid component of biogas residue **(**Table 5) and 200ml of total volume of solution, volume of water(V_w) and volume of glucose(V_g) required respectively are given by;

$$V_w = 200 - X/ 1.581$$

$$V_g = X/1.581 \quad \text{where, X is mass of glucose.}$$

Glucose used is D+ glucose-monohydrate in which one mole of water is found per mole of glucose. Thus, 18g of water/180.17g of glucose = 9.99% is water and the remaining 90.01% is dry glucose of which 72/180.17 = 39.96% are organic carbon (OC) on dry base analysis. Therefore the total mass of water (m_w) in the solution is both from glucose and water added to make the solution and is given as;

$m_w = 0.9975 *(200-X/1.581) + 9.99\% * X = 199.5 - 0.531X$.....1

Mass of OC = Molar mass of carbon * n (mole of carbon) / mole of glucose * 0.9001*mass of glucose added . And, = 12g/mol*6mole of C/ mole of glucose*0.901*X = 0.3996*0.901*X = 0.3600X 2

From the composition of TOC in biogas residue (.i.e. 10.77%), the following equation can be obtained.

10.77% = {Total organic carbon} / {Total mass of solution}.....3

From equation 1, 2 and 3 above; 10.77% = 0.36X/(199.5 - 0.531 + 0.901) 4

Then solving for X gives the amount of glucose added to keep the total organic carbon in the solution at 10.77% and equal to X = 67.1124g. Therefore, mass of all the other components are computed and tabulated below in **Error! Reference source not found.**.

Table A. Mass and volume of sample feedstocks and utilities used for HTC of pure glucose solution

Utilities	Measured Value	Calculated Value
Mass of water added	157.299	157.1588
Water from Glucose	6.7057	6.7045
Total mass of water	164.0047	163.8633
Mass of glucose	67.1240	67.1124
Mass of glucose in dry base	60.4787	60.4683
Mass of TOC	24.1673	24.1631

Calculation for experiment with ammonium chloride additives

Assume to add X amount of ammonium chloride solution in 200ml of solution with 10.77% total organic carbon (TOC). And the concentration of ammonium chloride in the solution is needed to be 186.4mg/L, solid component of biogas residue from Liu Hang analysis. So after adding the ammonium chloride the total volume of solution is give by

$$200ml + X/ 1.53$$

Where X is mass of ammonium solution added, 1.53 is density of ammonium chloride in g/ ml. Hence, the concentration of ammonium chloride in the solution is $X/ (200 + 0.6536X) = 186.4mg/ L$ Therefore x is calculated to be =0.03728g . The total volume of solution is then = 200.02437ml.

Determination of KCl additives

The concentration of Potassium salt in the biogas residue, from Liu Hang analysis 311µg. Doing the same calculation above, the total volume of solution after adding potassium chloride 200ml of glucose water solution 200ml + (X/ 1.98) * 200ml, where X is mass of potassium chloride to be added and 1.98 is density of potassium chloride in g/ ml. Then X is calculated to be = 62.21µg. Therefore 62.2µg of potassium chloride should be added to have a concentration of 311µg/ L in 200ml glucose water solution. And finally the total volume of solution equals 200ml + 62.2µg/1.98g/ml = 200.0314ml.

Calculation for amino acid additives

For Mixtures :- Assume glucose solution with TOC of 10.77% is to be made with additives , a mixture of amino acids

Let g = glycine = 0.13%

P = phenylalanin = 0.11%

a = glutamic acid =0.29%

We have to use the amount of solution used in the first experiment and adjust the TOC and calculate the amount of each amino acid used in such a way that TOC is still 10.77%.. Hence the mass of glucose

water solution with TOC 10.77% is 224.3316g, from experiment 1. When we consider a mixtures of all the three amino acids with composition stated above(in db mass percentage), we can compute the mass percentage of each components as,

$$0.13 = 100g/ (224.3316 + g + a + p + X)$$

$$0.11 = 100p/ (224.3316 + g + a + p + X)$$

$$0.29 = 100a/(244.3316 + g + a + p + X)$$

$$0.1077 = (0.36X + 24.1631)/ (224.3316 + g + a + p +X)$$

when x is the amount of glucose added to keep the amount of TOC at 10.77% in the solution. Here water from glucose is also added and then should be taken in to consideration in total mass of water calculation.

In these four equation we have four variables, i.e. 4 equation and 4 variable, it can be solved using substitution. After solving the equations the values for each variable are shown in the following table.

Table B. Amount and concentration of amino acids, water and glucose in the solution

Component	Weight(g)	Concentration of additives in the solution [%]
Glutamic acid(a)	0.6555	0.1291
Phenylalanin(p)	0.2502	0.11069
Glycine(g)	0.2919	0..2900
Total Mass of water(g)	163.9129	72.5192
Mass of glucose in dry bas	60.9196	27.1925
Mass of glucose in wet base	67.6133	
Total mass of solution	226.0301	

Table C. Mass of additives water and glucose in the solution

Utilities	NH_4Cl	KCl	Amino acids (AA)		
			Phenylalanine	Glutamic acids	Glycine
Mass of additives [g]	0.0373	$6.2*10^{-7}$	0.2502	0.6555	0.2919
Mass of water[g]	157.313	157.229	157.2921		
Mass of glucose [g]	67.1168	67.1124	67.6133		
M_{total}[g]	224.4671	224.332	226.103		
V_{total}[ml]			200		

Table D. Experimental results on solid recovery

Temperature [°C]	Expt. no	Solid recovery [%]			
		Glucose Solution[GS]	With NH_4Cl	With amino acid [AA]	With KCl
180	1	6.250	11.86	14.68	8.73
	2	7.68			
	3	7.343			
200	1	41.10	41.86	52.00	42.44
	2	40.67	42.78	51.3	43.70
	3	41.96	41.43	54.00	45.4
	4			49.05	
210	1	44.06			
	2	44.53			
220	1	46.06	44.53	47.30	54.07
	2	46.92	45.44	46.10	55.46
	3	46.44	44.39	46.30	51.83
	4	44.77			
240	1	52.02	41.77	46.62	49.11
	2	50.20	41.53	46.63	51.83
	3	49.59	42.05	46.48	49.63
260	1	45.87	42.34	46.20	52.25
	2	45.63	41.62	46.30	55.36
	3				51.54
300	1	41.29	36.52	41.80	52.21
	2	42.15	39.76	42.72	50.02
	3	46.92	40.03	41.91	49.80

Table E. Elemental analysis on nitrogen and carbon

Temperature [°C]	GS		With NH_4Cl		With AA		With KCL	
	N	C	N	C	N	C	N	C
180	<0.1	63.2	< 0.1	ND*	1.66	62.4	N.d	61.9
200	N.d*	64.5	N.d	68.83	0.5	64.4	N.d	66.8
220	N.d	66.9	N.d	74.78	0.753	67.6	N.d	68.2
240	N.d	68.6	N.d	72.12	0.803	69.1	N.d	68.3
260	N.d	70.0	N.d	73.85	0.803	71.4	N.d	71.1
300	N.d	73.9	N.d	74.53	0.859	75.7	N.d	75.5

N.d*: Not detected, ND*: Not determined

Table F. Solid balance and carbon distribution for HTC of glucose with KCl additive

Temperature [°C]	**Mass of char [g]**	**Solid recovery [%]**	**Carbon distribution among the three phase of products[%]**		
			solid	Liquid	Gas
180	0.183	8.70	13.50	58.66	0.19
200	0.890	42.40	73.10	1.133	1.61
220	1.134	54.00	91.80		3.80
240	1.197	57.07	86.00		5.76
260	1.161	55.36	94.40		4.54
300	1.105	52.60	95.7		6.40

Table G. Functional group and their corresponding absorption bands in IR spectroscopy

Wavenumber, cm–1	**bond**	**functional group**
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	primary, secondary amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C(triple bond)C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	Aromatics
3100–3000 (m)	=C–H stretch	Alkenes
3000–2850 (m)	C–H stretch	Alkanes
2830–2695 (m)	H–C=O: C–H stretch	Aldehydes

2260–2210 (v)	C(triple bond)N stretch	Nitriles
2260–2100 (w)	–C(triple bond)C– stretch	Alkynes
1760–1665 (s	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	alpha,beta–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	alpha,beta–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	Alkenes
1650–1580 (m)	N–H bend	primary amines
1600–1585 (m)	C–C stretch (in–ring)	Aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	Aromatics
1470–1450 (m)	C–H bend	Alkanes
1370–1350 (m)	C–H rock	Alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1300–1150 (m)	C–H wag (–CH2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	Alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	primary, secondary amines
900–675 (s)	C–H "oop"	Aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	Alkanes
700–610 (b, s)	–C(triple bond)C–H: C–H bend	Alkynes
690–515 (m)	C–Br stretch	alkyl halides