A descriptive study of hydrochar prepared from *Seasame oilcake* and *Groundnut oilcake*- An ecofriendly approach

Elanchimuthu.S

(16PCH004)

Thesis Submitted to

Avinashilingam Institute for Home Science and Higher Education for Women,

Coimbatore-641 043

In Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE IN CHEMISTRY

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Signature of the Head of the Department

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LIST OF ABBREVIATION

SOC	Seasame Oilcake
GOC	Groundnut Oilcake
HC	Hydrochar
HTC	Hydrothermal carbonization

1. INTRODUCTION

Energy demand in the world continues to increase with increase in population and economic development .The necessity to supply the increasing energy demand and also to concur with the related to environmental pollution is an enormous task in the present global scenario. The use of biomass as a renewable source to combat these energy issues is becoming more and more relevant.

Biomass has emerged as a potential alternative source of specialty chemicals, gaseous and liquid fuels and thermal energy. Among different processing routes, the transformation of lignocellulosic biomass into liquid bio-oil through the fast pyrolysis process is receiving increased attention **(Negahdar *et al.*, 2016)**.

Porous carbons are derived from various biomasses by thermal pyrolysis, chemical activation or hydro hydrothermal carbonization (HTC), followed by carbonization or chemical activation (**Zhu *et al.*, 2014),**investigated the characteristics and tetracycline adsorption behavior of a novel porous carbon prepared using HTC. High activation temperatures ranging from 300 to 700 ^{0}C were found to work well for hydrochar carbonization and the produced materials exhibited high surface area.

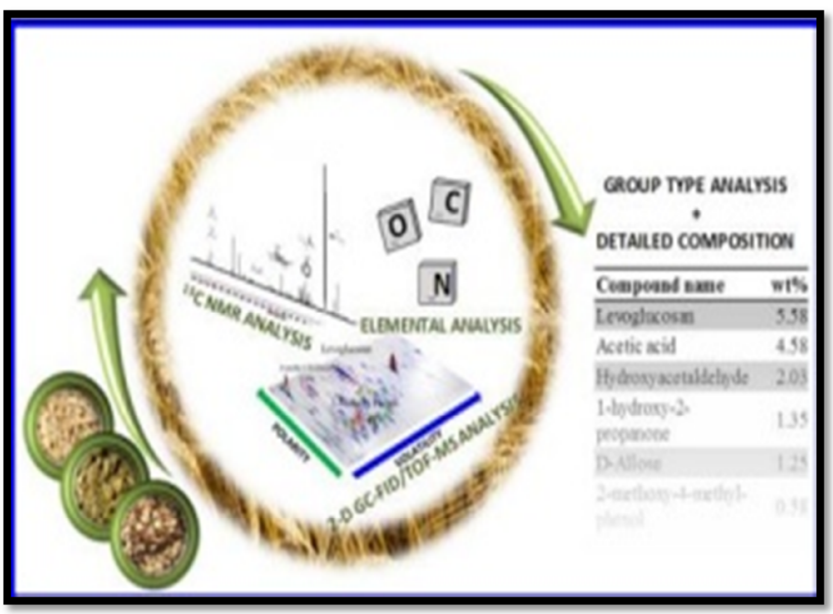


Fig1.1: Courtesy (ACS) hydrochar

Hydrothermal carbonization process is a wet process that converts food wastes to a valuable energy and then low temperatures compared to the pyrolysis **(Parshetti *et al.,* 2015)** used hydrothermal carbonization method to prepare hydrochars from urban food wastes for removal of textile dyes from the contaminated water **(Mehmet Koc 2017)**.

Thermo chemical biomass conversion process such as pyrolysis, gasification and liquefaction are the most appropriate. Here gasification of agricultural waste is more difficult because of bad transport facilities, partial ash sintering, non-uniform flow distribution and the presence of a muddy phase in the effluents. The pyrolysis process conditions can be optimized to maximize the production of liquids, solids and gases .It is dependent on the experiments conditions applied especially temperature and heating rate **(Bani *et al.,* 2016).**

Fig1.2: Ancient hydrochar production method

Fig 1.3:Environmental impact of Carbonization

http:treehuger.com

Since the last few decades, the research interest in renewable energy is increasing throughout the world. Utilization of biomass resources for biofuel production is at the top of all forms of renewable energy.

There are two technologies available to produce biofuel from biomass, thermo-chemical and biochemical methods. Thermochemical processes include pyrolysis, combustion, gasification and hydrothermal processes **(Pramanik, 2003)**. Thermochemical processes are distinguished from each other by process conditions such as use of oxygen or the amount of heat used. On the other hand, biochemical processes use enzymes as a catalyst to convert biomass into biofuel. Biochemical processes include fermentation, anaerobic digestion, transesterification and composting **(Lee and Ofori -Boateng, 2013).**

Thermochemical processes are preferred over biochemical methods because of advantages such as no pretreatment is required for the biomass in hydrothermal carbonization process. Biochemical processes need pretreatment of biomass material by different pretreatment methods such as chemical, physical, biological and physiochemical to improve the accessibility of enzymes **(Kumar, 2010).**

The old method for producing the hydrochar in pit or trench method and otherwise it is created by terra preta in dark soil. This method is still utilized in rural areas the producing the hydrochar. Hydrochar production process can utilize most of the agricultural biomass residues, including wood chips, corn Stover, rice or peanut hulls, tree bark, paper mill sludge, animal manure, and recycled organics.

The first evidence of charcoal being used as a soil amendment in the Amazon Basin of South America over 2,500 years ago. Archaeological evidence suggests that ancient people used the piled and covered wood in earthen pits, then burned it slowly with limited air and then, this method was widely used and still this method was followed in developing countries. The disadvantage of this method is it creates considerable smoke and releases half of the carbon dioxide (CO_2) in the original biomass along with other greenhouse gasses (GHG's). The atmosphere and all that heat energy is wasted.

In recent years, biofuel production has increased due to the environmental impact of fossil fuels. It is worth mentioning that first-generation biodiesel is produced generally from vegetable oils which include rapeseed, sunflower, soybean and palm oils.

Biomass energy is a type of the alternative energy produced from the renewable resources and then the valuable products are obtained by the pyrolysis and carbonization of biomass sources. Hydrochar and bio-oil products are maximum used to the alternative fuel to fossil based fuels. Hydrochar as the source for carbon and then producing different carbon materials. Hydrochar production systems differ from the most biomass energy systems because the technology is a carbon-negative and it removes net carbon dioxide from the atmosphere.

Hydrochar is always created naturally as a result of vegetation fires and intentionally by humans in burn pits and hand-made structures. When the charcoal is made for the purpose of adding to the soil as an amendment, it's called biochar.

It has been a research focus in recent years due to its potential roles in soil amendment, carbon sequestration and then heavy metal sorption. Hydrochar is equal to the black carbon and it is prepared by the pyrolysis of biomass under limited condition otherwise absence of oxygen condition. It is mainly applied to the soil for the agricultural and this is increasing the soil fertility and then crop production reducing the greenhouse gases by reducing nitrous oxide emissions from the soil and also it improves the soil microbial activity, high stability of the hydrochar relative to other forms of soil carbon.

Pyrolysis is a thermal decomposition of materials at elevated temperatures in an inert atmosphere such as a vacuum gas. It involves the change of chemical composition and is irreversible. Pyro means “fire” and lysis means “separating”.

Pyrolysis is most commonly applied to the treatment of organic materials. The most processes involved in charring wood, starting at 200-300 °C (390-570 °F). In pyrolysis of organic substances produced the volatile products and leaves a solid residue and then enriched in carbon, char.

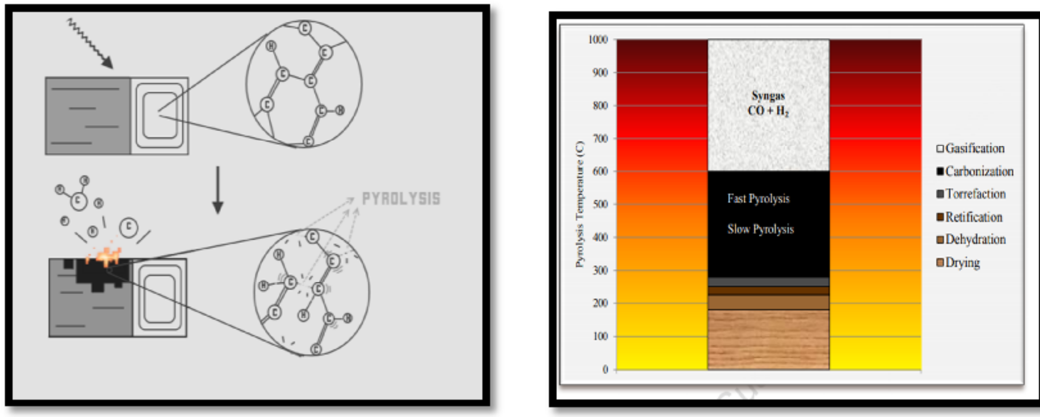


Fig1.4: Fast and slow Pyrolysis method

There are two types of pyrolysis. One is fast pyrolysis and then other one is slow pyrolysis. Fast pyrolysis yields 60%bio-oil, 20%biochar, and 20%syngas .These are can be done within the seconds and then the slow pyrolysis is taken a lot of time and hours.

Pyrolysis and hydrothermal liquefaction are mostly used to increase bio-oil yield. Hydrothermal gasification is preferred for maximum gaseous product. Slow pyrolysis can produce solid fuel, but the yield percentage will be lower than that of the HTC. Besides, water acts as a solvent in HTC thus, pre-drying of biomass is not required as it is needed for pyrolysis **(Kang et al., 2012)**. HTC can handle both wet and dry biomass types, therefore saving the energy, cost, and time that are needed for dry biomass. It is an environmentally friendly process than pyrolysis because of the fewer emission of volatile matter **(Cakan, 2008; Titirici *et al.*, 2008; Titirici, Thomas, & Antonietti, 2007; Titirici, Thomas, Yu, et al., 2007).**

Syngas created by the modern pyrolysis and then output energy is 3-9 times these amount of energy is required to the run. Alternatively, microwave technology has recently been used to efficiently convert organic matter to hydrochar on an industrial scale, producing ~50% char. The below diagram depicts the production of hydrochar using pyrolysis.

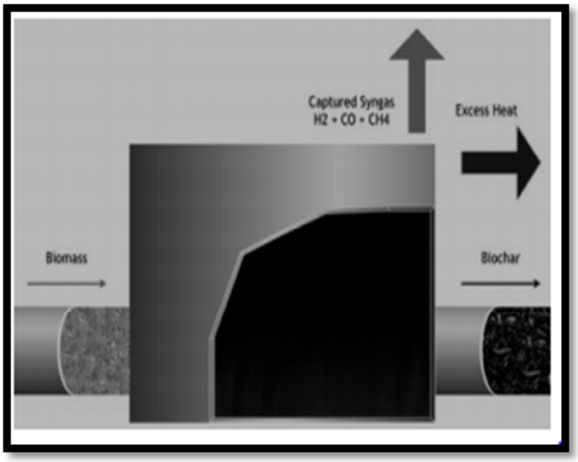


Fig1.5: Simplified pyrolysis process flow diagram

(Source: www.biochar.info.com)

Hydrochar can be produced either from small, simple mobile units or from larger, stationary ones. Small-scale systems for biomass inputs of 50 to 1000 kilograms per hour can be used. While large units of up to 8000 kilograms per hour can be operated by large industries **(Odesola *et al.,* 2010).**

Hydrothermal carbonization -way to carbonize biomass

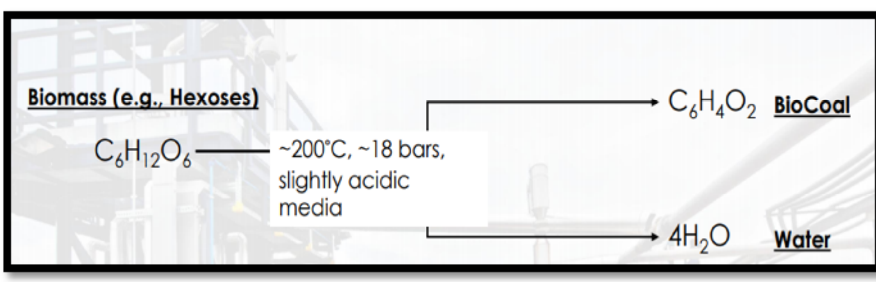


Fig 1.6: Example for hydrothermal carbonization

The great advantage of this process is that it takes place in a water solution, so humidity of biomass is not a problem. The waste product contains no toxics. The excess of processed water contains soluble components which have fertilizer effect on growing plant. The components are N, K, and Fe and it is present in all carbon molecules in original biomass. Exothermic reaction and thermal energy consumption is very low, mainly for startup. HTC is very low in hydro-soluble chemicals (which are washed away with the water) such as sulfur, chlorite and potassium.

Hydrothermal carbonization Process characteristics

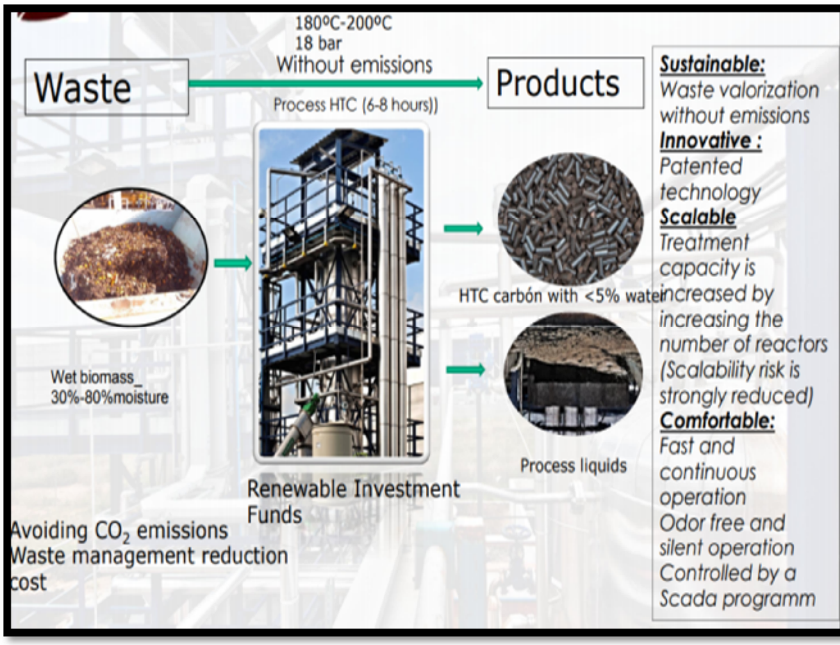


Fig 1.7: Characteristics of HTC process

Industrial hydrothermal plant

Fig 1.8: Hydrothermal industrial process

Carbonization several bio-mass

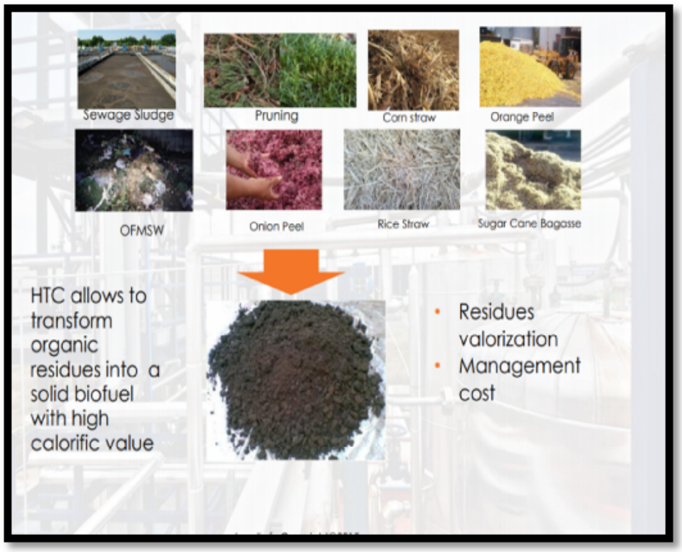


Fig 1.9: Biomass for raw material (www.ingelia.com ,Brussels,2015)

The raw materials obtained from the biomass wastes are wood, sawdust, straw, palm shell, coconut shell, rice hull, peanut shell, etc. These are the renewable source for the biomass materials are quite common and cheap in the market, which can reduce the cost of bio charcoal production equipment.

One process that has re-emerged in the last five years is biochar, a solid material obtained from the thermo chemical conversion of biomass in an oxygen-limited environment—which creates a fine-grained, highly porous charcoal. Interest in hydrochar has increased recently as horticulturalists are looking for sustainable ways to improve soils and decrease their use of chemical fertilizers. Benefits of hydrochar include reduced soil bulk density, increased nutrient and water retention, and decreased nutrient leaching. It can also be used for remediation and protection against particular environmental pollution and as an avenue for greenhouse gas (GHG) mitigation.

Before looking at new research on hydrochar in soils, let’s examine the origins of biochar. The concept was originated, thousand years ago in the Amazon Basin, where islands of rich, fertile soils called terra preta (“dark earth”) were created by indigenous people. Anthropologists speculate that cooking fires and kitchen middens along with deliberate placing of charcoal in soil resulted in soils with high fertility and carbon content, often containing shards of broken pottery. These soils continue to "hold" carbon today and remain extremely nutrient rich compared to the surrounding soils. Hydrochar can be found in soils around the world as a result of indigenous soil management practices and natural vegetation fires. Natural hydrochar from historic prairie fires is a key element of the fertile Midwestern soils in the US **(Kyoung S.Ro, 2016)**.

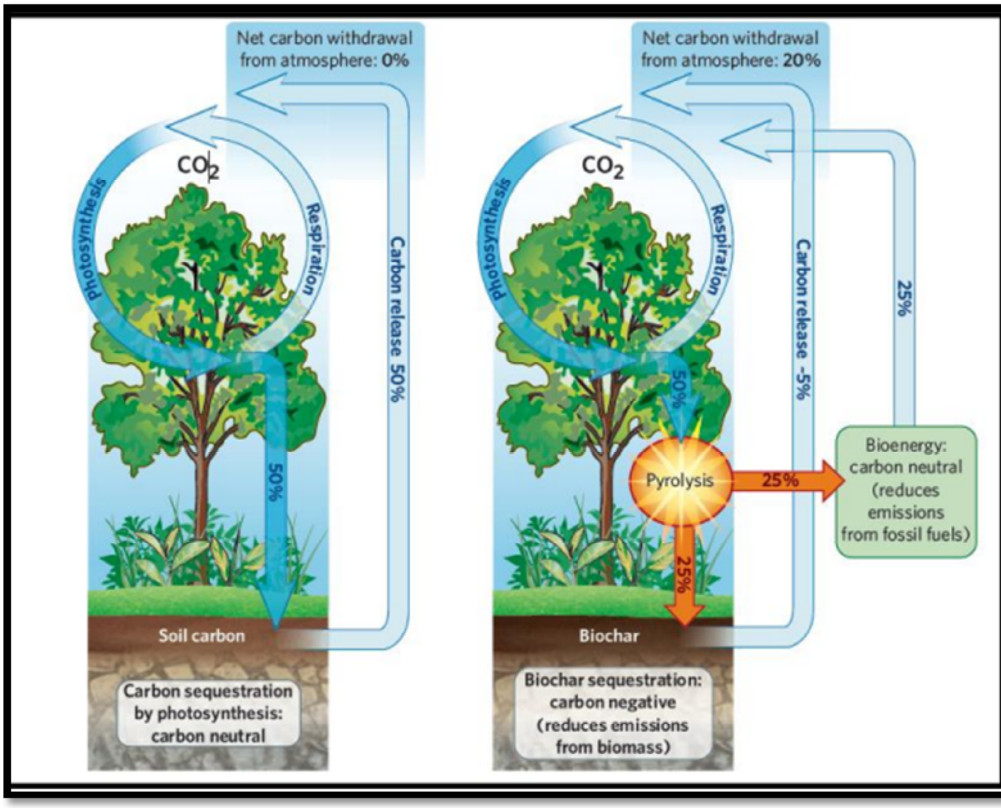


Fig 1.10: Hydrochar mechanism for soil

$$\textbf{Biomass} \xrightarrow{\textbf{Yields}} \textbf{water + unreacted residue}$$

$$\textbf{Unreacted residue} \xrightarrow{\textbf{Yields}} (\textbf{Volatile + Gases})_1 + (\textbf{Char})_1$$

$$(\textbf{Char})_1 \xrightarrow{\textbf{Yields}} (\textbf{Volatile + Gases})_2 + (\textbf{Char})_2$$

Hydrochar enhances soil and protects water quality

Increased Nutrient and Water Retention: Hydrochar has the ability to attract and retain water along with nutrients in all other organic soil material and in addition it holds in to phosphorus and agrochemicals. Due to this, Plants are healthier and less fertilizer run off from surface water is noticed.

Persistence: Hydrochar is relatively inert and therefore, persists in soil far longer than any other organic soil additives. Hydrochar lasts 100s to 1000s of years, its benefits of nutrient and water retention and overall soil porosity keep working, unlike common fertilizers and conditioners.

Less Fertilizer Needed: When added to soil, hydrochar improves plant growth and crop yields while reducing the total fertilizer required. Nitrous oxide, a greenhouse gas, released from certain fertilizers is 310 times more potent than carbon dioxide CO_2. Hydrochar conditioned soils reduce N_2O off-gassing by 50-80%.

Hydrochar fights climate change

Burning biomass releases CO_2 into the atmosphere and the plants are reabsorbing it; this active carbon cycle has been in balance for millennia. Burning fossil fuels puts excessive CO_2 into the air, more than can be absorbed naturally. This traps heat in the Earth's atmosphere. Reducing atmospheric CO_2 is critical to combat climate change.

A Perfect Circle Solution - burning of biomass through pyrolysis to produce energy (heat and power) instead of burning fossil fuels as it is a carbon neutral process; it neither adds to the climate-change problem nor reverses it.

Hydrochar holds 50% of the biomass's carbon and when applied to soil, sequesters that carbon for centuries, reducing the overall amount of atmospheric CO_2 by removing it from the active cycle. Hydrochar also enhances the plant growth which absorbs more CO_2 from the atmosphere. Overall, these benefits make the hydrochar process carbon negative as long as biomass production is managed sustainably.

Hydrochar from waste

The hydrochar is the main product generated from organic wastes. There are many forms to valorize the coal for energy, through combustion or gasification. Besides the properties as energy carrier, the hydrochar is raw material for the following processes:

- Filter (of activated carbon)
- Dyestuffs Electrodes for Batteries
- Fuel cell
- Fotocatalizators.

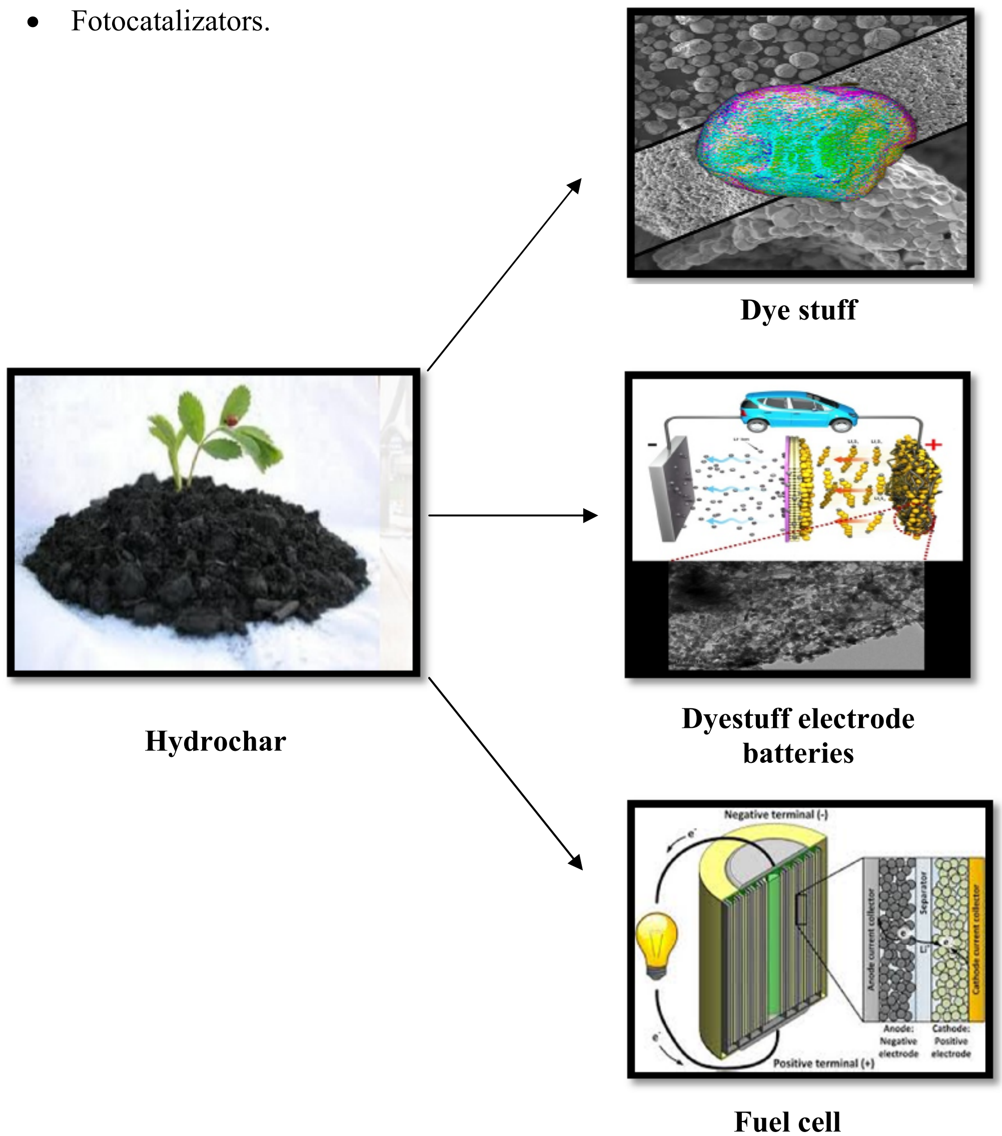


Fig 1.11: Hydrochar applications

The hydrochar has good properties also for soil amelioration, due to its porous structure and its capacity to retain water and nutrients, in form of filter cake.

In this view the present study focuses a utilization of waste oilcakes for production of hydrochar.

Types of oilcakes: 1. Edible oilcake

2. Non-edible oilcake.

Table 1.1: Types of oilcakes

Edible oilcake	Non-edible oilcake
• This type of oilcake is used for feeding of cattles along with other meals in different ratio. • Some common used oil cakes are mustard oilcakes, groundnut cake, seasame oilcake, linseed oilcake, coconut cake, etc…	• This type of oilcake is not suitable for feeding to cattle and mainly used for manuring purpose. • These are good source of nitrogenous manure. The amount of nitrogen varies with the type of oilcake.
	

For the present project work-a renewable source of biomass Seasame **oilcake** and **Groundnut oilcake** has been selected for the preparation of hydrochar.

Description of selected biomass:

Vegetables oils and then the olive oil cake ,castor oil cake can be considered as an alternative source of fuel and then most important which do not contain sulfur. It provides a clean, renewable source of energy that could dramatically improve the environment bioenergy does not contribute to climate change through the emissions to the atmosphere of carbon dioxide **(Bani *et al.,* 2016).**Oilcakes are the by-products of oilseeds crops.

Seasame oilcake

(a)

(b)

(c)

Fig1.12: (a) Sesame plant (b) sesame seed (c) seasame oilcake

Sesame (*Sesamum indium*) is one of the world's most important oil seed crops. The genus sesamum is a member of the family Pedaliaceae, which contains 16 genera and 60 species. Sesame is an oilseed plant in the genus Sesamum. It is an annual plant, grows up to 50 to 100 cm with an entire margin; they are broad lanceolate, to 5 cm broad, at the base of the plant, narrowing to just 1 cm broad on the flowering stem. The flowers are white to purple, tubular, 3 to 5 cm long, with a four-lobed mouth. Seasame oilcake , a waste of Seasame oil mill can be utilized as a precursor to generate the biomass Seasame oil cake is available in large amounts at very low cost .

Sesasmum indicum seed consists of a spermoderm, endosperm and cotyledon. The outer epidermis composes a single layer of cells which contain a mass of calcium oxalate crystals in the outer ends of the cells. The endosperm consists of two to five cell layers with thick rigid walls and is separated from the spermoderm by a membrane. These cells contain oil drops and small aleurone grains.

Seasame-oil cake, the biomass remaining as a byproduct of industrial processes after extracting removal of oil by pressing, was used in the work. Oilcakes are the by- products of oilseeds crops.

Sesame Oilcakes are one of the important animal fodders as it contains quick acting organic nitrogenous manure. It also contain small amount of phosphorous and potassium, magnesium, calcium, sodium. It shows the difference on some physical properties, proximate, mineral, and anti-nutritional and antioxidant compositions. The seeds contained 5.7% moisture, 20% crude proteins, 3.7% ash, 3.2% crude fiber, 54% fat, 13.4% carbohydrate **(Nagendra *etal.*, 2012).**

Groundnut oilcake

(a) (b) (c)

Fig 1.13: (a) Groundnut plant (b) Ground seed (c) Ground oilcake

Groundnut is particularly valued for its protein content (26%). Groundnuts contain more protein content than meat and double the time in egg.

Being an oil seed crop, it contains 40 to 49% oil. In addition to protein, groundnuts are a good source of calcium, phosphorus, iron, zinc and boron. The groundnut oil cake contains trace amount of vitamin-E and vitamin B complex.

Oil cake from oil mill industry has a great potential for being used as a precursor for hydrochar production. It is a waste available in plentiful quantity from the oil mill industry.

Objectives:

- The present study has been carried out improve the agricultural waste management and ascertain the utilization of sesame oilcake and groundnut oilcake minimizing environmental pollution.
- To prepare of hydrochar from seasame oilcake and groundnut oilcake waste using a direct hydrothermal carbonization.
- To study the individual effect of each parameter of HTC such as reaction time and biomass to water ratio on the yield percentage and quality of hydrochar produced.
- To study the physical characteristics of hydrochar.
- To characterize the synthesized hydrochar using FT-IR, TGA, SEM and optical surface analyzer.

2. REVIEW OF LITERATURE

Waste biomass with significant moisture content is nowadays utilized due to their eco-friendly and biodegradable natue.Traditional thermo chemical processes can be applied to this kind of waste biomass after a severe drying up pre-treatment which can makes the whole process unsustainable from energy an energy point of view. Hydro thermal carbonization consists in reacting substrates in a liquid water environment in order to obtain a carbon rich solid fraction. It can be utilized in co-combustion with low rank fossil coals, which can be very effective and economically feasible way to exploit hydrochar for energy production. It can be utilized as soil amendenment, as precursor for activated carbon, for the generation of nano-structured materials, as a catalyst and for CO_2 sorption and sequestration based on the above observations, the present review highlights the salient findings of recent research carried out in this field.

- **Lee (1997)** in his review **"Biological conversion of lignocellulosic biomass to ethanol"** highlighted the technologies required for the successful biological conversion of lignocellulosic biomass to ethanol. According to the author the biological process of ethanol fuel production utilizing lignocellulose as substrate requires: (1) delignification to liberate cellulose and hemicellulose from their complex with lignin, (2) depolymerization of the carbohydrate polymers (cellulose and hemicellulose) to produce free sugars, and (3) fermentation of mixed hexose and pentose sugars to produce ethanol.
- **Kuo (1967), Owusu *et al.,* (1970), Devuyst(1963)** highlighted the chemical composition and amino acid composition of SOC and GOC.

Table 2.1Chemical composition of SOC and GOC

Content	Drymatter	Crude protein	Crude fibre	Ash	Calcium	Phosphorus	Ref
SOC	83.2	35.6	7.6	11.5	2.45	1.11	Kuo (1967)
GOC	92.6	49.3	5.3	4.5	0.11	0.74	Kuo (1967)

Table 2.2: Amino acids compositions for SOC and GOC

Amino acids	SOC	GOC
Arginine	12.8	11.0
Cystidine	2.1	0.9
Glycine	5.3	6.0
Histidine	2.9	2.5
Isoleucine	3.6	3.0
Leucine	7.5	6.1
Lysine	2.9	3.6
Metidine	3.1	0.4
Phenylalanine	4.3	4.9
Threonine	3.2	2.8
Tryotophan	1.4	-
Tyrosine	3.9	3.7
Valine	4.0	3.7
Ref	De vuyst(1963)	Owusu-Domefeh *et al.* (1970)

- **Phukan *et al*., (1999)** presented the development of a method for the isolation and refining of microcrystalline wax from press mud waste of the sugar industry. Physico-chemical and XRD analyses were made for characterization of isolated micro wax. The yield of hard wax was found to be from 3.50 to 4.10%.According to the authors this method enabled high grade refined sugar cane micro wax to be obtained**.**
- **Kumar *et al.,* (2008)** evaluated the efficient method of harnessing energy efficiently from corn stover. According to the authors, this research was carried out to determine selected physical and chemical properties of corn stover related to thermo chemical conversion. Thermo gravimetric analyses were performed at heating rates of 10, 30, and 50 °C min^{-1} in nitrogen (inert) and air (oxidizing) atmospheres. The parameters of the reaction kinetics were obtained and compared with other biomass. The weight losses of corn stover in both inert and oxidizing atmospheres were found to occur in three stages.

- **Kobayashi** ***et al.,*** **(2008)** successfully produced a fuel and pellet fuels from sunflower oilcake .This depended on the conditions of compression process .The calorific values for the oilcake was 20.99MJ/kg.
- **Ramachandran** ***et al.,*****(2009)** obtained their application in the Weld of fermentation technology has resulted in the production of bulk-chemicals and value-added products such as amino acid, enzymes, mushrooms, organic acids, single-cell protein (SCP), biologically active secondary metabolites, etc.
- **Boateng** ***et al.,*** **(2010)** highlighted the pyrolysis processes carried out in two different cakes camelina and pennycress. High yields and high energy dense liquid fuel intermediates were produced.
- **Ruiz** ***et al.,*** **(2010)** indicated that hydrothermal processes were an eco-friendly processes that provide an interesting alternative for chemical utilization of lignocellulosic materials, in which water and crop residues were the only reagents. In this work the effect of process conditions (size distribution of the wheat straw, temperature and time) was evaluated against production of fermentable products. The use of milled wheat straw fractions as a raw material containing blends of different particle size distribution showed that the latter had an influence on the final sugars in the hydrolysate. Improved values of glucose (21.1%) and xylose yields (49.32%) present in the hydrolysate were obtained.
- **Cao** ***et al.,*** **(2010)** produced hydrochar from dairy manures by heating at low temperatures (500 °C) and under abundant air condition. The resultant biochar was characterized for physical, chemical, and mineralogical properties specifically related to its potential use in remediation. Overall the results indicated that dairy manure can be converted into hydrochar.
- **Odesola** ***et al.,*** **(2010)** reported from cocoa pod husk a small scale production of biochar. This equipment was evaluated by comparing its output with a single barrel method of production. The results obtained during the test indicated that the efficiency of the equipment based on its output per kg cocoa pod husk was 79.9%.The authors were able to produce 18.3 kg of biochar from the cocoa pod husk per day using 1 bag of local charcoal.
- **Issac** ***et al.,*** **(2010)** successfully proposed an alternative method for the small scale biochar production technologies using the single container to two barrels.

- **Sui Lam *et al.,* (2011)** carried out the Physical and chemical properties of pellets made from untreated and steam-exploded ground softwood, Canadian west coast Douglas fir were investigated. Over all this research must be extended to steam treatment of the mixture of bark and stem wood and then assess the economic value of steam treatment in improving the durability of pellets.
- **Andrew *et al.,* (2011)** observed that pyrogenic carbon (biochar) may be used to increase soil fertility while sequestering atmospheric carbon. However, both increased and decreased C mineralization was observed the biochar additions to soils. Overall the soils, C mineralization rate increased after biochar amendment, but decreased after a few months. During early incubation, soil generally stimulated the release of biochar-C, likely due to co-metabolism. During later incubation, biochar generally suppressed the release of soil C, likely due to sorptive protection.
- **Berge *et al.,* (2011)** reported the environmental implications associated with carbonization of representative municipal waste streams (including gas and liquid products), to evaluate the physical, chemical, and thermal properties of the produced hydrochar, and to determine carbonization energetics associated with each waste stream. Results from batch carbonization experiments indicate 4975% of the initially present carbon .Process energetics suggests feedstock carbonization is exothermic.
- **Chen *et al.,* (2011)** highlighted the Biochar derived from agricultural biomass waste may be utilized as a multifunctional material for agricultural and environmental applications. The results suggested that the magnetic biochar is a potential sorbent to remove organic contaminants and phosphate simultaneously from wastewater.
- **Mukherjee *et al.,* (2012)** studied the biochars made from oak (*Quercus lobata*), pine (*Pinus taeda*) and grass (*Tripsacum floridanum*) at 250 °C in air and 400 and 650 °C under N_2, micro pore surface area (measured by CO_2 sorptometry) increased with production temperature as volatile matter decreased, indicating that VM was released from pore-infillings. Overall no anion exchange capacity was measured in the biochars.

- **Wang *et al.,* (2012)** obtained development activated carbon materials with a high specific surface area, and large pore volume using potassium hydroxide (KOH) activation of fossil-based materials.

- **Ahmad *et al.,* (2012)** indicated the Biochar developed from soybean stover at 300 and 700 °C and peanut shells at 300 and 700 °C were used for the removal of trichloroethylene (TCE) from water. Overall the Pyrolysis temperature influenced crop residue-derived biochar (BC) properties.
- **Mahtab *et al.,* (2012)** used mussel shell, cow bone, and biochar to reduce lead (Pb) toxicity in the highly contaminated military shooting range soil. Bioavailability and bio-accessibility determine the level of metal toxicity in the soils. Mussel shell, cow bone, and biochar decreased Pb toxicity in shooting range soil. Soil dilution aided the amendments in reducing Pb toxicity.
- **Duleeka (2012)** reported the bulk density of rubber wood chip. The gas compositions obtained for three different throat diameters are comparable with typical producer-gas composition and then analyzing the effect of fuel size, more trials should be done. The exit gas temperature of the gasifier was around 250 °C and 1.653 kW waste heats available for energy efficient measures like air preheating. Approximately 2.583 kW was lost through char-ash at the maximum char-ash generation rate. This char-ash may be used as a soil conditioner as charcoal.
- **Inyang *et al.,* (2012)** revealed the two bio chars converted from digested biomass to sorbs heavy metals using a range of laboratory sorption and characterization experiments. Initial evaluation of DAWC (digested dairy waste biochar) and DWSBC (digested whole sugar beet biochar) showed that both bio chars were effective in removing a mixture of four heavy metals (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) from aqueous solutions. According to the authors DWSBC demonstrated a better ability to remove Ni and Cd.
- **Hui Li *et al.,* (2012)** carried out studies to identify the energy consumption and pellet properties. Energy consumptions for compacting torrefied sawdust into pellets were significantly higher than untreated sawdust at the same compression temperature. The hardness of pellet was reduced in the torrefaction process, while the hardness of pellets decreased with increasing the severity of torrefaction. The moisture adsorption of torrefied pellets was lower than pellets from untreated

sawdust, while the moisture adsorption of torrefied pellets decreased with increasing the severity of torrefaction.

- **Pak Sui Lam *et al.,* (2012)** reported the particles were exposed to high pressure saturated steam (200 and 220^0 C for 5 and 10 min) to improve the durability and hydrophobicity of pellets produced from them. The effect of steam treatment on the drying rate, moisture adsorption rate, and the equilibrium moisture content of untreated and steam treated Douglas fir were investigated.
- **Uras *et al.,* (2012)** evaluated the biochar from sugar cane bagasse seems to be a promising sorbent and soil conditioner due to its high surface area, high surface acidity and micro porous structure. This biochar can be applied to a wide pH range of soils for enhancing nutrient and water retention. Overall Vacuum pyrolysis contributed to the development of C$=$O groups on biochars surface.
- **Cegri *et al.,* (2012)** observed the effect of hydrothermal pretreatment at 25, 100, 150 and 200 ^{0}C on fiber composition and the biomethane potential of sunflower oil cake (SuOC). An increase in pretreatment temperature from 25 to 200^0 C caused a decrease in hemicellulose content in the solid pretreated fraction from 13 to 6% while the lignin content increased by 16%. Overall hydro thermal pretreatment at 100^0 C was the best option to improve the anaerobic digestion of SuOC and its methane yield.
- **Zhang *et al.,* (2012)** studied the application of abundantly of available renewable materials the corn residues (cobs, leaves and stalks) as an energy source in gasification and combustion systems. A positive relationship between the average particle size and the porosity was observed for the corn residues. The differences in the physical properties among the corn residues (cobs, leaves and stalks) observed in this study were due to variations in the compositions and structures of these materials.
- **Nizamuddin (2012)** investigated hydrochar has been successfully produced from the oil palm shell using HTC process and the results of statistical analysis suggest that the optimized conditions for maximum yield hydrochar production during HTC process were reaction temperature at 180^{0}c reaction time 30 minutes and biomass to water ratio of 1.6%**.**

Table 2.3: FT-IR spectral peaks in oil palm shell

Oil palm shell	Hydrochar 260 ^{0}C	Hydrochar 280 ^{0}C	Hydrochar 300 ^{0}C	Functional groups	Vibration	Wave Number (cm^{-1})
3452.3	3443.6	3441.7	3442.1	Alcoholic, Carboxylic Phenolic	O-H (Stretch)	3700-3000
2919.1	2922.5	2922.7	2923.1	-CH2, -CH3	C-H (Stretch)	3000-2800
1645.9	1616.6	1610.7	1611.4	Aromatic ring	C=C (Stretch)	1650-1510

- **Balagurumurthy *et al.,* (2013)** indicated that hydropyrolysis of deoiled cake was carried out at various pressures of hydrogen at 450^{0}c.The optimum value of pressure was found to be 40 bar for obtaining maximum bio-oil yield and then FTIR &SEM analysis of hydro pyrolysis are also carried out in macro molecular network and loss of functionalities present in the feed stocks.
- **Lei *et al.,* (2013)** indicated that hydrothermal pretreatment method was applied to lignocellulosic substrate, represented by the prairie cord grass, and comparison between different conditions based on the yield of glucose after enzymatic hydrolysis. The treatment did not involve any chemicals usage. Enzymatic hydrolysis was performed in order to examine the amount of glucose which was released from pretreated materials.
- **Chin *et al.,* (2013)** investigated the effects of torrefaction treatment on the weight loss and energy properties of fast growing species in Malaysia biomass. The biomass was torrefied at three different temperatures 200, 250 and 300 ◦C for 15, 30 and 45 min. The torrefied biomass occurred more suitable than raw biomass in terms of calorific value, physical and chemical properties. The results of this study could be used as a guide for the production of high energy density solid biofuel from lignocellulosic biomass available in Malaysia.
- **Kurt Spokas (2013)** carried out in the observations of decreased greenhouse gas production from the biochar amended soils. These are used to further substantiate the environmental benefit of biochar production and soil incorporation strategies.

- **Oladeji *et al.,* (2013)** compared the experimental and predicted results from generalized and empirical equations of some densification characteristics of corncob briquettes. Seven mathematical models were developed for the briquettes produced from corncobs. The regression analyses for the seven models had regression coefficients R^2 = 0.72, 0.81, 0.85, 0.84, 0.77, 0.86 and 0.81 for the maximum density, relaxed density, compaction ratio, density ratio, relaxation ratio, axial expansion and lateral expansion respectively. The t-statistics was less than t-critical both at one and two-tail with 95% confidence level for all the physical parameters examined in this study.
- **Ying *et al.,* (2013)** reported that Sludge thermo gravimetric analysis was conducted to get 180^0 C as the upper-limit hydrothermal temperature. The higher the hydrothermal temperature, the better was the dewater ability character. The water contents of solid products were positively correlated with the hydrothermal holding time at predetermined temperature .overall the Separated liquid can be anaerobic digested to produce methane for energy recovery or discharged back into water treatment plants.
- **Zhou *et al.,* (2013)** synthesized the chitosan-modified bio chars in efforts to produce a low-cost adsorbent for heavy metal environmental remediation. Characterization results showed that the coating of chitosan on biochar surfaces could improve its performance as a soil amendment or an adsorbent. Overall this work suggested that chitosan-modified bio chars may be used as an effective, low-cost, and environmental-friendly adsorbent to remediate heavy metal contamination in the environment.
- **Ahmad *et al.,* (2014)** revealed that Biochar was a stable carbon-rich by-product synthesized through pyrolysis/carbonization of plant- and animal-based biomass.

- **Anukam *et al.,* (2014**) observed the computer stimulation of a downdraft biomass gasifier performed on sugarcane baggase and results showed that several characteristics affect the gasification process and performance of sugarcane baggase including moisture content and particle diameter as well as gasifier operating parameters such as throat angle, diameter, and temperature of input air. The study finally established that a laboratory scale as well as a large scale gasifier.

- **Chen *et al.,* (2014)** studied the properties of corn stalk and cotton stalk after torrefaction, and the effects of torrefaction on product properties obtained under the optimal condition of biomass pyrolysis poly generation. According to the studies, improved grind ability increased the carbon content and decreased oxygen content.

- **Dominic *et al.,* (2014)** indicated the coproduction of biofuel with the biochar can be provide carbon-negative bioenergy .It can improve fertility and thus simultaneously address issues of food security, soil degradation, energy production and then climate change.
- **David Yarrow (2014)** synthesized biochar using moisten, micronized, mineralize, microbe inoculation, cultures, colonies and inoculate. The small amount of the material by ways that target and concentrate char near crop roots .The author stated that this can be used to seed dressing ,bonding ,side dressing, root drenches, vegetables growers get top value blending biochar in potting mixes for seedlings .biochar compost to occupy its microspores.
- **Ferreira *et al.,* (2014)** reported the pyrolysis process on *Chorella vulgaris* and *scenedesmus obliquus* pyrolysis carried out in the fixed bed reactor in the with and without catalyst. The use of carbonate catalyst increased the gas and decreased the bio-oil productions for both microalgae used.
- **Greg Roth *et al.,* (2014)** reported that corn cobs were once viewed as an important biofuel feedstock .Its dense and relatively uniform, and they have a high heat value, with low N and S contents, and can be collected during corn grain harvest. Its appear to be a relatively sustainable, but relatively low-yielding, feedstock that can be used effectively in cellulosic ethanol, gasification. Two of the limiting issues were the need for a significant local resource base and the development of harvesting equipment, which is compatible with current corn-harvesting systems.
- **Hao (2014)** evaluated the hydrothermal treatment on grass cutting, horse manure, beer waste, biosludge. Overall the hydrothermal biomass had special characteristics and then the structure and properties of hydrothermal biomass and then the activated carbon with embedded iron oxide nanoparticles could be easily separated from a water suspension by a magnet.

- **Jiang *et al.,* (2014)** carried out the effects of process parameters on pellet properties for the co-pelletization of sludge and biomass materials. The pellet density was increased with the parameters increasing, such as pressure, sludge ratio and temperature. High hardness pellets could be obtained at low pressure, temperature and biomass size.
- **Khursheed *et al.,* (2014)** observed that solid char comprised of macro and nanoparticles having porous structures and various functionalities .Press mud thermal pyrolysis with and without up gradation of the vapor products was studied and the production of hydrocarbons .The comprising gases, liquids, and solid residue were characterized .The results inferred that the in carbon nanoparticles obtained may be used to remove pollutants and heavy metals from the waste water.
- **Liu *et al.,* (2014)** proposed an alternative method for production biochar prepared from the raw material. The authors demonstrated that hydrothermal carbonization (HTC) combined with pelletization provides an alternative for solid biofuel production from biomass resources, especially for the abundant agricultural residues**.**
- **Liang *et al.,* (2014)** investigated the Pyrolysis of *Spartina alterniflora* (smooth cordgrass) by thermo gravimetric analysis in a nitrogen atmosphere at heating rates of 5, 10, 20, and 40 C/min. Main weight-loss was observed in smooth cordgrass at temperatures ranging from 200^0 C to 360 ^{0}C, owing to release of 72% to 74% of total volatiles.
- **Salviano *et al.,* (2014)** studied the hemicelluloses present in jatropha seed cake the proportion of 2.3 tons of cake for each ton of jatropha curcas seed oil extracted; it would be possible to produce 88.5 l of ethanol.
- **Shan-wen du *et al.,* (2014)** evaluated the utility potential of pretreated biomass in blast furnaces, the fuel properties, including fuel ratio, ignition temperature, and burnout, of bamboo, oil palm, rice husk, sugarcane bagasse, and Madagascar almond undergoing torrefaction and carbonization in a rotary furnace were analyzed and compared to those of a high-volatile coal and a low-volatile one used in pulverized coal injection (PCI).

- **Kalderis** ***et al.,*** **(2014)** reported the carbon rich product obtained when biomass such as wood, manure or leaves is heated in a closed container where air is not available.
- **Nunes** ***et al.,*** **(2014)** inclined to develop an analysis of the current situation of the production of pellets, mainly with mixed biomass types, and the possible uses they have, with the main emphasis on the review of different combustion processes.
- **Zhou** ***et al.,*** **(2014)** highlighted the thermal decomposition behavior of coal gangue, peanut shell, wheat straw and their blends during combustion. The addition of biomass in the coal gangue was found to improve the thermo chemical reactivity with suitable proportion and heating rate. Overall of this study was vital as it provides an insight into the future utilization of agricultural biomass and coal gangue as a renewable resource.
- **Cao** ***et al.,*** **(2015)** observed that two kinds of biomass materials were torrefied and mixed with oil cake for co-pelletization. The energy consumption during pelletization and pellet characteristics including moisture absorption, pellet density, pellet strength and combustion characteristic, were evaluated. Overall the complementary performances of the torrefaction and co-pelletization with castor bean cake provide a promising alternative for fuel production from biomass and oil cake.
- **Feng** ***et al.,*** **(2015)** studied the biochar prepared from cassava dreg at 350^0C, 450^0C, 550^0C, 650^0C and 750^0C.This results showed that the kinetic data were fitted to the pseudo second order model. Sorption sites on the biochar surfaces rather than the solution. Overall this work constituted a basis for further research considering the bioavailability and toxicity of antibiotics in the presence of the biochar.

- **Parshetti** ***et al., (*****2015)** Obtained low-cost carbonaceous adsorbents with a remarkable carbon dioxide uptake capacity from empty palm fruit bunch feedstock using HTC and chemical activation.

- **Hussein** ***et al.,*** **(2015)** studied the formation of biochar based on the fast pyrolysis, slow pyrolysis, intermediate pyrolysis and gasification. The produced biochar were further studied to determine the influence of production conditions on the yield and the environmental stability of biochar.

- **Pengfei *et al.*, (2015)** highlighted the biochar coated with magnetic F_{e3O4} nanoparticles and then finding the potential of the developed magnetic biochar for use as a sorbent in the treatment of cationic crystal violet polluted waste water.
- **Wang *et al.*, (2015)** observed the need for the development of low-cost adsorbents to removal arsenic (As) from the aqueous solutions. In this work, a magnetic biochar was synthesized by pyrolyzing a mixture and then naturally-occurring hematite mineral and pinewood biomass. The resulting biochar composite was characterized with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDS).
- **Nizamuddin (2015)** indicated the hydrochar has been successfully produced from oil palm shell using hydrothermal process and then the results of statistical analysis suggest that the optimized conditions for maximum yield of hydrochar production during hydrothermal process were reaction temperature at 180^0c.
- **Falah *et al.*, (2016)** studied the pyrolysis of olive biomass in a stainless steel reactor. This process was carried out in externally heated by the electrical furnace in which the temperature measured by a thermocouple inserted into the bed. The catalyst ratio to the biomass (5%, 10%, 15%, 20%, 30%, and 40%) on the pyrolysis yield was investigated and then compared with the uncatalysed pyrolysis yield product. Overall this work the chemical characterization showed that the bio-oil obtained from olive -oil cake might be potentially valuable as a fuel and then the chemical feedstock.
- **Liang *et al.*, (2016)** in their study carried out the pyrolysis of mixture of torrefied camphor wood and caster bean cake was determined by thermo gravimetric analysis .Here thermal and kinetics suggested that torrefaction and co-pelletization increased the efficient heat transfer and contributed to the stable pyrolysis.
- **Lih Teo *et al.*, (2016)** reported the application of high surface area activated carbon derived from the rice husk as a super capacitor electrode .The three

different samples of activated carbon with different surface areas were prepared at different activation temperatures and studied electrochemically using cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy.

- **Trivedi *et al.,* (2016)** characterized eight different biomass ashes such as soya bean plant ash, mustard plant ash, maize ash, groundnut plant ash, cotton plant ash, pigeon peas ash, groundnut shell ash, wheat plant ash, and their chemical properties were discussed .All samples had a predominance of K_2O and CaO contents except wheat plant ash. The K and Ca compound containing ashes might be added to the soil to increase the micronutrient content.
- **Kalinke *et al.,* (2016)** evaluated the biochar samples prepared from castor oilcake using different temperatures of pyrolysis and then voltametric procedures based on the carbon paste modified electrode was investigated the effect of temperature of pyrolysis on the adsorptive characteristics of Pb, Cd and Cu.
- **Elaigwu *et al.,* (2016)** proposed an alternative method that implies that the microwave -assisted hydrothermal approach is a fast and simple approach for preparing time from hours few minutes.
- **Kyoung S.Ro (2016)** studied the animal manure produced the biochar with multiple beneficial and then used for the improving soil quality and the environment .This energy could be used for the local power generation.
- **Magdalena *et al.,* (2016)** observed the agricultural biomass in the form of oilcake, which is formed as a result of oil seeds processing, had perfect fodder properties (considerable content of fat) results indicated that they may be used as a valuable energy carrier.
- **Negahdar *et al.,* (2016)** highlighted the characterization and Comparison of Fast Pyrolysis Bio-oils from Pinewood, Rapeseed Cake, and Wheat Straw Using 13C NMR and Comprehensive GC × GC. The rapeseed cake bio-oil was chemically more stable and relatively noncorrosive when compared with the two other bio-oils. In addition, valuable phenol compounds were identified and quantified in all bio-oils.
- **Young *et al.,* (2016)** reported the hydrochar was produced from CO_2 assisted hydrothermal treatment from corn stover black liquor. The optimal condition

was determined by using Response Surface Methodology with the operational parameters set as the following the activation temperature (205^0 C), duration (28 mins), LiquidSolidRatio with Pb^{2+} removal capacity reaching 47 mg/g. The combination of hydrothermal temperature and duration was found to be significant to the response. The prepared hydrochar showed a comparable Pb^{2+} removal capacity at ambient temperature.

- **Anukam *et al.,* (2017)** investigated corn cob and to determine the gasification of potential .The corn cob was analyzed using proximate analysis, ultimate analysis, FTIR, TGA, SEM.
- **Chen *et al.,* (2017)** revealed that thermo chemical process may help in the conversion of organic components from municipal solid waste into different energy carriers and reduce the negative impacts on the environment .Municipal solid waste were treated with four steps of device a hot char filter, a condenser cooled with ice water, a cooking oil scrubber and then finally sodium carbonate solution scrubber .overall the performance of each unit and then the effects of system for removing particles, tars ,gaseous pollutants like H_2S,NH_3,HCl high quality syngas for practical applications.
- **Onorevoli *et al.,*(2017)** indicated that energetic tobacco a type of modified tobacco with a focus on energy residual cake can be thermally degraded to the bio-oil or biochar through the pyrolysis method, acid alkaline extraction of bio-oil and then analysis of bio-oil of the residual cake of the energetic tobacco and alkaline extract using gas chromatography can be performed in a fixed bed reactor.
- **Sliva *et al.,* (2017)** carried out the preparation of bio-based catalyst derived from residual jatropha curcas cake using a combination of low temperature conversion and then chemical treatment to be applied for the epoxidation of vegetable oil. The catalyst was characterized and its performance for epoxidation of cotton seed oil was evaluated and then compared with cationic resin VPOC 1800.
- **Chen *et al.,* (2017)** evaluated the prepared hydrochar in pre-hydrolysis step. The majority of hemicellulose were removed and then dissolved in the liquor along the some organic compounds.

- **Takaragawa *et al.,* (2017)** carried out the baggase produced biochar and then these are slight alkalinity and then sunflower residues also produced biochar and then these characterized by high values of pH and potassium concentration tended to be higher than that of any other minerals in the baggase .In sunflower potassium concentrations were higher than 10,000mg.
- The physicochemical properties of biochar, hydrochar and pyro-hydrochar were compared by multi-analysis including the characterization by elemental composition, BET, FTIR, XPS, SEM, chemical oxidation method by $K_2Cr_2O_7$ and H_2O_2. The results showed the pyro-hydrochar was newly developed rich carbon material with large specific surface area, rich functional groups, high aromatization degree and strong chemical oxidation stability **(Liu *et al.,* 2017).**
- **Shemsedin *et al.,* (2017)** carried out the proximate and ultimate analysis of rubber seed cake and rubber seed shell and confirmed that both are rich in hydrocarbon content and can be suitable for bio-oil and biochar production and then increase in activation energy for pyrolysis process.
- Solid char, bio-oil and gaseous products were obtained from mauha deoiled seed cake.600^0c is maintained in the pyrolysis process and then biochar yield fell slightly with increasing temperature .The biochar also increased with increasing particle size of the sample and the presence of carbon 73.7%, nitrogen 1.6%, phosphorus 0.48%help to plant growth **(Mulimani *et al., 2017).***
- **Mehmet (2017)** observed that Food industry generated voluminous and serious amounts of food wastes and by-products due to rapid urbanization, industrialization and population growth. Conversion of these food wastes and by-products into value added products are very important for not only economic aspect but also social and environmental sides. Overall the Food wastes and by-products can be converting into valuable products through thermal, chemical and biological methods. The appropriate conversion method was selected with respect to composition of food wastes and by-products.
- **Fang *et al.,* (2017)** indicated that hickory and peanut hydrochars were chemically activated with KOH and H_3PO_4 and tested for their ability to remove methylene blue and lead from aqueous solutions. The physicochemical

characteristics of the activated hydrochars namely surface area, pore volume, and elemental composition were determined. Kinetics and isotherm studies were then conducted on methylene blue adsorption. Compared to their non activated counterparts, the chemically activated hydrochars had higher surface areas and more functional groups. Overall hydrothermal carbonization is more energy efficient than dry pyrolysis, the use of AHCs may prove to be a more cost-effective water treatment applications. For instance, AHCs may be used in soil remediation to immobilize toxic chemicals including heavy metals and organics to reduce their mobility and bioavailability.

- **Guangzhi *et al.*, (2017)** produced porous carbon from camphor leaves (CLs) by hydrothermal carbonization (HTC) and sequential potassium hydroxide activation. The morphology, porous structure, chemical properties, and CO_2 capture capacity of the produced materials were investigated. The influence of HTC temperature on the material structure and capture capacity was studied. Overall the porous carbon materials derived from CL biomass via hydrothermal carbonization and chemical activation had a potential use in carbon capture and storage.
- **Sayg *et al.*, (2017)** reported the production of powdered activated carbon under optimized conditions from a 30 novel precursor, carob industrial processing residues, by zinc chloride (ZnCl2) chemical activation. The production influenced. The of impregnation ratio carbonization temperature and carbonization duration on the some textural properties of produced carbons and the best production conditions were determined.
- **Nikolas *et al.*, (2018)** compared biochar and activated carbon, both materials could produced from the same feedstock using different impregnation ratios and burn-off rates, respectively, producing comparative series from non-activated to fully activated biochar/activated carbon will allow an overall economic evaluation.

3. MATERIALS AND METHODS

In any research work the materials and methods adopted are the aspects, which decide and determine qualitatively and quantitatively the outcome of the research. In the present investigation, efforts have been taken to study the hydrochar prepared by *Seasame oilcake and Groundnut oilcake*. The design of the present investigation consisted of the following steps.

3.1. Selection of sample

Seasame oilcakes, groundnut oilcake were collected from V.V.V Sons & edible oil factories located in around the city of virudhunagar in the south of Tamilnadu. The industrial process after extracting removal of oil by pressing was selected.

3.2. Preparation of sample

The samples were dried outdoors at an average temperature of about 30^0C to lower its moisture content .This was followed be milling to a size required by the instruments that were used for analyses .The dried and milled SOC, GOC was preserved in a desiccators.

3.3. Hydrochar Production

Seasame oilcake and Groundnut oilcake feedstocks were milled to particle sizes of 0.5^{-1}mm and added to a pressurizable lidded stainless-steel pot to a height of about one inch from the top. Deionized (DI) water was added to the same level. The pots were then sealed and heated on a hotplate to 200 °C for six hours, which were the HTC conditions that produced hydrochar with the highest yield and surface area.

The resulting hydrochars were rinsed for one hour by submersion in tap water and ten minutes in DI water to remove water soluble volatile matter, and oven dried for 24 h at 70 °C.

For activation, the hydrochar was mixed in a 1:1 w/w ratio with either KOH solution or 85% H_3PO_4 solution. The mixture was stirred on top of a hotplate for 2 h at 85 °C, and the resulting slurry was oven dried for 24 h at 100 °C. The dried slurry was then activated in a tube furnace for 1 h at 600 °C under N_2 gas flowing at a rate of 150 ml.

The Activated hydrochar was then allowed to cool to room temperature, and were washed with DI water in order to remove any residual chemicals. They were rinsed repeatedly with DI water until the pH of the AHC water mixture stabilized **(Fang *et al.*, 2017)**.

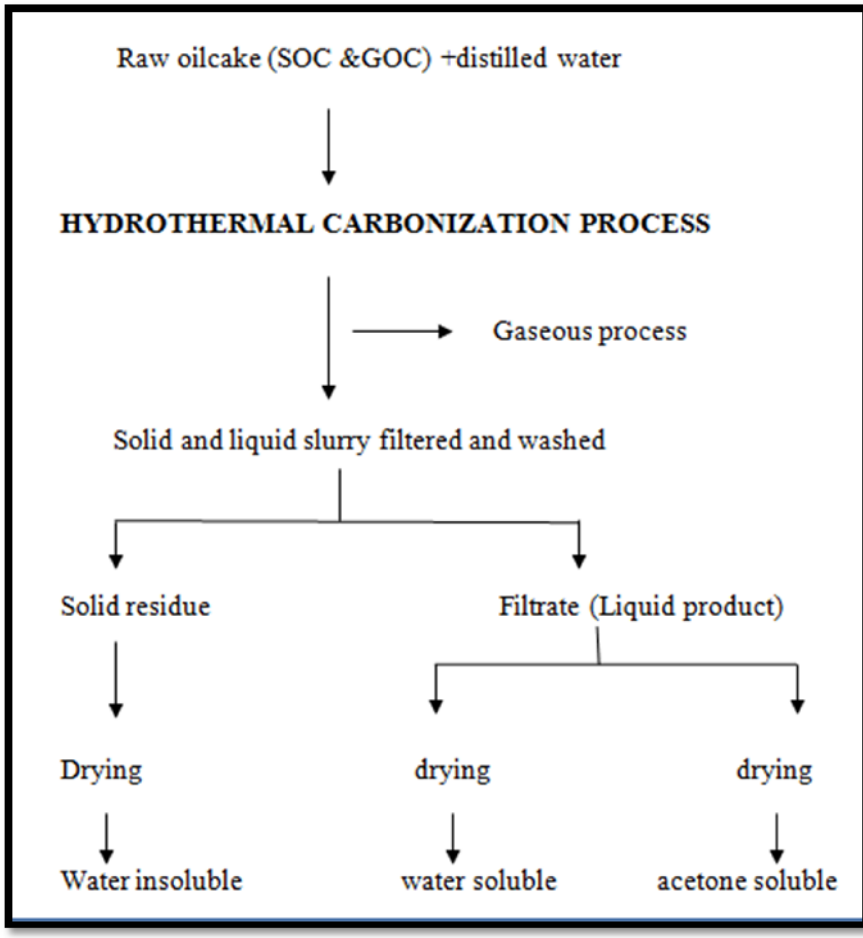


Fig 3.1: Schematic diagram for hydrothermal carbonization process

3.4. Characterization of hydrochar

Hydrochar, which is called solid product of biomass carbonization, is used in many commercial applications such as, metallurgical, domestic and chemical .It can be used to produce activated carbon and different carbonaceous materials .It can be alternative to the conventional fuels partially due to their high fixed carbon content and high calorific value.

The following characterization techniques were carried out

3.5. Physical characteristics

Water adsorption capacity

0.2 g of SOC-H,GOC-H was taken and added in10ml of water and then this mixture was allowed to the react for 3hr in shaker and then they remained water is decanted and measured .Initially 10ml water is taken finally the hydrocarbon is adsorbed the water. These volumes are noted.

Bulk surface acidity and basicity

Approximately 0.1g of prepared SOC and GOC hydrochar were treated with 50ml of **0.01N NaOH and 0.01N HCl**. The samples were shaken at 30^0C in constant temperature water bath shaker for 24hr.

The mixture was filtered and back titrated with **0.01N HCl and 0.01N NaOH**. The concentration of the bulk acidic substituent group on the surface was expressed in millimole gram.

Fig 3.2: Visualization for bulk surface acidity

Fig 3.3: Visualization for bulk surface basicity

Effect of biomass to water ratio

Slurry of 5g of biomass SOC and GOC 5, 10, 15ml of water was loaded into autoclave. A stream of N_2 gas was used to purge air from the autoclave and to maintain initial internal pressure into 1MPa. The autoclave was heated to the target temperature. The target temperature ranging from 200 to 300^{0}C, was automatically adjusted .Once the target temperature was reached, the sample was held for 30 min before autoclave was cooled to the ambient conditions. The slurry of hydrochar and water was filtered .The solid part was dried in an oven at 150^{0}c for 4hours to yield the final solid product .The experiments repeated for biomass -water ratio 5%, 10%, 15% at 250^{0}c and residence time 30min.

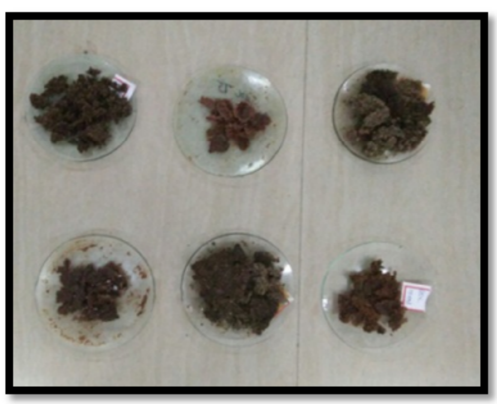


Fig 3.4 Visualization of water ratio of biomass

Effect of reaction time

A Slurry of 5g of biomass SOC, GOC and 75ml of water was loaded into autoclave. A stream of N_2 gas was used to purge air from the autoclave and to maintain initial internal pressure into 1MPa; the autoclave was heated to the target temperature. The target temperature ranging from 200 to 300^0C, was automatically adjusted .Once the target temperature was reached, the sample was held for 30 min before autoclave was cooled to the ambient conditions. The experiments repeated for biomass - reaction time 30mins to 180 mins at 250^0C at varying time intervals.

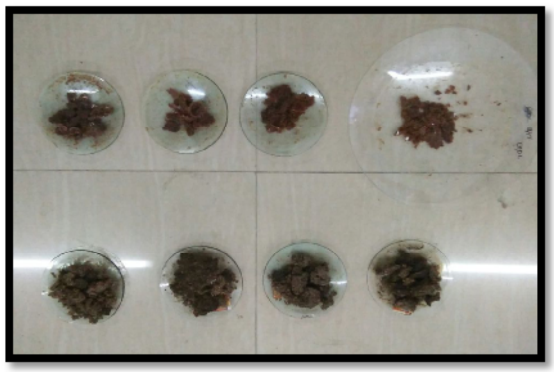


Fig 3.5: Reaction time for biomass

Energy value for SOC and GOC

Plants convert energy from the sun into chemical energy that is stored in the structural components of the biomass by using CO_2 in the atmosphere. The energy value of SOC and GOC was determined to evaluate the amount of energy available for conversion, which is a very important property of biomass because conversion efficiency of a gasification process depends on it. The energy value, also known as heating value and reported in terms of higher heating value (HHV) of SOC and GOC, was calculated from the mass fractions of the elemental components obtained from CHNS analysis.

$$HV\ (MJ/kg) = -1.3675 + 0.3137 \times C + 0.7009 \times H + 0.0318 \times O$$

Proximate analysis:

Proximate analysis (ash and moisture content) for the oil cake and produced hydrochar is measured by using Model: Mettler Toledo TGA/STDA 851e. This equipment is a robust, flexible and easy to use. It has the SDTA function which is similar to the DSC. Both the reference temperature and sample temperature are measured. Any difference between the reference temperature and sample temperature shows a change in enthalpy of the sample. The system records the mass of the sample, the temperature of the sample, furnace (reference) temperature and the time continuously during measurement. As the mass of the sample is lost, the lost mass becomes smoke and gas.

It is the most widely used method for solid and liquid fuels characterization such as moisture content (MC), ash content (AC). The solid samples were prepared. For each analysis, the crucible was dried at respective operating temperature (i.e., for moisture content at $105 \pm 1\ ^0$C, ash content at 575 ± 25^0 C and volatile matter at 950 ± 25^0 C) for 30 min and placed in desiccators. For moisture determination, sample 2 g of SOC and GOC was placed in the dried crucible and then oven-dried again for 16 h at 105 ± 1^0 C, and MC is calculated using the following mass balance expression

$$MC\ (\text{mass }\%) = \frac{(W_c + W_0) - (Wc + W_{fr}) \times 100}{W_0}$$

Where W_c, W_o and W_{fr} are the mass of empty crucible, raw sample and moisture-free (oven-dried) sample, respectively.

$$AC\ (\text{mass }\%) = \frac{W_a}{W_{OD}} \times 100$$

Where W_{OD} and W_A mass of oven-dried sample and ash obtained.

3.6. Chemical characteristics:

FT-IR Spectrometric analysis

FTIR spectroscopy is preferred for the determination of functional groups attached to the surface of the material because of its efficiency to analyze the functional groups and the lower cost. It may be applied to many areas which are difficult or nearly impossible to analyze by dispersive instruments

The samples for FT-IR studies were prepared by finely mixing the crude with spectroscopically pure KBr and then pressed by using a die so as to get a fine transparent pellet. The FT-IR spectrum was recorded for SOC-Crude SOC-HC, GOC-Crude, GOC -HC powder with a frequency ranging from 3600 to 600 cm^{-1} using **Perkin Elmer FT-IR spectrophotometer** with the **SOFTWARE - OPUS version 6.5**.

3.7. Thermal characterization

Thermogravimetric analysis

The amount and rate of weight changes in a material are measured by using TGA either as a function of temperature with increasing temperature or isothermally as a function of time. It is used to characterize any material which exhibits a weight change and detects phase changes due to oxidation, decomposition or dehydration. It is connected to a computer which acts as a controller to control the functions like to run data analysis 46 programs, store experimental data and to setup and control experiments. Moisture content and presence of volatile species can be determined by this technique. Computer controlled graphics can calculate weight percent losses. The dynamic thermogravimetric is carried out on samples (about 10 mg) with an airflow rate of 300 cm3 /min. The maximum temperature was 800 °C and the typical heating rate was 10 °C per minute. The TGA was used to study the thermal stability of the products in order to distinguish the deposited carbons according to their different thermal stability level.

Seasame oilcake and groundnut oilcake crude and hydrochars were analyzed using a thermogravimetric analyzer. The analyzer provides continuous recording of thermogravimetry and differential thermogravimetry in terms of temperature increment per second. In each experimental run the samples are placed inside the thermal analyzer. Then the experiment run was carried out at heating rates of 10,20,30 and 40^0c/min with temperature ranging from 30^0C to 800^0C.To maintain the inert environment ,nitrogen was used as the carrier gas during thermal analysis.

3.8. Microstructural characterization

Optical Profilometer

Surface profiles and pores were studied using a **Zeta-20 3D Optical Profiler**. The samples were mounted on sample holder under the objective of the Optical Profiler and the 3D photos were taken from the 100x magnified surface via operating program on computer.

Scanning Electron Microscope

Scanning electron microscopy (SEM) **JEOL MODEL JSM 6360** was used to examine the morphology of the prepared SOC and GOC hydrochar surface. It is a potential technique for studying morphology of solid fuel particles. SEM analysis has been especially used to evaluate the structural variations in hydrochar particles after different thermal treatment and SEM images are very useful to obtain accurate details about pore structure of hydrochars (**Ozcimen & Mericboyu 2010)**. SEM was carried out to study the characteristics of hydrochar and to determine the dimensions of the synthesized SOC, GOC surface.

EDAX

This analysis was carried out using the vario micro cube model to determine the composition of carbon, hydrogen, nitrogen and sulfur. It is used for identifying the elemental composition of the specimen. The specimen is bombarded with an electron beam inside the scanning electron microscope. A EDAX spectrum plot not only identifies the element corresponding to each of its peaks.

4. RESULTS AND DISCUSSION

The present study entitled **“A descriptive study of hydrochar prepared by *Seasame oilcake* and *Groundnut oilcake* -an ecofriendly approach”** deals with the in depth assessment of nature of hydrochar prepared from seasame oilcake and groundnut oilcake.

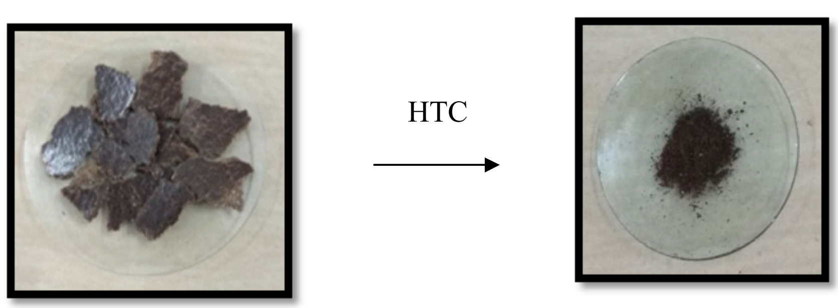
Among the thermo-chemical processes available, hydrothermal carbonization (HTC) is selected to study and find out its effects on the seasame oilcake and groundnut oilcake. HTC is an environmentally friendly method which converts raw biomass into a high yield percentage and higher quality hydrochar.

Seasame oilcake and Ground oilcake are vastly used as fodder for animals. In this project, these oilcakes considered as waste was converted into value added products. To ascertain the applicability of hydrochar in several characterization techniques were carried out and the results are discussed under the following topics.

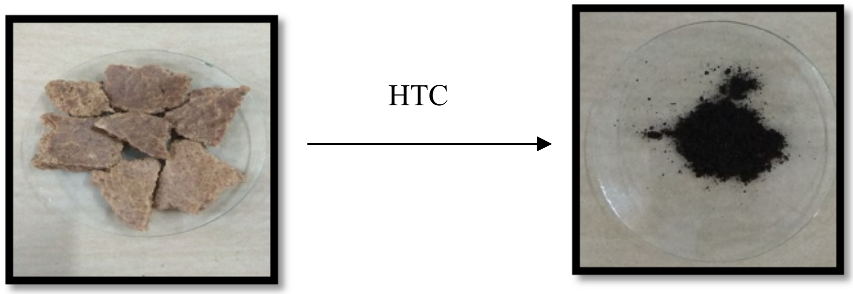
4.1: Physical characteristics

Preparation of hydrochar:

There are two main processes to produce solid fuel (hydrochar/biochar) from different biomass sources: pyrolysis and HTC. The difference between pyrolysis and HTC is the pyrolysis employs dry biomass and it is not environmentally friendly because of volatile matter emissions. The HTC is an environmentally friendly method and can handle both wet and dry biomass, therefore, saving the energy, time and cost required for drying of feed material.



Seasame oilcake **Hydrochar for seasame oilcake**



Groundnut oilcake **Hydrochar for Groundnutoilcake**

Fig 4.1: Visualization of SOC, GOC-crude and SOC, GOC-HC

The physical properties of the SOC and GOC used in this study were typically different from those of the reported agricultural biomass, such as corn silage, dry straw, cabbage residue, poultry manure, and bedding material. These types of agricultural biomass have a carbon content of 40.7-46.9% and oxygen content of 30.1-44.4%. SOC and GOC used in this study showed a lower carbon content and lower oxygen content compared to the reported agricultural biomass. This might be due to the fact that Oil cakes are rich in protein and energy contents.

Table 4.1: Physical properties for SOC and GOC

Parameters	**SOC**		**GOC**	
	Element	**Composition (%)**	**Element**	**Composition (%)**
	C	22.41	C	26.11
	Na	0.17	Na	0.04
	Mg	0.11	Mg	0.28

INFLUENCE OF WATER and REACTION TIME ON HYDROCHAR YIELD

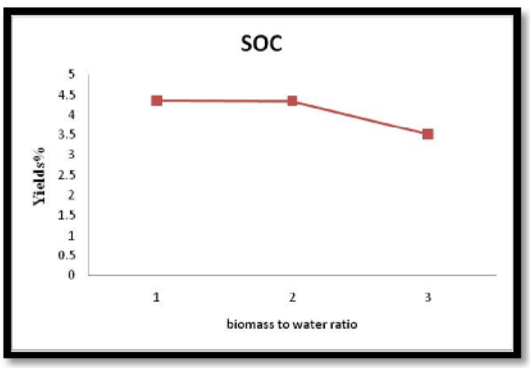
Impact of biomass to water ratio and reaction time on hydrochar products to analyze the influence of biomass to water ratio and reaction time on the percentage yield of the hydrochar, following experiments were carried out.

Effect of biomass to water ratio

Biomass to water ratio has little influence on the yield percentage, product distribution and quality of solid products. The effect of biomass to water ratio on the yield percentage of hydrochar from the HTC of the SOC and GOC. The higher amount of hydrochar was produced at lower biomass to water ratio. A slight decrease in the hydrochar yield percentage was observed as SOC biomass to water ratio decreased from 4.36 to 3.30wt. % and GOC biomass to water ratio decreased from 3.25 to 2.24 wt %. Similar observations were discussed in the literature that higher biomass to water ratios lead to a lower carbonization **(Román, et al., 2012)**. Besides, it is revealed from an earlier study, the biomass concentration and particle size have less effect on the mass yield **(Rogalinski, et al., 2008)**.

Table 4.2: Water ratio for SOC and GOC

Biomass to water ratio (wt %)	SOC (wt %)	GOC (wt %)
5	4.3	3.3
10	4.4	2.5
15	3.5	2.2



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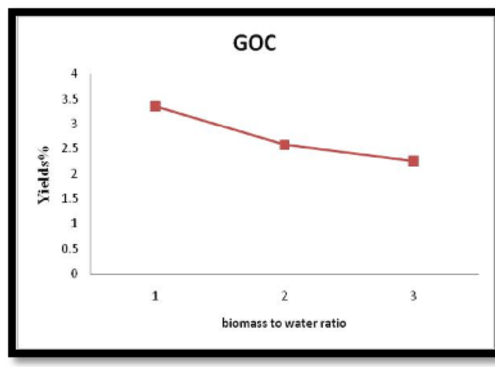


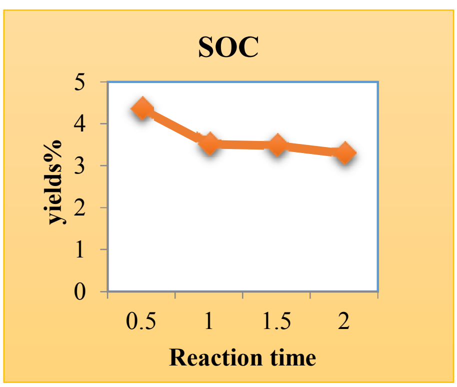
(b)

Fig 4.2: Water ratio graph for SOC and GOC

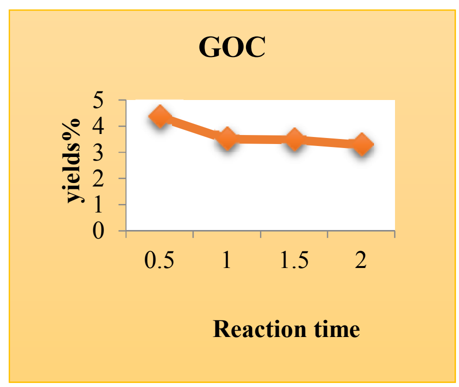
SOC biomass water ratio varied from 4.3664 to 3.5052 and GOC biomass varied from 3.2513 to 2.2496.

Effect of reaction time

HTC is a slow process and the reported reaction duration of HTC is from minutes to a few days. Reaction duration is interpreted as a parameter affecting product composition and the overall conversion of biomass. In supercritical state, the hydrolysis and degradation of biomass rates are comparatively fast (Sasaki, et al., 2003), therefore short time duration is needed to decompose biomass in an effective manner. Some studies have reported that higher reaction times support production of solid product by repolymerization of heavy oil (Overend *et al.,* 1985), but it was not observed in our study. The effect of reaction time on the hydrochar yield percentage. The higher amount of hydrochar is produced at lower reaction time. As the reaction time increases the yield percentage tends to decrease. Thus, there would be a decline in the hydrochar yield and increase in the carbon's porosity (Arami-Niya, et al., 2011). Additionally, the longer reaction time would support liquid production, with the exemption of high biomass to water ratio (Boocock and Sherman, 1985). A similar effect of reaction time on HTC of lignocellulose biomass was observed by (Hoekman, et al., 2011). They studied the effect of reaction time from 5 min to 60 min on mass recovery of hydrochar keeping temperature constant at 255 ^{0}C. It was found the HTC char recovery was more at lower reaction durations whereas it decreased with increasing holding time and the amount of water product and noncondensable gases increased with longer holding time.



(a)



(b)

Fig 4.3: Reaction time graph for SOC and GOC

SOC biomass varies from 4.3522 to 3.2828 and SOC biomass varies from 3.8056 to 2.3498 in the reaction time.

Water absorption capacity

0.2 g of HC prepared from SOC and GOC are taken and added 10ml of water and this mixture was allowed to react for 3h in shaker. After 3h the remaining water was decanted and measured for the water adsorption capacity of hydrochar.

Table 4.3: Water absorption capacity

Hydrochar	Water absorption(ml/g)
SOC	0.2
GOC	0.1

The results reflected the high tendency of the hydrochar to adsorb H_2O. This higher tendency to adsorb H_2O was due to high porosity of the hydrochar **(Trivedi *et al.*, 2016)**

Bulk surface changes:

Surface acidity and basicity

Approximately 0.1g of prepared SOC and GOC hydrochar were treated with 50ml of 0.01N NaOH and 0.01N HCl. The samples were shaken at 30^0C in constant temperature water bath shaker for 24hr. The mixture was filtered and back titrated with 0.01N HCl and 0.01N NaOH. The concentration of the bulk acidic substituent group on the surface was expressed in millimole gram.

Table 4.4: Titration values for bulk surface acidity bulk surface basicity

Hydrochar	Surface acidity (mmol/g)	Surface basicity (mmol/g)
SOC	1.2	8.9
GOC	1.1	8.0

Bulk surface acidity of SOC -hydrochar was 1.2mmol/g where as for GOC hydrochar it was 1.1 mmol/g. Similarly surface basicity was noticed at 8.9mmol/g for SOC-hydrochar and8 mmol/g for GOC-hydrochar.The results indicate that the total charge on the surface of hydrochar tend to have basic nature and showed very minimum total acidity on the surface

Characteristics of SOC and GOC

Table 4.5: Characteristics of proximate and element composition

Characteristics	Values	
	SOC	GOC
Proximate analysis (%Wt)		
Moisture content	6.93%	8.36%
Ash content	12.85%	5.14%
Composition (%Wt)		
CK	22.41%	26.11
NaK	0.17%	0.04
MgK	0.11%	0.28

Energy Value of SOC and GOC

Plants convert energy from the sun into chemical energy that is stored in the structural components of the biomass by using CO_2 in the atmosphere. The energy value of SOC and GOC was determined to evaluate the amount of energy available for conversion, which is a very important property of biomass because conversion efficiency of a gasification process depends on it. In this study, the energy value of SOC and GOC was measured as 19.9221 MJ/kg, a value that is in agreement with those reported by Danje, 2011 and Danish *et al*., 2015. It is therefore sufficient to allude that the energy value of SOC and GOC measured in this study is in agreement with most findings in the literature.

Proximate analysis

The parameters of proximate analysis are moisture, ash content. The proximate analysis of different materials was done according to a group of test methods ASTM D 5142, ASTM D 3172 and ASTM D 4442 for measuring moisture content, ASTM E 1755 for measuring ash content.

Determination of the moisture content of SOC and GOC

The moisture content of the SOC and GOC samples were determined by heating the samples at 120 ^{0}C till constant weight. The moisture was found to be 6.93% and 8.36%. Lower moisture content helps in combustion, whereas higher moisture hampers ignition and thus reduces the combustion temperature, which adversely affects reaction products of combustion and quality combustion **(Werther *et al.,* 2000)**.

Determination of the ash content of SOC and GOC .The ash content of SOC and GOC samples were determined. The ash content was found to be 12.85% and 5.14%.

Table 4.6: Proximate analysis

Proximate analysis	Moisture content (%)	Ash content (%)
SOC	6.93	12.85
GOC	8.36	5.14

Ash content value represents the residue after combustion fuel. Ash contents also give the total mineral composition of a solid fuel. Minerals may have a catalytic effect on the reactivity of solid fuels such as coal.

4.2: Chemical characterization:

FT-IR spectroscopy

The FT-IR spectra of the obtained hydrochar were carried out to identity for all groups present in the hydrochar. The functional groups present on the surface of hydrochar show the biodegradability and have an important role in a sorption process. The FTIR spectroscopy is conducted to identify the functional groups attached to the surface of biomass and biofuel. It also determined the changes occurred during processing of biomass **(Ofori-Boateng *et al*., 2014)**.

SOC-Crude

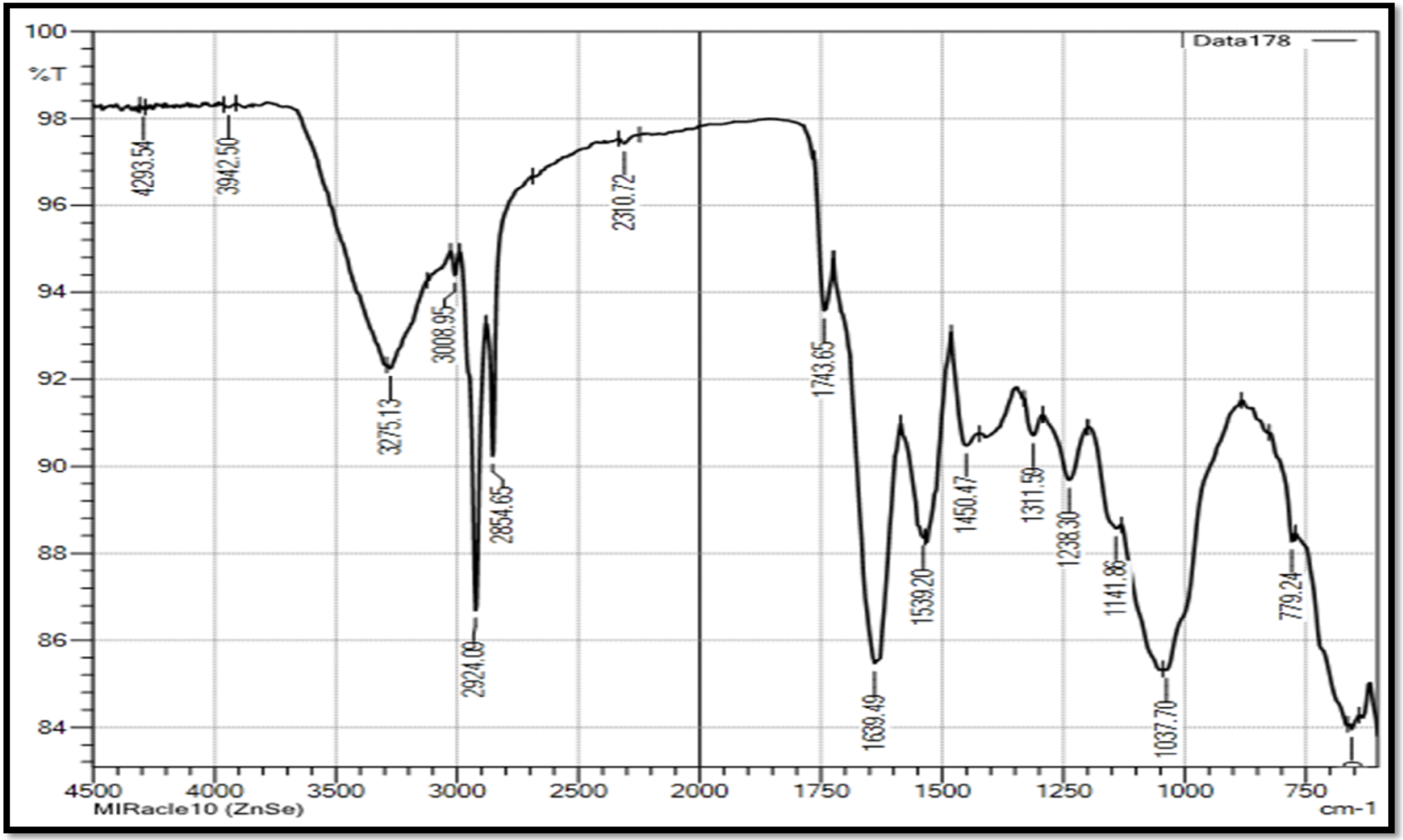
The bond at 2924 cm^{-1} belonged to the C-H stretching in methyl and methylene groups**(Ozhan *et al.,2010*)**.The C=O stretching in lactones and C=C stretching in olefins could be found at 1700 cm^{-1} and 1610 **(Shafryan *et al.,* 2010)**. A peak at about 1510 cm^{-1} was observed due to the C-O stretching in carbonyls, carboxylic acid and lactones.

SOC-Hydrochar

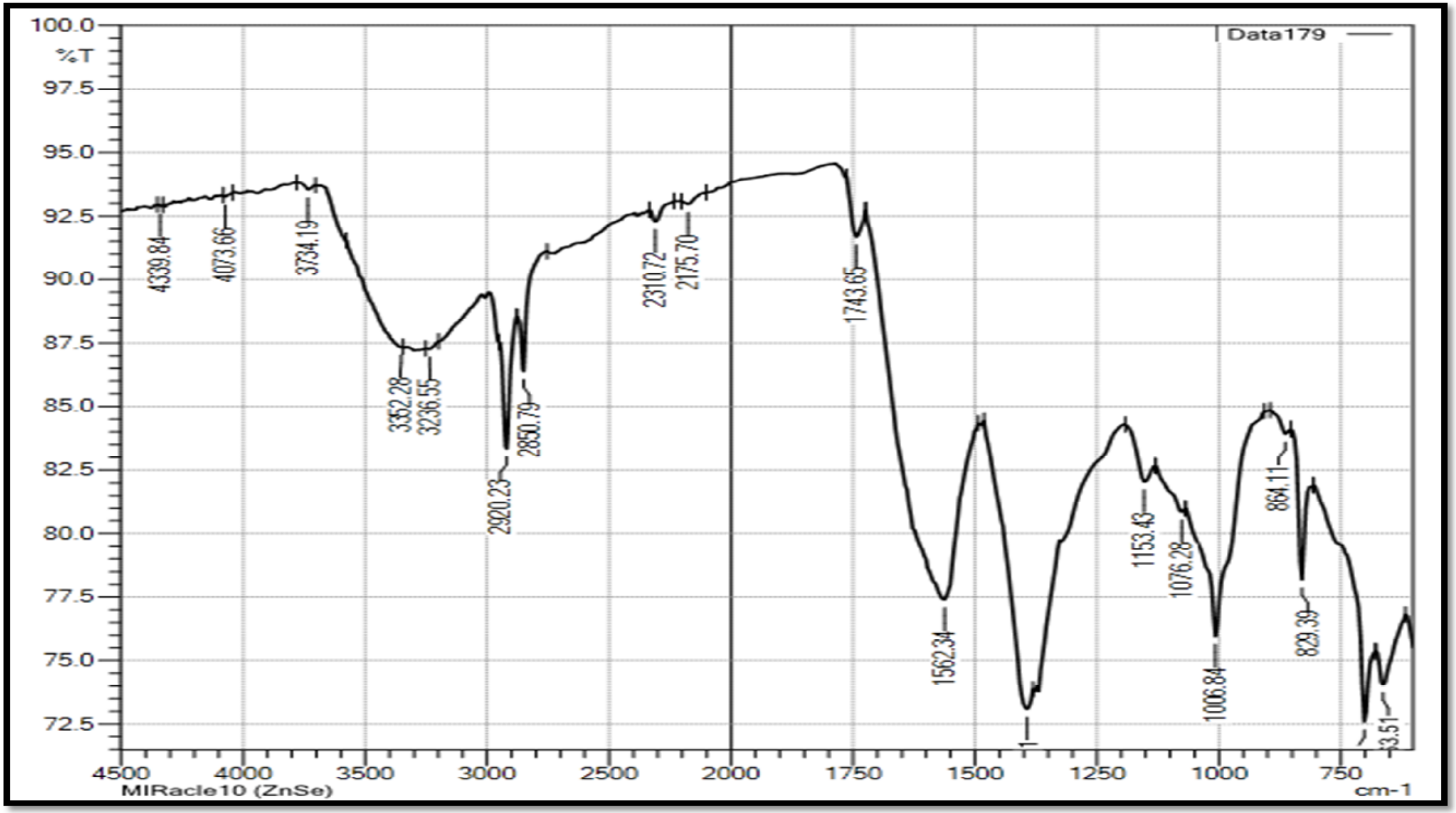
A broad adsorption band between3237-3362 cm^{-1} corresponded to O-H stretching indicating the presence of carbonization points such as phenols, alcohols. The peak at 1007 reperesence of inorganic matter -SO_4 , indicating the band at about 2920 cm^{-1} belonged to the -CH symmetric stretching .The O=C=O stretching in carbon dioxide could be found at 2310 cm^{-1}.The absorbance peak at about 1743 cm^{-1} C=O stretching. The peaks located in the range 2175 cm^{-1} belonged to the S-C=N stretching.

Table 4.7: FT-IR ranges for SOC

SOC-Crude			SOC-Hydrochar		
Frequency cm^{-1}	**Assignment**	**Functional Groups**	**Frequency cm^{-1}**	**Assignment**	**Functional Groups**
3008	=C-H Symmetric stretching	Alkane	3237-3362	O-H stretching	Phoenols, alcohols.
2924	C-H stretching	Aliphatic compound	2920	C-H stretching	Aliphatic compound
2854	-C-H stretching	Aliphatic compound	2310	O=C=O stretching	Carbon dioxide
2310	O=C=O stretching	Carbondioxide	2175	S-C=N stretching	Thiocyanate
1743	-C=O stretching	Esters ,aldehyde	1743	-C=O stretching	Esters, aldehyde
			1007	-SO_4	C-F
			1400	Aromatic ring stretching	CH_3 bend



(a) FT-IR SOC-Crude



b) SOC-HC

Fig 4.4: FTIR Peaks for SOC Crude and SOC- HC

FT-IR Spectroscopy of GOC:

GOC-Crude

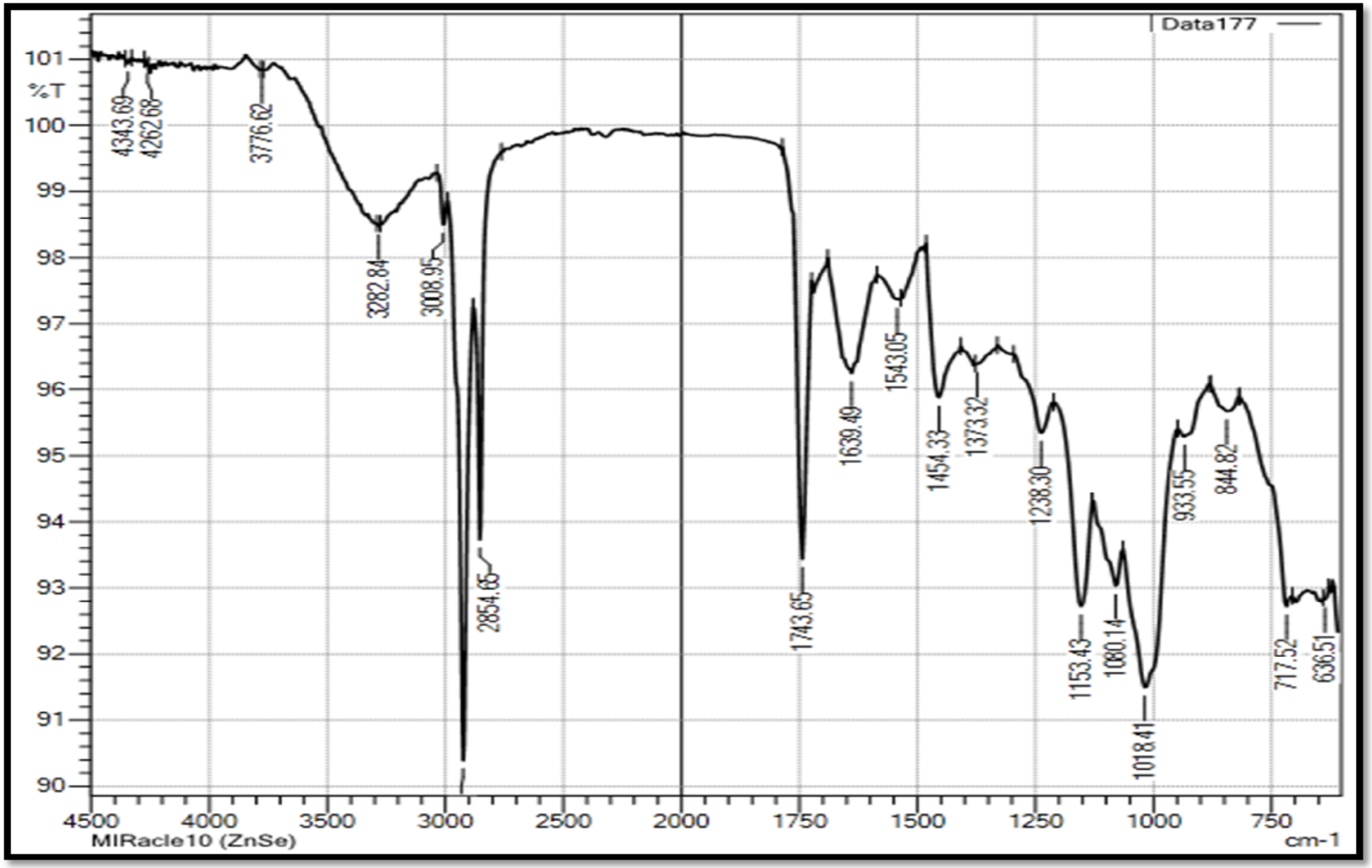
The peaks located in the range of 3282 cm^{-1} was attributed to the alkyne functional groups. The bands located in the range of phenol **(Martins *et al.,* 2007).** The peak at about 2854cm^{-1} belonged to the C-H stretching in methyl and methylene groups, aldehyde **(Ozhan *et al.,* 2010**). The C=O stretching in lactones and C=C stretching in olefins could be found at 1743cm^{-1} and 1639**(Shafryan *et al.,* 2010).** The peak at about 1743 cm^{-1} due to the C=O stretching in carbonyls, carboxylic acid and lactones, cyclopentane.

GOC-Hydrochar

The peaks located in the range of 3736cm^{-1} attributed to the alcohol functional groups. The band at about 2920 cm^{-1} belonged to the -CH symmetric stretching .The N=O stretching in nitro compound could be found at 1558 cm^{-1}.The peak at about 1323 cm^{-1} due to the O-H stretching. The bands located in the range 2175 cm^{-1} belonged to the S-C=N stretching.1450 cm^{-1} aromatic ring stretching vibration,1007,698,667 cm^{-1} represented SO_4 indicating the presence of inorganic matter.

Table 4.8: FT-IR ranges for GOC

GOC-Crude			GOC-Hydrochar		
Frequency cm^{-1}	**Assignment**	**Frequency cm^{-1}**	**Assignment**	**Frequency cm^{-1}**	**Assignment**
1743	C=O stretching	Cyclopentane	1323	-O-H bending	Alcohol
2854	C-H stretching	Aldehyde	1558	N-O stretching	Nitrocompound
3008	-CH stretching	Alkane	2175	S-C=N stretching	Thiocyanate
3282	-CH stretching	Alkyne	2920	-CH stretching	Aliphatic compound
3776	-OH stretching	Alcohol	3736	-OH stretching	alcohol
1743	C=O stretching	Cyclopentane	1323	-O-H bending	Alcohol



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1743.65
1639.49
1543.05
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1373.32
1238.30
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1080.14
1018.41
933.55
844.82
717.52
636.51
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3500
3000
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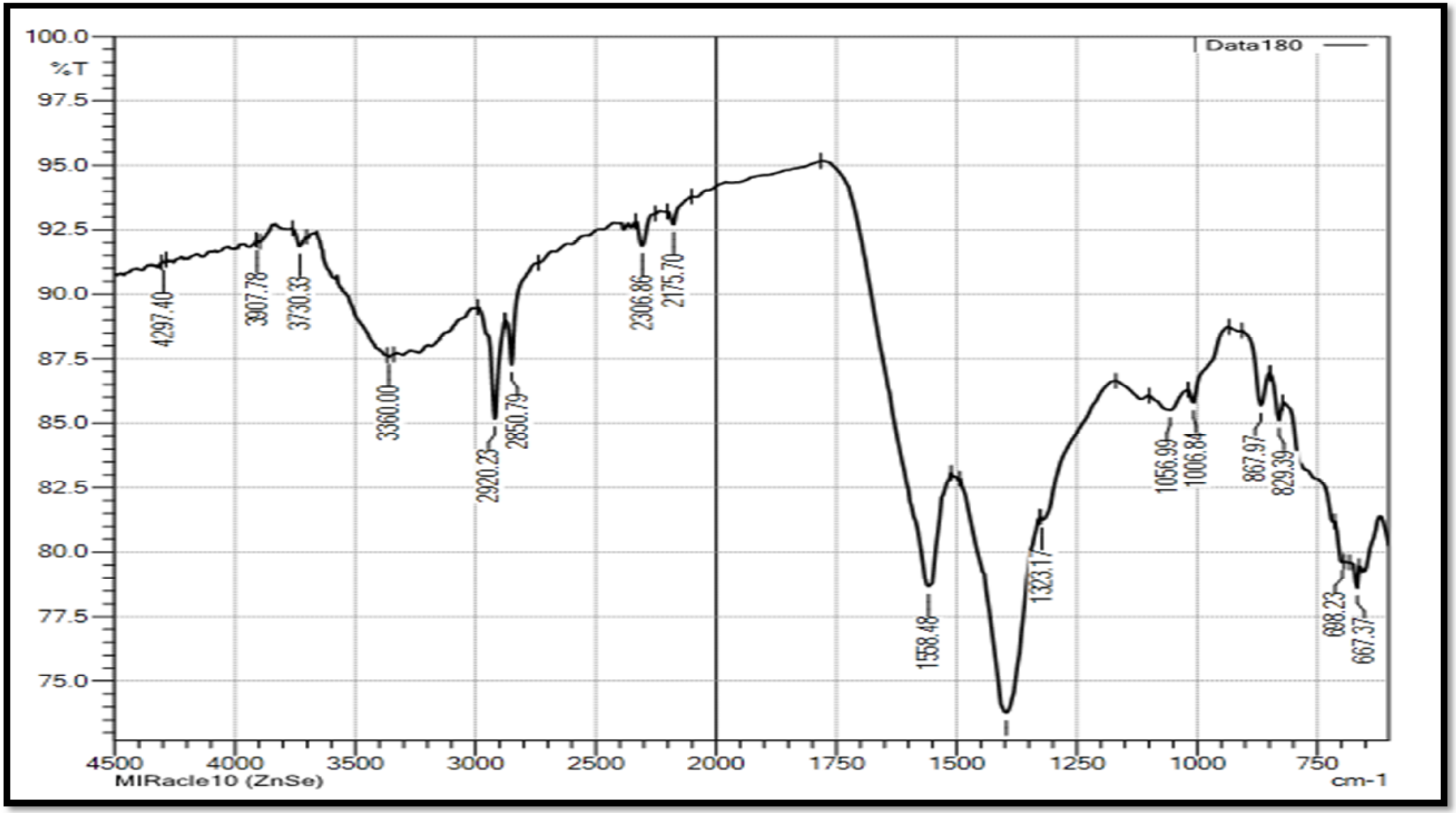
2000
1750
1500
1250
1000
750
MIRacle10 (ZnSe)
cm-1

(a) GOC-Crude



(b)GOC-HC

Fig 4.5: FT-IR peaks for GOC

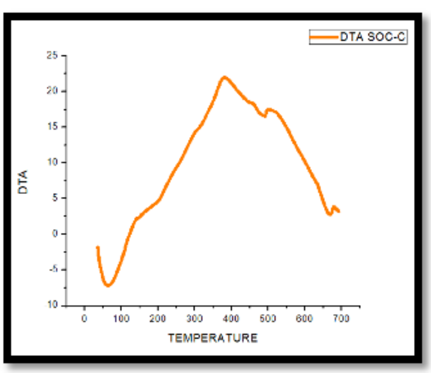
4.3: Thermal characterization:

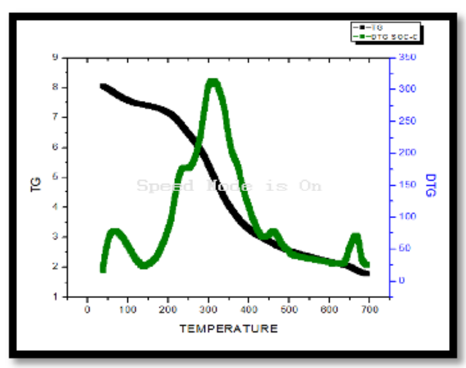
Thermo gravimetric analysis

The thermal behavior of biomass materials SOC and GOC was measured by a thermo gravimetric analyzer (TGA). It measured the percentage weight loss of the biomass as a function of temperature and the resulting thermo gram has a peculiar shape for biomass materials. In addition to studying the thermal behavior of SOC and GOC, this analysis was undertaken in order to establish the thermal parameters that would impact on the gasification of the material. It is worth noting that most TGA experiments are conducted under a chemically inactive environment (of which nitrogen or argon is often used) to show the effect of heat degradation that includes carbonization; oxygen is highly reactive and usually not recommended during analyses involving TGA because it reacts with sample components, leading to loss of original sample in the process. A 7.81 mg of the sample was combusted in a SDT Q600 TGA instrument under a nitrogen atmosphere at a flow rate of 35 ml/min between 35 and 1000^0 C. Nitrogen was used to create a chemically inactive environment so as to prevent the TGA instrument from overheating. A heating rate of 10 ^{0}C/min was used during TGA because this is characteristic of gasification systems using the downdraft gasifier.

SOC-Crude

DTA curve showed in the figure (a) decomposition peaks at 98^0C and 668^0C. DTG curve showed (b) exothermic peak at 150^0C, 300^0C and 430^0C.TG curve of SOC the weight loss of SOC started at 208^0C and completely decreased at 580^0C.



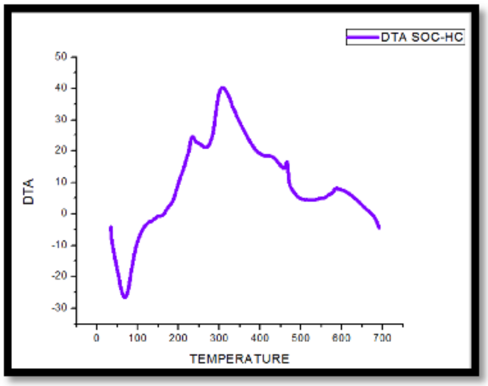


(a) **(b)**

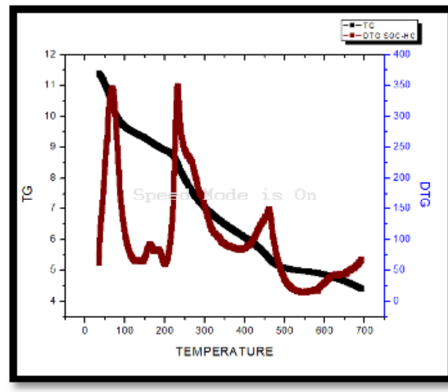
Fig 4.6: (a) DTA-SOC-C (b) TG+DTG-SOC

SOC -HC

DTA curve showed in the figure (a) decomposition peaks at 90^{0}C and 558^{0}C. DTG curve showed (b) exothermic peak at 120^{0}C, 250^{0}C and 530^{0}C.TG curve of SOC the weight loss of SOC started at 245^{0}C and completely decreased at 480^{0}C.



(c)

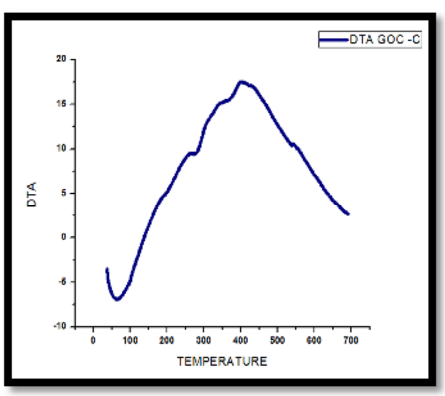


(d)

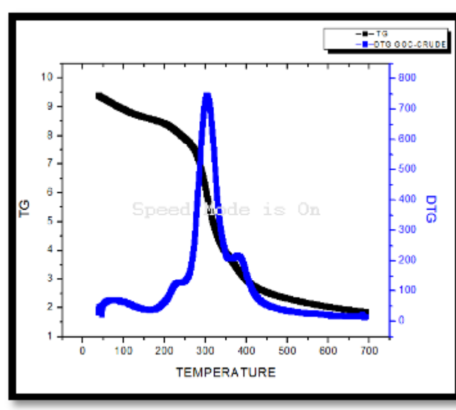
Fig 4.7: (c) DTA-SOC- HC (d) TG+DTG-SOC-HC

GOC-Crude

DTA curve showed in the figure (a) decomposition peaks at 98^{0}C and 440^{0}C. DTG curve showed (b) exothermic peak at 140^{0}C, 300^{0}C and 410^{0}C.TG curve of SOC the weight loss of SOC started at 190^{0}C and completely decreased at 480^{0}C.



(a)

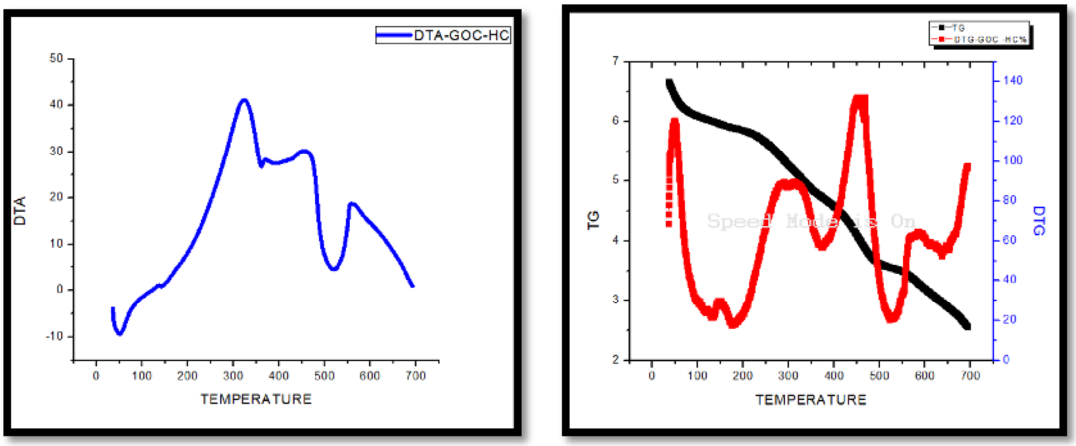


(b)

Fig 4.8: (a) DTA -GOC -C (b) TG+DTG-GOC-C

GOC-HC

DTA curve showed in the figure (d) decomposition peaks at 68^0C and 568^0C. DTG curve showed (d) exothermic peak at 300^0C,430^0C and 600^0C.TG curve of SOC the weight loss of SOC started at 220^0C and completely decreased at 580^0C.



(c) (d)

Fig 4.9: (c) DTA-GOC-HC (d) TG+DTG-GOC-HC

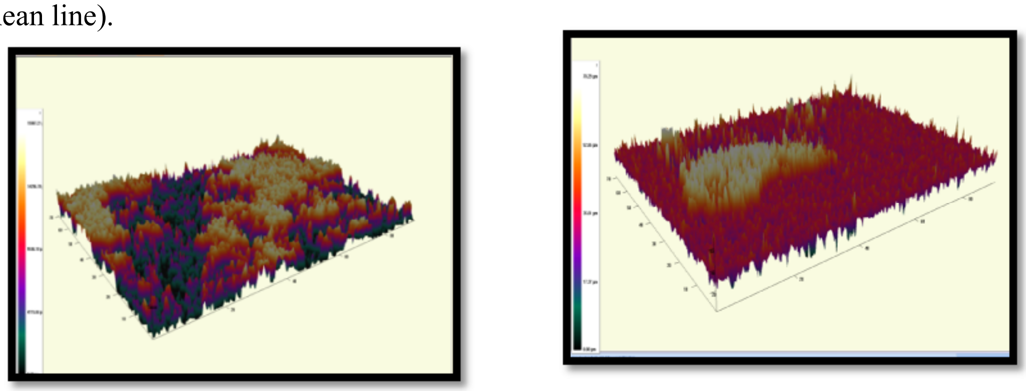
DISCUSSION

(a) Removal of water content and light volatile components which occur at a temperature less than 120^0 C (b) degradation of hemicellulose takes place at 220-315 ^{0}C (c) decomposition of cellulose and lignin at 315-400^0C (d) degradation of lignin at greater than 450 ^{0}C (**Sanchez-Silva *et al.*, 2012; Yang *et al.*, 2007**). According to Rodriguez-Reinoso and Molina-Sabio (1992) three stages can be identified during the thermal decomposition of lignocelluloses materials. (a) Evaporation of absorbed water in the range of 27-300 ^{0}C, (b) primary pyrolysis in the range of 300-500^0C where most of the gases are released and early structure of hydrochar develops and (c) further consolidation of cross-linked product structure between 500-850 ^{0}C with slight loss of weight. TGA-DTG for oil cake crude and hydrochar produced at 200^0C, 220 ^{0}C and 240 ^{0}C for 60 minutes reaction time was carried out in TGA-Q500 to measure and compare the thermal behaviour and weight loss kinetics of hydrochar with flow of pure nitrogen (99.999%). 10 mg of hydrochar sample was placed in a pan. Weight loss kinetics was almost similar for both oil palm shell and hydrochar. The minor weight loss was observed between 50-100 ^{0}C, which corresponds to the removal of water absorbed and when the temperature was in the range of 200-750^0C, the fast rate of decomposition was observed which is attributed to decomposition and pyrolysis of hemicellulose and cellulose. The 75 lower lignin content is also inferred from the less marked decomposition at higher temperatures **(Lapuerta, *et al*., 2004; Mohammed, *et a*l., 2012).** The weight loss taking place at 190-305 ^{0}C is because of pyrolysis of hemicellulose whereas the pyrolysis of lignin and cellulose occurs at 305-404 ^{0}C **(Li *et a*l., 2008)**. The profile between 750-850^{0}C remained almost flat, indicating the removal of all volatiles, hence remained as a residue. The temperatures at which maximum rate of weight loss takes place were defined by the position of peaks in the DTG curve. The first DTG peak for oil palm shell was observed at ~290 ^{0}C, which was probably due to the decomposition of hemicellulose (El-Sayed and Mostafa, 2014). The second peak for the oil palm shell was observed at ~350^{0}C, which attributed to the decomposition of cellulose (Asadieraghi and Wan Daud, 2014). The combustion of oil cakes involves mainly combustion of volatile matter, which ignited at lower temperature due to its high reactivity. The rapid weight loss of oil palm shell at lower temperature range suggested that an incomplete combustion took place with low efficiency, causing high pollutant emissions **(Liu *et al.*, 2014)**.

4.4: Micro Structural Characterization:

3D Optical profilometer

3D Optical Profilometer image analysis was performed to obtain the average roughness, Ra,(the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq, (the average of the measured height deviations taken within the evaluation length and measured from the mean line).



(a) SOC-Crude (b) SOC-HC

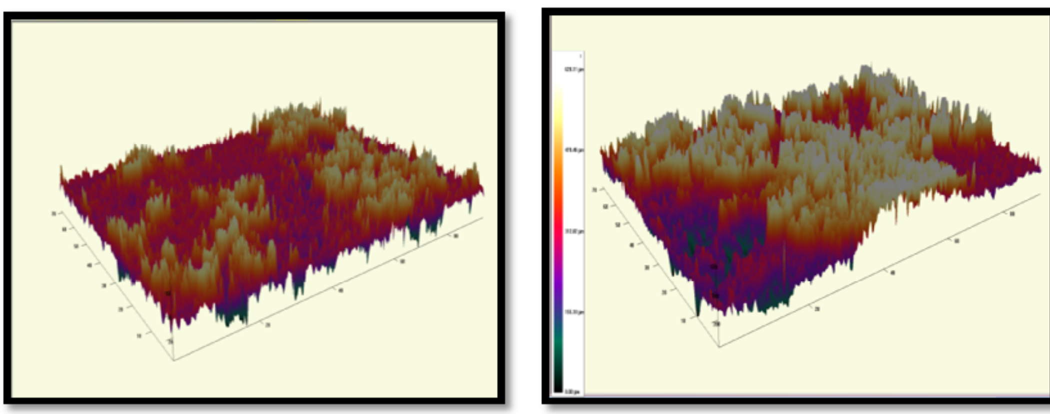
Fig 4.10: Optical profilometer for SOC-C, SOC-HC.

Table 4.9: Optical profilometer R_a and R_q values for SOC

Samples	**R_a (µm)**	**R_q (µm)**
SOC -Crude	2926.9	2506.57
SOC-HC	3.35	9.812

In fig (a) the surface topography of seasame oilcake crude surface is shown. The value for the crushed seasame oilcake crude surface reference sample was obtained R_a -2926.9 µm and R_q-2506.57 µm.

In fig (b) the seasame oilcake hydrochar surface is shown. The value for the SOC hydrochar reference sample was obtained R_a -3.35 µm and R_q-9.812 µm.



(c) GOC-Crude (d) GOC-HC

Fig 4.11: Optical profilometer for GOC-C, GOC-HC.

Table 4.10: Optical profilometer R_a and R_q values for GOC

Samples	R_a (µm)	R_q (µm)
GOC -Crude	88.27	178.11
GOC-HC	8.874	11.55

In fig (c) the surface topography of groundnut oilcake crude surface is shown. The value for the crushed groundnut oilcake crude surface reference sample was obtained R_a -88.27 µm and R_q-178.11 µm.

In fig (d) the groundnut oilcake hydrochar surface is shown. The value for the GOC hydrochar reference sample was obtained R_a -8.874 µm and R_q-11.55 µm.

These values inference that the produced hydrochar relatively smooth in nature.

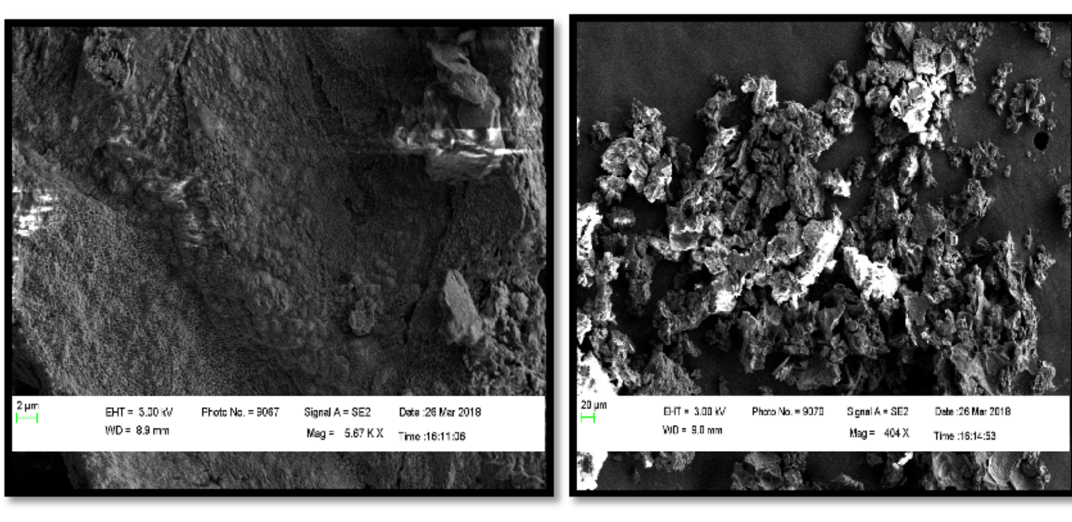
SEM

Since the physical properties affect the combustion characteristics of solid fuels **(Blake *et al*., 1967),** the physical properties of hydrochar samples such as porosity,total pore volume and surface area should be determined. For instance, the porosity can help combustion event because more porosity causes more active combustion **(Ozcimen, 2010).** Scanning electron microscopy is a potential technique for studying morphology of solid fuel particles. SEM analysis has been especially used to evaluate the structural variations in hydrochar particles after different thermal treatment and SEM images are very useful to obtain accurate details about pore structure of hydrochars (**Ozcimen & Mericboyu., 2010)**

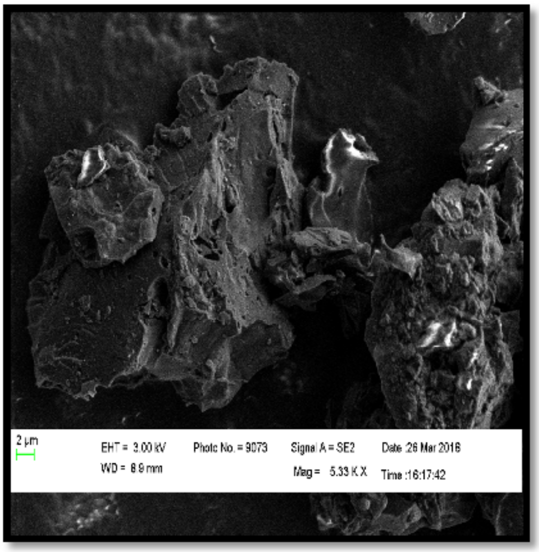
This led to the generation of large specific area activated carbns.The SEM images presented well developed pores acused by removal of moisture and the vaolatile matter content from the biomass

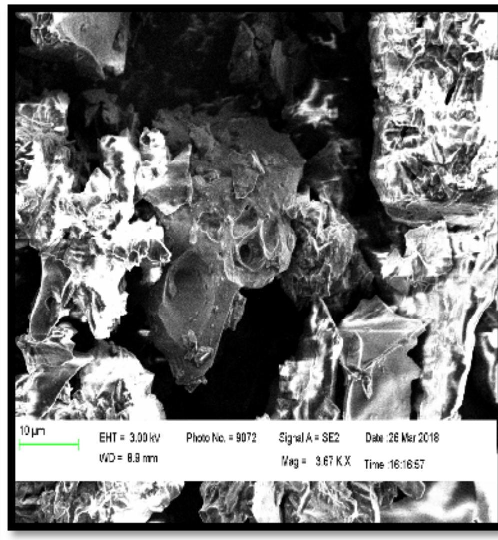
(a)SOC -HC contained carbon nanoparticles in the size range of 20µm.

(b)GOC-HC contained carbon nanoparticles in the size range of 10µm.



(a)SOC-HC





(b)GOC-HC

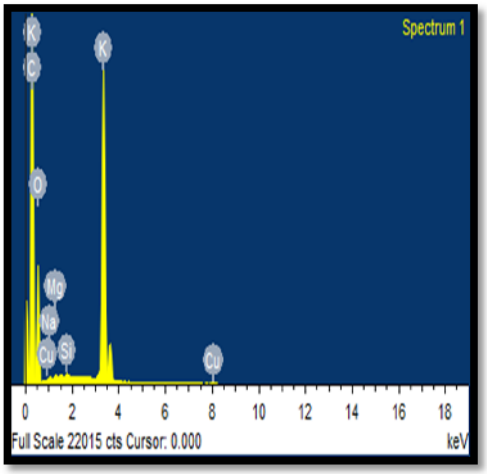
Fig4.12: SEM images for SOC -HC and GOC-HC

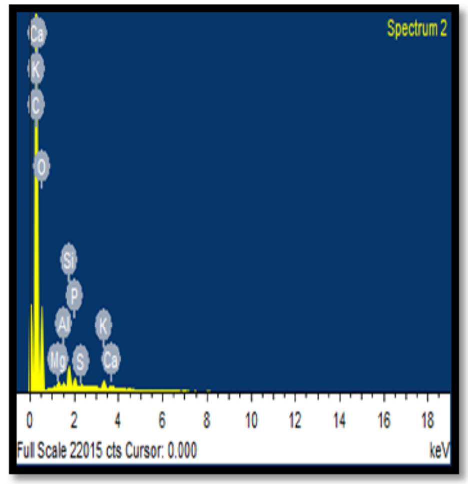
EDAX

EDAX analysis indicated the presence of entrapped soil into the hydrochar. These spectra were employed to determine the elements on the surface of carbon present in the SOC and GOC. This can be seen by the increase in Al, O, K, Si presumably from soil minerals .Hydrochar influences the EDAX chemical composition results , as hydrochar is not homogeneous substance and then samples increasing the sample heterogeneity

SOC-HC: It contains C, Na, Mg. The highest value is carbon then the other elements.

GOC-HC: It contains C, Na, Mg, Al, Si, P, S. The highest value is carbon then the other elements





(a)SOC-HC **(b)GOC-HC**

Fig 4.13: EDAX images for SOC-HC and GOC -HC

Table 4.11: EDAX Values for SOC -HC and GOC-HC

SOC-HC			**GOC-HC**		
Element	Wt%	At%	Element	Wt%	At%
C K	22.41	30.20	C K	26.11	32.34
Na K	0.17	0.12	Na K	0.04	0.02
Mg K	0.11	0.07	Mg K	0.28	0.17
			Al K	0.13	0.07
			Si K	0.79	0.42
			P K	0.37	0.18

5. SUMMARY AND CONCLUSION

The activated carbon production from hydrochar of hydrothermally treated seasame oilcake and groundnut oilcake was investigated. It is also a need to understand the properties of hydrochar that are critical in mitigating its harmful impacts on the environment. It is clear that hydrochar has potential application under growing environmental challenges. It is a need for more balanced evaluation of the adverse environmental risks associated with hydrochar, especially the soil pollutants and reduction in agrochemical effectiveness. In this study, major macroporous SOC, GOC based porous carbon was successfully prepared by combining HTC and KOH activation.

The bulk surface acidity and basicity data indicated a more basic change on the surface of all the ashes.

In optical profilometer the SOC, GOC crude sample R_a and R_q values are higher than the SOC, GOC hydrochar values.

Edax analysis of our samples confirmed that the ashes are a source of Al, Si, Ca, Mg and K in groundnut oilcake. The potassium and calcium compound containing ashes can be added to the soil to increase the micronutrient.

Proximate analysis of SOC and GOC confirm that both SOC and GOC are rich in hydrocarbon content and can be suitable for feedstock for hydrochar production.

To harvest maximum potential in the future sustainability in hydrochar technology needs to be considered including sourcing of the feed stock biomass, the production process and its application ,to ensure that there is a net positive impact when the social, economic and environmental perspectives are considered.

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