

Production of Bio-oil by Pyrolysis of Municipal Sewage Sludge (MSS)

A thesis submitted to Gujarat Technological University
For award of

Doctor of Philosophy
In
Chemical Engineering

By
Dharmesh V. Kapatel
(Enroll No: 139997105004)

Under the Supervision of
Dr. Yogesh C. Rotliwala



Gujarat Technological University

Ahmedabad

June 2022

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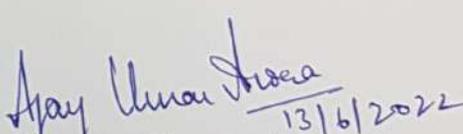
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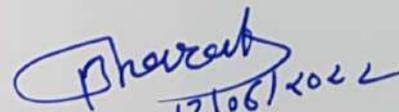
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ABSTRACT

The management of municipal sewage sludge (MSS) is a difficult and expensive issue. Due to major environmental concerns such as huge space requirement and leachate contamination in soil, landfilling of MSS is not a preferred solution, while land application as a fertilizer leads to toxic metals accumulation in soil. Incineration had been investigated as an efficient route for the resourceful disposal of waste. However, the huge cost of pretreatment and pollution control is not a preferred option. Hence, increasing generation of MSS needs a technique providing a techno-economic feasible solution for its proper disposal. Pyrolysis is one of the thermal decomposition methods used to recover energy from sewage sludge and biomass. It has attracted lots of attention from researchers. It produces high valued products, i.e. dark brown liquid (also known as bio-oil), char, and gaseous fuel. The yield of MSS-derived bio-oil observed 50-60 wt%, is a complex mixture of water, oxygenates, hydrocarbons, nitrogen, and sulphur containing compounds. Thus, bio-oil need to be upgraded by lowering oxygenates and also needs to reduce nitrogen and sulphur containing compounds. The search for new upgraded alternative fuels and simultaneously reduces the negative environmental impact of MSS has led to the idea of studying co-pyrolysis of MSS with one of the solid residues (biomass) from a sugar mill, namely sugarcane bagasse (SCB).

In order to evaluate the influence of SCB in pyrolysis with MSS (i.e., co-pyrolysis), kinetic was established using thermogravimetric analysis (TGA) and differential thermogravimetry (DTG).

In order to evaluate the influence of SCB in co-pyrolysis with sewage sludge, thermogravimetric analysis (TGA) in the presence of argon was studied. Pyrolysis experiments were carried out for MSS, SCB, and MSS/SCB mixtures (1:1 mass ratio) in the temperature range of 30 °C to 800 °C at a heating rate of 10°C per minute. Kinetic analysis was determined by using the Arrhenius equation and showed a change in activation energy, i.e., 27-52 kJ/mol, 29-46 kJ/mol, and 20-39 kJ/mol in the three stages of temperature ranges for MSS, SCB and those for MSS/SCB mixtures, respectively. The behavior of material degradation is attributed to this variation of activation energy. In contrast to pyrolysis of only-MSS, co-pyrolysis mixtures (MSS/SCB) offer improvement in the highest rate of degradation by 100%, the shift of peak temperature to lower value by 2-13%, reduced quantity of residue

left behind by 41%, and alteration in activation energy by -60 to +30% suggest a synergism upon addition of SCB in MSS.

Then after, the yield of products and characterization bio-oil was investigated in this study.

Co-pyrolysis of MSS with SCB at various proportions was performed at 500 °C in a batch reactor in the presence of nitrogen under atmospheric pressure to produce bio-oil. In comparison with only MSS pyrolysis, the yield of the bio-oil and gas improved by 100% and 14%, respectively. Furthermore, the yield of char (residue) decreased by 42%. GC/MS analysis of bio-oil showed that the co-pyrolysis afforded a reduction of sulphur and nitrogen compounds significantly. Physical characteristics of bio-oil demonstrated that MSS-derived bio-oil exhibited alkaline nature, whereas, SCB shows acidic nature. The density, viscosity, and water content of bio-oil marginally reduced. Such a property of bio-oil favors its use as a transport fuel. The pH of co-pyrolysis derived bio-oil decreases. Thus, the co-pyrolysis technique has a potential to modify the properties of bio-oil significantly.

Besides this, the application of residue resulting from co-pyrolysis of MSS and SCB, i.e. bio-char was activated through the chemical activation method using phosphoric acid to explore its application for wastewater treatment.

In this study, the solid residue (bio-char) produced from co-pyrolysis of MSS- SCB was activated through a chemical activation method using phosphoric acid. The resulting activated bio-char was utilized for the removal of chemical oxygen demand (COD) and colour of pulp and paper industry wastewater obtained from the conventional secondary treatment process to explore the recycling potential in the pulp and paper manufacturing process itself. In contrast to bio-char, activated bio-char showed higher surface area (50 times), total pore volume (10 times), and lower average diameter (5 times). Honeycomb shape in SEM (Scanning electron microscope) image and the existence of functional groups in FTIR (Fourier Transform Infrared Spectroscopy) spectra attributed to such a significant improvement. Results of adsorption experiments revealed that maximum COD and colour were reduced by 84.61% and 98.03%, respectively 3 pH with activated bio-char doses of 0.14 g/L in 20 h. However, COD and colour were reduced by 68.8% and 86.31%, respectively at an optimized pH 3 with an activated bio-char dose of 0.14 g/L in a duration of 5 hours. Moreover, Langmuir and Freundlich isotherm model was observed best suited to obtained equilibrium.

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List of Abbreviation

Abbreviation	Meaning
APHA	American Public Health Association
ASTM	American society for testing and materials
BET	Brunauer-Emmett-Teller
BSS	British standard society
CEC	Cation Exchange Capacity
CHP	Combined heat and power
COD	Chemical oxygen demand
cP	Centi poise
DAEM	Distributed activation energy model
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
EU	European Union
FTIR	Fourier Transformed Infrared Spectroscopy
FWO	Flynn-Wall-Ozawa
GC-MS	Gas chromatography – Mass spectrometry
GCV	Gross calorific value
GHG	Greenhouse gas
HDO	Hydrodeoxygenation
HHV	High heating value
H-NMR	Proton Nuclear Magnetic Resonance
IBI	International bio-char initiative
ICP-MS	Inductively coupled plasma mass spectrometry
ID	Internal diameter
IUPAC	International Union of Pure and Applied Chemistry
KAS	Kissinger-Akahira-Sunose
LC	Liquid Chromatography
M-DAEM	Multiple normal distributed activation energy models

MLD	Million liter per day
MSS	Municipal sewage sludge
PAHs	Polycyclic aromatic hydrocarbons
PT	Peak temperture
Pt/Co	Platinum-Cobalt
PMC	Press mud cake
SCB	Sugarcane bagasse
SEM	Scanning Electron Microscopy
STP	Sewage treatment plant
TG	Thermogravimetry
TGA	Thermogravimetry analysis
TR	Temperature range
TS	Total solids
TSS	Total Suspended Solids
TWAS	Thickened waste activated sludge.
US	United states
WWTPs	Waste water treatment plants

List of Symbols

Symbols	Meaning
A	Pre-exponential (frequency) factor
E	Activation energy
R	Universal gas constant
T	The absolute temperature
D	Pyrolysis characteristic index
k	Rate constant
x	Degree of conversion
β	Heating rate ($^{\circ}\text{C}/\text{min}$)
AY	Actual yield
CY	Calculated yield
Y	Difference in actual and calculated yield
M_b	Mass of the activated bio-char sample (dry)
M_0	Mass of precursor (dry)
q_{eq}	Adsorption amount at equilibrium.
C_{eq}	Unadsorbed adsorbate concentration in solution at equilibrium
C_0	Initial liquid-phase concentrations of adsorbate (g/L)
C_e	Liquid-phase concentrations of adsorbate at equilibrium (g/L)
m	Mass of dry adsorbent (bio-char) (g)
V	The volume of solution (mL)
K_F	The adsorption capacity of solid surface
n	Favorability for adsorption,
q_m	Maximum adsorption capacity (mg/g)
K_L	Rate of adsorption
R_L	Separation factor

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CHAPTER 1

Introduction and Background

The management of municipal sewage sludge (MSS) is a difficult and expensive issue. Due to major environmental concerns such as huge space requirement and leachate contamination in soil, landfilling of MSS is not a preferred solution, while land application as a fertilizer leads to toxic metals accumulation in soil. Incineration had been investigated as an efficient route for the resourceful disposal of waste. However, the huge cost of pretreatment and pollution control is not a preferred option. Hence, increasing generation of MSS needs a technique providing a techno-economic feasible solution for its proper disposal. Pyrolysis is one of the thermal decomposition methods used to recover energy from sewage sludge and biomass. It has attracted lots of attention from researchers. It produces high valued products, i.e. dark brown liquid (also known as bio-oil), char, and gaseous fuel. The yield of MSS-derived bio-oil observed 50-60 wt%, is a complex mixture of water, oxygenates, hydrocarbons, nitrogen, and sulphur-containing compounds. Thus, bio-oil need to be upgraded by lowering oxygenates and also needs to reduce nitrogen and sulphur containing compounds. The search for new upgraded alternative fuels and simultaneously reduces the negative environmental impact of MSS has led to the idea of studying co-pyrolysis of MSS with one of the solid residues (biomass) from a sugar mill, namely sugarcane bagasse (SCB).

1.1 State of the art of the research topic

MSS is the major by-product of municipal sewage treatment plants. With the high growth rate of population and rapid urbanization, a massive quantity of sewage sludge is generated. Due to

the high risk of health and environmental issues associated with various disposal methods of MSS, such as landfills (Cao et al., 2010), fertilizer (Vasseur et al., 1999), and incineration (Mondala et al., 2009), they are not an attractive solution. Hence, MSS calls for the development of environmentally benign and energy-efficient techniques for its disposal in an eco-friendly manner.

Industrial biomass residue, e.g., sugarcane bagasse (SCB), a by-product generated from sugar manufacturing, is anticipated to be produced in huge quantities in India. In India, nearly 75-90 million tons of SCB produces annually from 377 million tons of sugarcane (Sugarcane statistics, 2020; Quereshi et al., 2020). SCB is mainly utilized as boiler fuel at sugar mills itself in cogeneration power plants during the 180 days of sugarcane crushing season in India with surplus quantities, typically 3-4% of the cane crushed, required to be stored in the offseason (Yadav and Singh, 2011; Umamaheswaran and Batra, 2008). Thus, there is a need to explore resource recovery from a surplus quantity of SCB.

The search for alternative fuels and simultaneously reduces the negative environmental impact of MSS has led to the idea for studying resource recovery potential of these two materials available in massive quantities in India, i.e., MSS and SCB.

Pyrolysis is one of the thermal decomposition methods used to recover energy from sewage sludge and biomass. It has attracted lots of attention from researchers (Demirbas, 2005; Kim and Parker, 2008; Jahirul et al., 2012). It is a method that occurs in an oxygen-deficient environment for the decomposition of the organic mass of biomass (i.e., MSS and SCB), leading to a reduction in the volume of the biomass and stabilization of the organic mass. It produces high valued products, i.e. dark brown liquid (also known as bio-oil), char, and gaseous fuel (Hossain and Davies, 2013; Bilgen, 2016; Henkel et al., 2016). Different proportions of these products were investigated at various conditions, e.g., type of pyrolysis (slow or fast), the configuration of reactor (augur, batch, etc.), catalyst, medium (N₂, argon, etc.), feedstock, etc. (Li et al., 2004). Flash pyrolysis of sewage sludge studied at 500 °C to decompose the organic content (proteins, lipids, and carbohydrates) of the sewage sludge, yielded 43 % wt. bio-oil (Pokorna et al., 2009). The high energy density of bio-oil is exhibited as a potential fuel and its oxygenates content supports application as a fertilizer and resins (Inguanzo et al., 2002). Furthermore, pyrolysis of sludge demonstrated residue generation with a stabilized carbonaceous matrix (Caballero et al., 1997).

1.2 Definition of the problem

The bio-oil obtained from only-MSS pyrolysis is a complex mixture of oxygenates, water, and hydrocarbons, which imparts heterogeneity, leading to instability. Moreover, nitrogen and Sulphur-containing compounds in the bio-oil lead to the issue of NO_x and SO₂ emission in exhaust gases and limit its application as a fuel (Samanya et al., 2012). Thus, the up-gradation of bio-oil is needed by reducing oxygenates along with nitrogen and Sulphur-containing compounds (Alvarez et al., 2015). Various researchers have investigated different up-gradation techniques, mainly including hydro-deoxygenation, catalytic cracking, emulsification, steam reforming, esterification, and reactive rectification (Zhang et al., 2007A). Nevertheless, these are so complicated techniques due to certain reasons, including complex equipment for hydro-treatment, catalyst deactivation, reactor clogging, and the high cost of emulsification. The present work narrates the co-pyrolysis as an in-situ hydrogenation technique for the production of up-graded bio-oil.

As referred to these problems, we had attempted pyrolysis of MSS with SCB as a second material, known as “co-pyrolysis technique”. Co-pyrolysis of sewage sludge and lignocellulosic biomass (in 50% wt.) studied in a conical spouted bed reactor, showed a significant synergistic effect in terms of reduced oxygenates and nitrogen-containing products. Moreover, it was seen free of sulphur containing compounds (Alvarez et al., 2015). Significant reduction in pyrolytic temperature and apparent activation energy investigated for catalytic co-pyrolysis of paper sludge and municipal solid waste with metal oxides, such as MgO, Al₂O₃, and ZnO (Fang et al, 2016). Co-pyrolysis of sewage sludge too was reported with oil shale showed improvement in gas generation, in particular methane (Lin et al, 2016).

To address in-depth co-pyrolysis operation at a larger scale, the study of kinetic is required to determine. Thus, TGA for this co-pyrolysis mixture (MSS and SCB) was carried out for the evolution of kinetic parameters, mainly activation energy, regression coefficient, and pre-exponential factor. Various authors had investigated significant synergistic effects using sewage sludge with different biomass residues in co-pyrolysis, e.g. lignocellulosic biomass, rice straw through TGA (Zhang et al., 2009; Alvarez et al., 2015). Change in activation energies reported for the mixture of sewage sludge and bagasse at a heating rate of 20°C per minute (Lin et al., 2018A). Moreover, noteworthy synergetic interaction between two materials, i.e. rice bran (low heating value) and plastics (high heating value material) was investigated by TGA and studied

the change in activation energy, residue generation, and decomposition rate (Rotliwala and Parikh, 2011).

In line with this, a comprehensive study on co-pyrolysis of MSS and SCB in terms of the existence of synergism upon addition of SCB in MSS for the highest rate of degradation, peak temperature, residue generation, and change in activation energy is little reported. Moreover, characterization of bio-oil derived from MSS, SCB, and its mixture (50% by mass) in terms of area % of oxygenates, nitrogen, sulphur, hydrocarbon (HC), and steroids (cholestenes) along with the application of bio-char for wastewater treatment rarely reported.

To overcome the issues associated with the pyrolysis of only-MSS, the objective of the study was to evaluate the influence of the addition of SCB in co-pyrolysis with MSS. Thus, the co-pyrolysis behavior and synergistic effect of these two materials were studied with the help of the thermogravimetric method along with its kinetics. Yield and characterization of the upgraded bio-oil were evaluated. Further to this, the application of bio-char for wastewater treatment was referred.

1.3 Objectives and Scope of work

1. To study synergistic effect upon addition of SCB with MSS (50% by weight) with the help of thermogravimetric analysis (TGA) and its kinetics.
2. To evaluate the yield of different products (i.e., bio-oil, char, and gases) obtained from batch type pyrolysis reactor (slow heating rate) upon addition of SCB in various proportions with MSS (0 to 100% by mass).
3. Comparison study of Physico-chemical characterization of bio-oil, derived from pyrolysis of pure MSS, SCB, and their mixture (50% weight).
4. To investigate chemical activation of the bio-char generated from the co-pyrolysis of MSS-SCB (50% weight) and its characterization.
5. To study the application of activated bio-char for the removal of chemical oxygen demand (COD) and colour of pulp and paper industry wastewater obtained from the conventional secondary treatment process to explore the recycling potential in the pulp and paper manufacturing process itself.

6. Determination of gases composition from co-pyrolysis would be the future scope of work. Moreover, downstream application of bio-oil other than fuel needs special attention.

1.4 Original contribution by the thesis

The present research work addresses the potential application of co-pyrolysis as a waste management technique to exploit MSS and SCB as a source of energy materials such as bio-oil and substitute of activated charcoal, e.g. bio-char.

To overcome the issues associated with the pyrolysis of only-MSS, the influence of the addition of SCB with MSS was studied with the help of TGA and its kinetics. It showed improvement in the highest rate of degradation, the shift of peak temperature to lower value, reduced quantity of residue, and alteration in activation energy. Thus, the significant influence of SCB addition in co-pyrolysis with MSS was observed.

In contrast to merely MSS pyrolysis, upon the addition of SCB in MSS (50% weight), the yield of bio-oil and gas increased, whereas the yield of char (residue) decreased. Moreover, the Physico-chemical characterization of bio-oil showed that bio-oil derived from co-pyrolysis favors the use of bio-oil as a transport fuel. Apart from this, resource recovery from activated bio-char was established for wastewater treatment.

1.5 Presentation and layout of the thesis

The present research work explores the potential of co-pyrolysis as a waste management technique of solid waste such as MSS and SCB and to produce biofuels such as bio-oil and biochar. This thesis has been organized into six chapters with appropriate sections, subsections, references, appendices, and a list of research publications.

The first chapter covers the introduction and background of project work. It also describes the problem definition and objectives of the present research work.

The detailed literature review is covered in chapter 2. It included the fundamentals of the pyrolysis process, products of pyrolysis, effect of various process parameters on pyrolysis products. A detailed discussion on characteristics of bio-oil derived from MSS pyrolysis, co-pyrolysis of MSS with various biomass with operational conditions are presented. The characteristics and potential utilization of biochar are described.

The research work in this thesis is mainly divided into three sets of experiments and analyses, which are discussed in the subsequent chapters.

Chapter 3 describes the kinetic study for co-pyrolysis of MSS and SCB. In this work, the detailed kinetic analysis of the co-pyrolysis process is investigated, and kinetic parameters are evaluated based on the results of the thermogravimetric analysis.

Chapter 4 highlighted the experimental setup and methods for pyrolysis/co-pyrolysis of feedstock for producing bio-oil. This chapter provides a complete set of operating parameters and their effect on the yield of products and suggests the optimum condition for maximum yield of bio-oil. The physico-chemical characterization of bio-oil also evaluated.

Chapter 5 is about an application of bio-char, solid residue of co-pyrolysis. It includes activation of bio-char using phosphoric acid followed by treatment of pulp and paper industry wastewater (secondary discharge) with activated bio-char for removal of chemical oxygen demand (COD) and colour. The effect of various parameters for removal of COD and colour is described along with adsorption. This chapter highlighted the applied aspects of pyrolysis product.

Chapter 6 contains findings and major conclusions drawn from this investigation with the future scope of the study. Also detail of major publications of the concerned subject along with conferences presentation mentioned.

CHAPTER 2

Literature Review

2.1 Municipal Sewage Sludge: Generation, Treatment and Disposal

2.1.1 Generation of MSS

Sewage sludge defined as the residual, semi-solid substance that is generated as a byproduct from the wastewater treatment plants (WWTPs) as a result of the treatment of wastes released from a variety of sources including homes, industries, medical facilities, street runoff, and businesses (Harrison et al., 2006). More specifically, the sewage sludge is formed as a by-product of the different treatment stages of wastewater from domestic households, and sometimes it also includes industrial and commercial effluents (Williams, 2005). In general, sewage sludge is also known as biosolids. The major types of sewage sludge are primary sludge and secondary sludge. Primary sludge is collected from the primary settling tanks used in WWTPs and Secondary sludge, known as biological sludge, is produced from the biological treatment of the wastewater drained from the primary settling tanks (Smith et al., 2009).

MSS is produced in large quantities worldwide. Approximately 8910, 6510, 2960, 650, 580, 550, and 370 thousand metric tonnes of sludge (dry basis) is reported annually for EU-27, USA, China, Iran, Turkey, Canada, and Brazil, respectively (Mateo-Sagasta et al., 2015). Considering the development of population, urbanization, and industrialization in India, sewage generation is expected to increase at a faster rate, which will, in turn, lead to the generation of massive quantities of municipal sewage sludge (MSS) produced from the sewage treatment plant (STP). The Ministry of Environment, Forest, and Climate Change of India reported generation of sewage water close to 61948 million liters per day (MLD)

with an equivalent amount of sludge from the Indian urban area in 2018 (MoEFCC, 2019). The quantity of dry sludge produced from conventional sewage treatment plants was reported to be 55 to 170 kg per million-liter treatment of sewage water. Accordingly, MSS generation purely from the urban areas of India is estimated to be nearly 4 million tons (Karia and Christian, 2013). It is estimated that the projected wastewater from urban centers may cross 120,000 MLD by 2051 and that rural India will also generate not less than 50,000 MLD in view of water supply designs for community supplies in rural areas (Kamyotra and Bhardwaj, 2011). Disposal and management of sewage sludge are one of the key issues in the world (Syed-Hassan, 2017; Swierczek 2018).

2.1.2 Sewage Sludge composition and Characteristics

Sewage sludge is a complex heterogeneous mixture of microorganisms, undigested organics such as paper, plant residues, oils or fecal material, inorganic material, and moisture (Degremont, 1979). The undigested organic materials contain a highly complex mixture of molecules coming from Proteins and peptides, lipids, polysaccharides, plant macromolecules with phenolic structures (e.g. lignins or tannis} or aliphatic structures (e.g. cutins or suberins), along with organic micropollutants such as polycyclic aromatic hydrocarbons or dibenzofurans (European Commission, 2002). The inorganic materials present in the liquids come mainly from the soil but also synthetic polymers of anthropogenic origin (Laternus et al., 2007). Table 2.1 shows the constituents present in sewage sludge.

Table 2.1 Constituents present in Sewage Sludge (Bharathiraja et al., 2014)

Sewage Sludge Constituents	
Microorganisms	Pathogenic bacteria, virus and worms eggs
Biodegradable organic materials	Oxygen depletion in rivers, lakes, and fjords
Other organic materials	Detergents, pesticides, fat, oil and grease, colorings, solvents, phenols, cyanide
Nutrients	Nitrogen, phosphorus, ammonium
Metals	Hg, Pb, Cd, Cr, Cu, Ni
Other inorganic materials	Acids, for example, hydrogen sulfide, bases

The origin, the purification treatment applied to the wastewater (mainly active mud or bacteria beds), and the stabilization and conditioning treatments applied to the sewage sludge affect significantly: 1) the level of decomposition of the organic materials, 2) the presence of certain constituents, such as the inorganic materials coming from synthetic polymers of anthropogenic origin, and 3) also the relative proportion of the sewage sludge constituents, such as the extractives content or the moisture content of the sewage sludge.

Furthermore, the wastewater purification treatments and the stabilization and conditioning treatments are not standardized in the wastewater treatment plants. For this reason, even when using the same treatments the composition of sewage sludge samples obtained from different urban wastewater treatment plants may vary significantly (Fonts, 2009A).

Due to the differences in the origin and treatments, the proximate and ultimate analysis of the sewage sludge samples used in these studies varies significantly (Table 2.2). The wide difference among the proximate and ultimate analyses of the different sewage sludge samples used is due to the different types of sewage sludge, although, as commented, even when sewage sludge samples are generated in the same treatments, their compositions vary significantly.

Table 2.2 Composition of various sludges from WWTPs (Fonts, 2012)

Ultimate analysis (wt %)		Proximate Analysis (wt %)	
C	23.1-39.9	Moisture	1.5-7.1
H	3.8-5.9	Ash	22.6-52.0
N	2.54-7.9	Volatiles	38.3-66.8
S	0.8-1.0	Fixed Carbon	0.84-19.7
O*	18.80-23.5		

*Oxygen calculated by the difference

The ash of the sewage sludge contains mainly minerals, such as quartz, calcite, or microline. These minerals are formed by some elements, such as, Fe, Ca, K, and Mg that can catalyze some pyrolysis reactions. Furthermore, in the sewage sludge can be also found some heavy metals (Cr, Ni, Cu, Zn, Pb, Cd, Hg) (Fonts, 2009A).

2.1.3 Characteristics of Primary and secondary sludge

Table 2.3 depicts the characteristics of primary and secondary sewage sludge. Primary sewage sludge is resulting after mechanical separation processes like screening, grit removal, sedimentation, etc. in a wastewater treatment plant. It contains mainly 93 to 99.5% water with suspended and dissolved solids (organic materials). The secondary sludge is resulting in biological wastewater treatment and it contains microorganisms which are complex organic matters. The total solids concentration in secondary sludge depends on the type of treatment process and it is in the range of 0.8 to 1.2%. (Tezel et al., 2011). The organic contents of secondary sludge are 59-88% (w/v) which are decomposable and responsible for unpleasant odors. A very small part of sludge is solid material while mainly it contains water (more than 95%). The organic matter of secondary sludge composition is like – Carbon 50-55%, Oxygen 10-15%, nitrogen 6-10%, hydrogen 1-13%, phosphorus and sulfur 0.5-1.5%. (Orhon and Artan, 1994). Additionally, it also

contains minerals and elements like Fe, Ca, K, Mg, Cr, Ni, Cu, Zn, Pb, Cd, and Hg (Fonts et al., 2009A).

Table 2.3 Characteristics of primary and secondary sewage sludge (Tchobanoglous et al., 2003)

Parameters	Primary Sludge	Activated Sludge
Total solids (TS), %	5-9	0.8-1.2
Volatile solids, VS (%TS)	60-80	59-68
Nitrogen (%TS)	1.5-4	2.4-5.0
Phosphorus (%TS)	0.8-2.8	0.5-0.7
Potash (K ₂ O, %TS)	0-1	0.5-0.7
Cellulose (%TS)	8-15	7-9.7
Iron (g/kg)	2-4	-
Silica (%TS)	15-20	-
pH	5-8	6.5-8.0
Grease and Fats (%TS)	7-35	5-12
Protein (%TS)	20-30	32-41
Alkalinity (mg/L as CaCO ₃)	500-1500	580-1100
Organic solids (mg/L as acetate)	200-2000	1100-1700
Energy content (MJ/kg TS)	23-29	19-23

The potential of energy recovery from the sewage sludge depends on the calorific value or heating value of the sludge. The heating value of the sewage sludge depends on the type and origin of the sample and its varying with organic matter content, moisture content, and ash content of the sludge. The higher heating value of dry and digested sewage sludge may range between 8.5 to 14 MJ/kg and, it can reach up to 23 MJ/kg when the sample has not been digested (Fonts, 2012). The calorific value of sludge is significant when thermal processes such as pyrolysis, gasification, combustion are considered.

2.2 Sewage Sludge disposal methods and challenges

Treated sludge contains large volumes of water or solution that need to be reduced for easier handling, transporting, and disposal (Werther and Ogada, 1999). The vacuum filters and centrifuge are commonly used for the dewatering of sludge. For further applications like incineration or agricultural use, further drying of sludge is done by using filter press or any other method to remove more excess moisture. However, the drying process involves significant energy consumption, which increases the cost of disposal considerably (Dominguez, 2006A). The cake after the removal of water is referred to as sewage sludge, which is the final solid residue from the sewage treatment process. In India, approximately 3955 thousand metric tons of dry sewage sludge are produced (Singh et al., 2020).

After the sewage treatment process, the solid sludge is to be disposed of according to country regulations. The most common ways to treat sewage sludge in Japan (Kasakura et al., 1993), European Union (EU), and the United States (US) (Girovich, 1996) are

agriculture use, incineration and disposed of in landfills. The key disposal practice among the various countries is landfilling depending on appropriate site availability. Landfilling is the most commonly used practice for the disposal of sewage sludge in various countries. Due to the production of a large volume of sewage sludge, the focus has shifted towards land application and production of other useful products out of it. More than 50% of sludge is utilized for agriculture applications in France, Spain, and Denmark. In the year 2010, an European countries sludge management reported that 27% of sludge was used in incineration, 42% sludge in recycling, 14% sludge in landfills, and 16% in other methods (Samolada and Zabaniotou, 2014). In the year 2020, it was predicted that 32% of the sewage sludge would be used for incineration and 44% by recycling methods. Landfilling is still, one the most used method for sludge disposal. 80-90% of sludge disposed of in landfills in Greece and Luxemburg (Samolada and Zabaniotou, 2014) while >70% of sewage sludge was incinerated in Japan due to lack of land for disposal. The methods are described in the following sections.

2.2.1 Incineration

Incineration of waste is the combustion of waste at high temperatures with the production of ash as residue in a combustor or combustion device. The volatile organic materials in sewage sludge are burned in the presence of oxygen. The incineration process is used to reduce the large volume of sewage sludge to a residue which is approximately 20 percent of the original volume (Forster, 2003). In Japan, about 70% of the sludge produced in wastewater treatment plants is incinerated and the resulting ash was landfilled and used as construction material, e.g., cement (Cao, 2011). In the united states and UK, 22% and 21% of sewage sludge produced, respectively, is incinerated (Forster, 2003). The incineration process destroys virtually all of the volatile solids and pathogens and degrades most toxic organic chemicals. This method minimizes the need for disposal space and reduces odors generated from landfills. Due to the high-temperature requirement, Incineration is quite an expensive method. It also generates CO₂, particulate matter, and other hazardous pollutants that need air pollution control types of equipment before being released into the atmosphere. Sludge incineration is expected to increase in countries where agriculture use is limited (Mininni, 2004).

2.2.2 Landfilling

A landfill is a sludge disposal method in which sludge is deposited in an allocated piece of land, alone or with other municipal waste, and buried beneath a soil cover. Landfilling is the key disposal practice among the various countries, depending on suitable site availability. The focus has shifted towards land application and production of other useful products due to the generation of a large volume of sludge. In Japan, more than 70% of the produced sludge is disposed of by landfilling before 1995 (Cao, 2011) but now 70% of their sewage sludge is incinerated due to lack of land for disposal (Singh et al., 2020). In European countries, only 14% of sludge generated is landfilled (Singh et al., 2020). Most of the countries still follow the traditional disposal method of landfilling sewage sludge. Greece and Luxemburg dispose of their 80-90% sewage sludge in landfills (Samolada and Zabaniotou, 2014). Landfilling is no longer considered a sustainable way of disposal from the environmental perspective (Forster, 2003). In India, most of the sludge produced is disposed of in landfill dumpsites. There is a lack of appropriate management or treatment facilities for sewage sludge in India (Singh et al., 2020).

2.2.3 Agriculture Application

For the last many decades, dewatered sewage sludge has been used as a fertilizer on agricultural farmlands. It contains nitrogen and phosphorous which are valuable for soil. Agricultural use of sewage sludge is considered to be the best disposal option which is environmentally friendly compared to other methods of disposal (Foster, 2003). Approximately 37% of sewage sludge is used in agricultural farmlands in EU countries and In Canada, of the biosolids produced each year, about half are applied to land reclamation (Fytili and Zabaniotou, 2008). In Japan, China, and USA, the application of sludge in agriculture takes 14%, 45%, and 13% of sludge produced, respectively (He, 2008; Forster, 2003; Cao, 2011). However, in many developed countries, there is increasing disapproval for the agricultural use of biosolids due to potential toxicity such as the presence of heavy metals, organic pollutants, and pathogens in the sludge (Bondarczuk et al., 2016). The average content of heavy metals in sewage sludge was reported higher than the average for most farming soils (Werther and Ogada, 1999). This implies that the uncontrolled addition of sludge to agricultural land may increase the concentration of heavy metals in the farmland, resulting in these components entering human beings

through plants and animals. Furthermore, public opinion about sewage sludge is generally negative, therefore it brings a negative impact on agricultural use of sewage sludge (Fytli and Zabaniotou, 2008). In summary of these factors results that agricultural use may not be a sustainable solution for the handling of sewage sludge.

2.2.4 Summary

In India, about 62000 MLD sewage is generated, out of which 20120 MLD is treated, for 3157 MLD, there are under construction facilities. There is no treatment facility for approximately 38722 MLD of sewage (CPCB, 2015). Annually, approximately 3955 thousand metric tonnes of dry sludge is produced, if all treatment facility available for all produced sewage. Municipal sewage sludge production will continue to increase in the future. Thus, it is high demands management of this huge quantity of sludge. The current disposal methods, incineration, landfilling, and the agricultural application does not completely remove the risk of contamination and facing more and more pressure due to land limitations and stringent regulations. In India, the majority of sludge is disposed of at disposal sites. Thus, it is important to develop a cost-effective and environmentally friendly solution to improve these traditional technologies. There is a lack of proper administration of sewage sludge in India (Singh et al., 2020). So. The energy recovery potential of sewage sludge has been explored in this study using thermal technology, pyrolysis. For example, in Japan, the inorganic content of sewage sludge is used in the manufacturing of bricks and cement. Organic parts are mainly utilized for thermal energy production and only a small part would be used as fertilizer. Another advantage is also to reduce the large quantity of CO₂ generated through the use of fossil fuels (Cao, 2011). There are various thermal technologies are used to produce the fuels such as combustion, gasification, pyrolysis, etc.

2.3 Alternate method for sludge disposal

One of the alternate methods to manage this huge quantity of sewage sludge of WWTPs (Wastewater Treatment Plants) is thermochemical conversion of sewage sludge and producing fuel and energy. These methods have an advantage in reduction of the large volume of sewage sludge (solid waste) and also reducing the various harmful microorganism (Pathogens) (Samolada and Zabaniotou, 2014). Additionally, the costly

metals and various nutrients can also be recuperated. In sludge management, thermo-chemical technologies are superior in terms of volume reduction of waste and energy recovery to the traditional methods of dumping and landfilling (Werther and Ogada, 1999). Sewage sludge pyrolysis is considered as one of the alternate methods for sludge disposal and is the environmentally friendly method where the sludge volume is effectively stabilized and reduced. Liquid products (bio-oil) and gas products of pyrolysis have high heating values and can be utilized as an alternative to fossil fuels (Inguanzo et al., 2002). Sewage sludge pyrolysis is generating very little pollution and producing bio-char (solid residue) and all heavy metals are present in bio-char. Bio-char has good potential to be used as high adsorption material (Font et al., 2001; Chen et al., 2002; Rozada et al., 2003). Bio-oil of sludge pyrolysis contains higher water quantity and has low heating value due to high ash and water content of sewage sludge of wastewater treatment plants.

2.4 Pyrolysis

2.4.1 Potential method for sludge disposal

Pyrolysis is the thermal breakdown of organic matter in the temperature range of 300 °C to 900 °C in the absence of air. Pyrolysis can convert biomass such as agriculture and land forestry residues into solids, liquid, and gaseous forms (Hossain and Davies, 2013). Production of biofuels from waste biomass can be achieved through gasification, pyrolysis, torrefaction, and incineration from biomass (Capareda, 2013). Of these technologies, pyrolysis is widely used primarily because of its ability to generate sustainable heat and power (Gao et al., 2014). The benefits of pyrolysis include the conversion of biomass such as sewage sludge into biofuel products: bio-oil, syngas, and bio-char (Pokorna, 2009). Besides, the bio-oil products can be used as raw materials for specialty and commodity chemicals, such as fertilizers, resins (Inguanzo et al., 2002), and light aromatics including benzene, xylene, toluene (Tian et al., 2011). Also, the pyrolysis process minimizes environmental impacts, such as the pollutants released into the atmosphere (Manara and Zabaniotou, 2012). Sewage sludge is a mixed composition of organic and inorganic materials and it is considered as a renewable biomass resource that contains volatiles and therefore identified as potential material for pyrolysis. Pyrolysis is one of the alternative methods to manage municipal sewage sludge.

In the Pyrolysis, recovery of bio-oil with low emissions of nitrogen and sulfur oxides. It is also observed that, the formation of toxic organic compounds such as dioxins is avoided with low operating costs compared to incineration. It is a source of quality oil that can be used in many chemical processes and a reduction of sewage sludge to small volumes of inert residues (Werther and Ogada, 1999). Pyrolysis process conditions such as temperature, reaction time, materials properties, operating pressure, the heating rate can be operated to favor the desired pyrolysis products i.e. solids bio-char, gas, or bio-oil as an end product (Khiari et al., 2004).

Moreover, there are many advantages of pyrolysis at relatively low temperatures over many other methods (Doshi et al., 2005). The significant reduction in the large volume of solid residue and the effective resistance for natural lixiviation of heavy metals present in the solids (Caballero et al., 1997). The thermal treatment provides an increase of gases and bio-oil generation with a high energy value, so they can be used as potential fuels. The chemical properties of bio-oil indicate its potential to be used as a range of specialty and commodity chemicals such as fertilizer and resins (Inganzo et al., 2002).

The enormous quantity of municipal sewage sludge creates its potential as raw material for the pyrolysis process to generate and recover fuels in the era of the challenge of availability of fossil fuels (Fonts et al, 2012). However, one of the studies shows that the use of sewage sludge as fuel may have a harmful impact due to the dioxin formation which affects unpleasant surroundings (Kim and Parker, 2008). There are various types of pyrolysis processes which include fast, intermediate, slow, and flash pyrolysis.

2.4.2 Types of Pyrolysis

Mainly there are two types of pyrolysis techniques: Fast and slow pyrolysis. Slow pyrolysis helps the solids i.e. bio-char production contrast to the liquid and gas yield. This process used for traditional charcoal production for many centuries and can also be carried out using modern new reactors. Slow pyrolysis is described by low heating rates, relatively long residence time of solid and vapor, and usually lower reaction temperature, 450 °C and below, compared to fast pyrolysis. On the contrary, Fast pyrolysis is characterized by high heating rates and short residence times. Generally, this process needs the fine size of raw materials and fast removal of the vapor from the presence of hot solids. Pyrolysis liquid (bio-oil) is the liquid condensed from vapors and aerosols. It also yields low calorific value noncondensable gases. The yield of bio-oil liquid decreases with high temperatures and

with longer residence time (Bridgwater et al., 1999B). The yield of bio-oil liquid in fast pyrolysis is 50-75% (wt). Typical feed particle sizes in slow and fast pyrolysis are 5-50 mm and < 1 mm, respectively (Maschio et al., 1992).

Table 2.4 Process parameters, yield of products for various pyrolysis processes (Bridgwater, 2004; IEA, 2010; Horne and Williams, 1996).

Technique	Temperature (°C)	Residence Time	Yield (wt%)		
			Liquid	Bio-char	Gas
Fast pyrolysis	500	Short hot vapor residence time ~ 1s	75	12	13
Intermediate pyrolysis	500	Hot vapor residence time 10-30 s	50	25	25
Slow - Torrefaction	290	Solids residence time: 30 min	-	82	18
Slow - Carbonization	400	Very long vapor residence time: hours-days	30	35	35
Flash pyrolysis	400	Short residence time: <0.5 s	65	24	10

In addition, pyrolysis types include intermediate pyrolysis and flash pyrolysis. In intermediate pyrolysis, the reaction takes place at controlled heating rates which evades the formation of tar. The tar is a higher molecular weight heavy residue of substance, which is undesirable if bio-oil is to be used as fuel. The feedstock particles' size and shape are less critical than in fast pyrolysis, which allows a wider variety of biomass feedstock. Whereas the low temperature of slow pyrolysis produces mainly bio-char. Intermediate pyrolysis operates in a medium temperature (450-500 °C) regime and with high heating rates to produce condensable vapors and aerosols (Hornung et al., 2011). Flash pyrolysis occurs with very fast heating rates of >1000 °C/s and uses even shorter residence time (<0.5 S) than fast pyrolysis. The typical operating temperature of flash pyrolysis is 800-1000 °C and the biomass is supplied in the form of dust (Maschio et al., 1992). This process gives similar product distribution as fast pyrolysis. A comparison of pyrolysis processes based on the wood is shown in Table 2.4.

2.5 Bio-oil

Bio-oil is the liquid product of the pyrolysis process which is generated on the condensation of vapors of pyrolysis. Bio-oil of sewage sludge pyrolysis is a complex mixture of mainly water and organic compounds. It is a complex emulsion of water, oxygenated, and nitrogenated compounds as well as hydrocarbons and sulfur-derived products (Fonts et al., 2012). It is a dark brown free-flowing liquid. Sometimes bio-oil can

give a dark green shade due to high nitrogen content (Thamburaj, 2000). Generally, the liquid product contains two phases: The aqueous phase, a lighter phase of low molecular weight, and a Non-aqueous phase called the organic phase of heavier molecules. The organic phase consists of mainly aromatics which is suitable to use as fossil fuel. The aqueous phase mainly consists of acetic acid and hydroacetone which generate an unpleasant odor and lower value of the flashpoint. Bio-oil contains both organic and inorganic compounds. Bio-oil contains a mixture of carbon, hydrogen, oxygen, acids, alcohol, aldehydes, esters, ketones, sugars, phenols, furans, lignin-derived phenols, and extractible terpene with multifunctional groups (Zhang et al., 2007A). Fig. 2.1 illustrates the potential uses of the bio-oil. (Hossain and Davies, 2013).

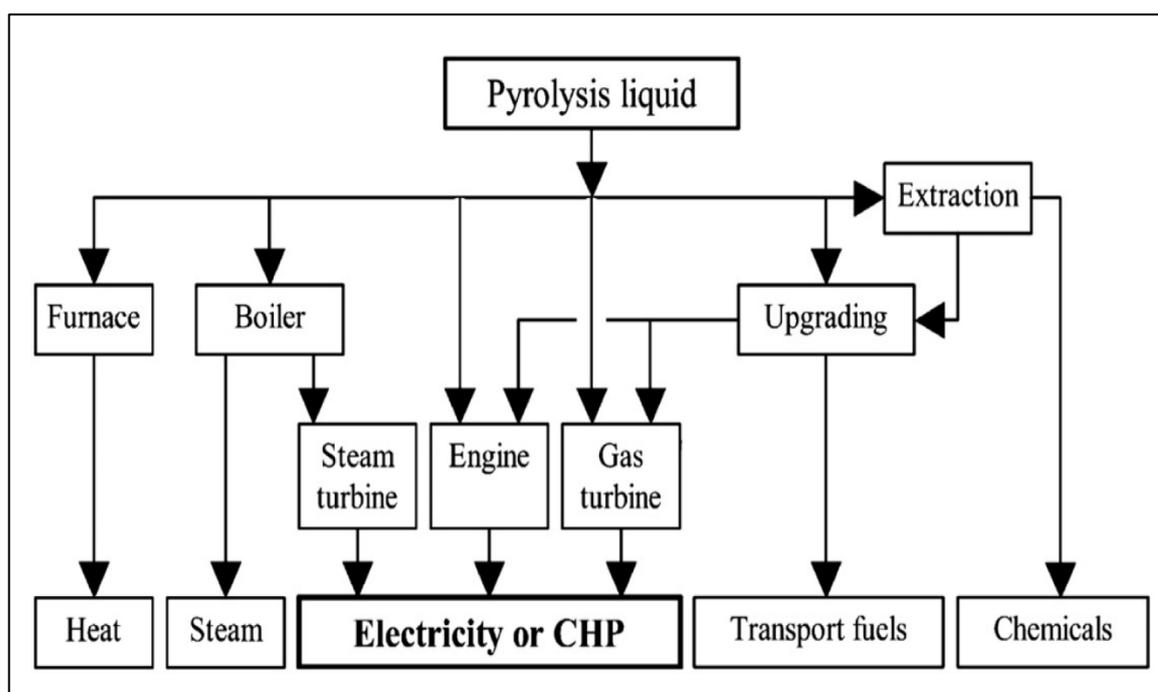


Fig. 2.1 Use of bio-oil produced by pyrolysis of various biomass waste. (Hossain and Davies, 2013)

2.5.1 Pyrolysis of Sewage Sludge: Operational conditions for bio-oil production

Various studies on bio-oil production from pyrolysis of sewage sludge have experimented in fluidized bed reactors to study mainly the fast pyrolysis process (Stammach et al., 1989; Shen and Zhang, 2003; Park et al., 2008; Fonts et al., 2008; Park et al., 2010). The experimental setup is a laboratory-scale plant prepared with a fluidized bed reactor where sand is used as inert material. The fluidizing medium is nitrogen, but many a time the non-condensable gases produced in pyrolysis are used as fluidizing agents (Park et al., 2008). After elimination of solids by using a cyclone separator, the product gas is condensed and

cooled and bio-oil (liquid product) is collected and stored. The operating conditions used by various researchers in fluidized bed pyrolysis setup are shown in Table 2.5.

Similarly, various experiments of pyrolysis of sewage sludge have also been performed in batch fixed bed reactors (Inguanzo et al., 2002; Kim and Parker, 2008; Dominguez et al., 2003; Dominguez et al., 2005; Dominguez et al., 2006A; Sanchez et al., 2009). In the typical setup, the stainless (Kim and Parker, 2008) or quartz (Inguanzo et al., 2002; Dominguez et al., 2003; Sanchez et al., 2009) made batch reactors were used and heated by electric heating (Inguanzo et al., 2002; Kim and Parker, 2008; Sanchez et al., 2009) or microwave furnaces (Dominguez et al., 2003; Domínguez et al., 2005, Domínguez et al., 2006B).

Table 2.5 Operating conditions for bio-oil production by pyrolysis of sewage sludge performed in fluidized bed reactor.

Type of sewage sludge	Size of feedstock (mm)	Pyrolysis Temperature (°C)	Fluidizing medium	Feed rate kg/h	Reference
Anaerobically stabilized Sewage Sludge from biological treatment	0.1 to 2	485-645	N ₂	1-5	Stammbach et al., 1989
Activated Sewage Sludge	0.2-0.3	300-600	N ₂	--	Shen and Zhang, 2003.
Digested dry sludge	0.45-0.75	800-1400	N ₂	0.3-0.66	Park et al., 2008
Anaerobically digested and dry sewage sludge	0.35-0.50	450-650	N ₂	0.18-0.36	Fonts et al., 2008; Fonts et al., 2009(B); Fonts et al., 2009(C).
Dried Sewage sludge	0.30-1.0	400-550	N ₂ and pyrolysis product gas	0.1-0.3	Park et al., 2010.
Sewage sludge after water treatments	0.25-0.60	400-600	--	--	Sun et al., 2015.

Fig. 2.2 shows the typical setup for the experiment of the fixed bed batch pyrolysis process for sewage sludge. The sewage sludge sample is fed in the reactor and heated at a specific heating rate to the desired temperature of pyrolysis in the presence of inert gas like nitrogen or argon. The gases/vapors produced during reaction passed through the condensing and cooling system, where the condensed liquid product, bio-oil, is collected. The un-condensed gas can be collected and analyzed for further research. The operating parameters for fixed bed batch pyrolysis are shown in Table 2.6.

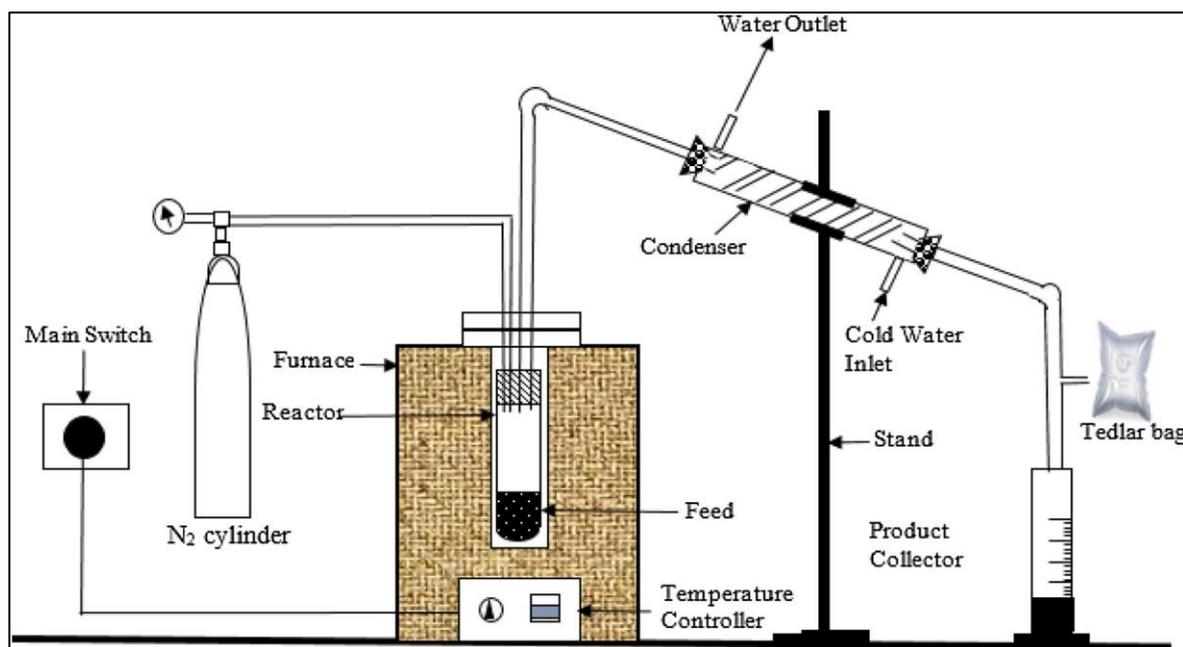


Fig. 2.2 Typical experimental setup for pyrolysis of biomass (Varma and Mondal, 2017)

2.5.2 Bio-oil yield: Impact of various parameters

The bio-oil produced by sewage sludge pyrolysis typically comprises organic components (organic phase) and water (aqueous phase). Many researchers reported bio-oil yield which includes both aqueous and organic phases together. (Inguanzo et al., 2002; Kim and Parker, 2008; Shen and Zhang, 2003; Fonts et al., 2008; Fonts et al., 2012; Jindarom et al., 2007) while many more researchers reported separate yields of the aqueous and organic phase (Park et al., 2008; Stammbach et al., 1989). The maximum bio-oil yield observed during pyrolysis of sewage sludge was in the range of 27-54 wt%. Bio-oil yield is influenced and studied by many process parameters like reaction temperature, heating rate, residence time, the particle size of dry sludge, sludge composition, catalyst, etc.

Many researchers observed that the temperature is the most effective operating parameter for a yield of products in the pyrolysis process (Fonts et al., 2012; Park et al., 2010; Mohan et al., 2006). It is very critical to predicting the temperature for the maximum bio-oil yield for pyrolysis. The yield of bio-oil is increased with temperature up to the maximum yield which is observed at a temperature between 450 and 500 °C in fluidized bed pyrolysis of sewage sludge (Shen and Zhang, 2003; Park et al., 2010; Fonts et al., 2012).

Similarly, it is also observed for pyrolysis of sewage sludge in fixed bed batch reactor that bio-oil yield increase with temperature. It is because of the non-condensable vapor

produced in each stage of temperature operated (Inguanzo et al., 2002; Kim and Parker 2008; Jindarom et al., 2007).

Table 2.6 Operating conditions for bio-oil production by pyrolysis of sewage sludge performed in fixed bed reactor.

Type of sewage sludge	Size of feedstock (mm)	Pyrolysis Temperature °C	Sample mass (g)	Rate of Heating (°C/min)	Inert gas flow rate (mL/min)	Reference
Anaerobically digested sludge	1-3	450-850	20	5-60	100 (N ₂)	Inguanzo et al., 2002.
Aerobically digested sludge	--	800-1200	--	74-300	10-15 (He)	Dominguez et al., 2003; Dominguez et al., 2005; Dominguez et al., 2006B.
Chemical and activated sludge and primary sludge	1	500	140	7	25 (N ₂)	Karayildirim et al., 2006.
Anaerobically digested sludge	--	250-500	5	--	50 (N ₂)	Kim and Parker, 2008
Anaerobically stabilized sludge	2-3	350-950	30	30	100 (He)	Sanchez et al., 2009.
Activated sludge	--	400-800	10	12	N ₂	Agarwal et al., 2015.
Dried Sludge	--	450-850	500-1000	10	N ₂	Karaca et al., 2018

The yield of bio-oil is also persuaded by the particle size of sludge used as raw material as the particle size is more crucial for pyrolysis reaction. Bio-oil yield is increased for smaller particle size of sludge (Park et al., 2008; Park et al., 2010; Stammbach et al., 1989) and it is also observed during pyrolysis of lignocelluloses biomass (Bridgwater 2007; Bridgwater et al., 1999A). However, the more gaseous product generated due to conversion of vapor to gas, for very small particle size which is less than 0.3 mm. The maximum bio-oil yield for sewage sludge pyrolysis was reported at particle size 0.7 mm (Park et al., 2008; Park et al., 2010). Furthermore, liquid yield is influenced by the sewage sludge composition such as primary sludge, secondary sludge, or activated sludge and digested sludge. Primary sewage sludge pyrolysis has a higher bio-oil yield than the secondary and digested sewage sludge due to the higher content of volatiles in primary sludge (Bridle et al., 1983). Sludge composition is also influencing the organic phase and water phase of bio-oil produced. More water yield is observed in the case of the high content of OH groups in sewage sludge composition (Fonts et al., 2009A; Agarwal et al., 2015). Some studies also mentioned that the water generated during pyrolysis could be caused secondary pyrolysis dehydration reactions of products of primary pyrolysis products which contain oxygen. (Agarwal et al., 2015; Murwanashyaka et al., 2001).

2.5.3 Physico-chemical properties of bio-oil

Pyrolysis liquid, bio-oil, is a complex mixture of water and oxygenated hydrocarbons. At room temperature, it is a dark-brown free-flowing liquid. Typically, bio-oil consists of two phases: an aqueous phase of lighter or low molecular weight and an organic phase of heavier molecular weight. The heavier or organic phase is mostly aromatics and is appropriate as a substitute for fossil diesel fuel. The lighter or aqueous phase comprises various chemicals such as acetic acid and hydroxyacetone, which are responsible for unpleasant odor and lower flashpoint. The bio-oil quality is determined by the physicochemical properties, which depend on the application targeted. It's not always necessary that the operating parameters for which bio-oil yield is maximum, the quality of bio-oil is also maximum. Therefore, optimization of both bio-oil yield and quality is always required (Westerhof et al., 2010). Due to this reason, it is highly essential to identify the bio-oil properties, composition, and effect of operating variables. The bio-oil properties and composition based on various research studies are discussed in brief in the following section.

2.5.3.1 Water content

Water content in bio-oil produced from sewage sludge pyrolysis is in the range of 20 to 70% (wt%) depending on the composition of sewage sludge and operating conditions. Water in bio-oil is mainly due to the presence of initial moisture in sewage sludge and the further reaction during pyrolysis. The water content of bio-oil is mostly measured by using the Karl Fischer titration method and azeotropic distillation. Piskorz et al. (1986), Fonts et al. (2009B) and Sanchez et al. (2009) observed the water content of bio-oil in the range of 21-32%, 40-69%, and 58-70%, respectively. They also investigated the water content of bio-oil with the effect of temperature. Fonts et al. (2009B) and Sanchez et al. (2009) observed minimum water content around 25 wt% and 58 wt%, respectively, at a temperature in the range of 520-560 °C and 450 °C, respectively. Sanchez et al. (2009) investigated the effect of temperature in water content of bio-oil in the range of temperature from 350 to 950 °C and observed minimum water content of 58% at 450 °C (Fonts et al., 2009B; Piskorz et al., 1986; Sanchez et al., 2009). The water reduces the high heating value of bio-oil, but it can also be beneficial by reducing viscosity and improving fluidity. Water content also lowers the flame temperature, which helps to reduce the NO_x emission. Moreover, due to the high-water content of bio-oil, erosion problem in the

injectors and fuel supply system is observed. It is difficult to remove homogeneously dissolved water from pyrolysis liquid by drying.

2.5.3.2 Viscosity

The viscosity of bio-oil is a very significant physico-chemical property because pumping and injecting of the fuel system are affected significantly by this property. Few studies reported different viscosity of bio-oil produced by pyrolysis of sewage sludge (Fonts et al., 2009B; Park et al., 2008; Gil-Lalaguna et al., 2010; Bahadur et al., 1995; Shen and Zhang, 2005). Some of the researchers reported viscosity for the organic and aqueous phases separately. One study reported bio-oil viscosity for two organic phases, which is 22 cP and 400-1500 cP, respectively, in both organic phases. The effective difference in the viscosity of both phases is due to its composition and more specifically, the amount of fatty acid present (Gil-Lalguna et al., 2010). The viscosity of bio-oil is claimed due to the fatty acid compounds. (Bahadur et al., 1995). Bio-oil viscosity is in the range of 22-1500 cP, which is very high compared to fossil diesel fuels.

2.5.3.3 Acidity and solids content

The pH of the bio-oil produced from sewage sludge pyrolysis varies among 8 and 10 which show alkaline nature, unlike biomass pyrolysis liquid, acidic characteristics. The basicity of bio-oil is mainly due to the existence of ammonia and nitrogen-containing compounds which might be resulted from the protein content of the sewage sludge. Due to the ammonia and nitrogen-containing compounds present in the aqueous phase of bio-oil, they can be used to prepare compounds that are useful for fertilizer manufacturing. The solid content of bio-oil of sewage sludge is very low (0.033 – 0.408 wt%) (Fonts et al., 2009A, Fonts et al., 2009C) and almost always lower than the proposed value of solids (less than 1 wt% and 0.25 wt%) in for its combustion in diesel engine and turbines (Oasmaa and Meier, 2005).

2.5.3.4 Heating value

To use the bio-oil as fuel, the heating value of bio-oil is very important. The heating value of fuel depends on its chemical composition and density. The heating value of pyrolysis liquid is 40-50% of that diesel oil due to the presence of oxygen and other components.

Various researchers have investigated the heating value of bio-oil produced by pyrolysis of various kinds of sewage sludge and reported values are presented in Table 2.7.

The higher heating value of bio-oil prepared by sewage sludge pyrolysis is mostly higher than 22 MJ/kg which is higher than the heating value of bio-oil prepared from lignocellulosic biomass. It is due to the presence of lipids and extractives in sewage sludge (Fonts et al., 2009A). Due to the presence of a significant concentration of oxygenated components and water in bio-oil, the heating value of bio-oil is lower than the of fossil fuel. Simultaneously, it also investigated that bio-oil of fast pyrolysis method could replace heavy and light fuel oils in industrial boiler applications based on flame combustion test. (Aguado et al., 2002; Bridgwater, 2005). To increase the heating value of bio-oil and reduce the weight of oil per unit of heat generated upon combustion, fractional condensation of biomass pyrolysis vapors can be used (Mohan et al., 2006). Many researchers reported the heating value of bio-oil over 40 MJ/kg which is quite near to the 45-46 MJ/kg, the heating value of commercial diesel fuels (Karayildirim et al., 2006; Fonts et al., 2009D). This very high heating value of bio-oil is due to the sewage sludge origin (Karayildirim et al., 2006).

Table 2.7 Heating value of bio-oil prepared from pyrolysis of various types of sewage sludge.

Sewage Sludge Type	High Heating Value (MJ/kg)	Operating conditions	Reference
Digested Secondary	22-28	Fixed bed, 450-850 °C	Inguanzo et al., 2002
Digested	24.7	Fixed bed, 500 °C	Pokorna et al., 2009
Digested	27.9		
Digested	27-34	Fluidized bed, 450-650 °C	Fonts et al., 2009C
Digested	31-32	Fluidized bed, 550 °C	Fonts et al., 2009A
Digested	33-42	Fluidized bed, 530 °C	Fonts et al., 2009B
Primary	36-38	Batch reactor, 250-500 °C	Kim and Parker, 2008
*TWAS	37		
Digested	38-39		
Dried sewage sludge	28-33	Fluidized bed, 400-500 °C	Sun et al., 2015
Anaerobically digested and thermally dried sewage sludge	19-32	Auger Reactor, 250-300 °C	Atienza-Martinez et al., 2014

*TWAS – Thickened waste activated sludge.

2.5.3.5 Ultimate Analysis

Elementary analysis of bio-oil is very essential to know the substance. Table 2.8 shows the elemental analysis of bio-oil produced by pyrolysis of sewage sludge in various studies. In the organic layer of bio-oil, the carbon fraction is higher than that in the aqueous phase and it is generally less than that in fossil diesel fuel, it's around 36-80 wt%. Hydrogen content is around 2.7 to 11.5 % (wt). The oxygen fraction is in the range of 6 to 59 wt% which is

much higher than in fossil fuel and biodiesel; equally, the bio-oil has less energy content and is almost 50% of the fossil fuel. Oxygen tends to make bio-oil unstable. The nitrogen and sulfur percentage composition are high which is due to the protein content of sewage sludge.

Table 2.8 Elemental analysis of bio-oil prepared by sewage sludge pyrolysis in various studies.

Type of Bio-oil	Wt %					Reference
	C	H	N	O	S	
Organic layer of bio-oil	49.4-62.6	9.8-11.5	5.1-5.6	20.4-34.9	0.4-0.6	Inguanzo et al., 2002
Bio-oil of Primary Sludge	62-74	2.7-8.5	9.5-9.9	8-22	n.r.	Kim and Parker, 2008
Bio-oil of TWAS	63-65	9.4-9.7	6.8-8.5	17-20	n.r.	
Bio-oil of digested sludge	69-74	9.7-9.9	5.6-6.3	8.4-15	n.r.	
The organic layer of bio-oil	36.3-60.8	4.5-9.8	4.2-9.1	24.6-45.7	0.6-1.6	Park et al., 2008
The aqueous layer of bio-oil	69	9.4	6.1	14.3	1.2	Pokorna et al., 2009
Organic layer of bio-oil	73.4	9.5	8	6.7	2.4	
Light Organic layer	75.6	10.5	2.4	11.3	0.2	Font et al., 2009D
Heavy Organic layer	62.2	8.4	8.8	19.6	1	
Aqueous layer of bio-oil	26.6	6.6	7	59	0.8	
Bio-oil of sewage sludge	65.2	8.6	8.4	17.4	0.4	Araza et al., 2017

n.r. – not reported.

2.5.3.6 Chemical Composition of bio-oil

Bio-oil obtained by pyrolysis of sewage sludge consists of compounds of diverse nature. These compounds are formed due to sewage sludge devolatilization and the secondary reactions of primary products formed during the reaction. The bio-oil is a complex mixture of water and organic chemicals. The chemical composition of bio-oil is studied by using various methods such as Gas chromatography coupled with Mass spectrometry (GC-MS), Fourier Transformed Infrared Spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (H-NMR), Liquid Chromatography (LC), solvent fractionation. Most researchers reported the chemical composition of sewage sludge pyrolysis bio-oil by using Gas chromatography coupled with Mass spectrometry (GC-MS) (Pokorna et al., 2009; Doshi et al., 2005; Fonts et al., 2009B; Park et al., 2008; Domínguez et al., 2003; Domínguez et al., 2005; Domínguez et al., 2006B; Karayildirim et al., 2006; Sanchez et al., 2009; Jindarom et al., 2007; Kaminsky and Kummer, 1989). The chemical composition of bio-oil was investigated for the whole bio-oil, organic phase, and aqueous phase. Many of the

researchers studied the whole bio-oil chemical composition (Fonts et al., 2009B; Shen and Zhang, 2003; Karayildirim et al., 2006; Park et al., 2010; Jindarom et al., 2007; Fullana et al., 2005; Cao et al., 2010.) Many other researchers studied organic phase of bio-oil (Kaminsky and Kummer, 1989; Dominguez et al., 2003; Dominguez et al., 2005; Domínguez et al., 2006B; Park et al., 2008; Pokorna et al., 2009; Sanchez et al., 2009) and few authors reported for aqueous phase composition (Park et al., 2008; Fonts et al., 2009; Kaminsky and Kummer, 1989). From the various studies, it is observed that the whole bio-oil liquid and organic phase of bio-oil consist of main alkane, alkene, aromatic compounds, fatty acids, carboxylic acids, ketones, aldehyde, steroids, nitriles, and amides. Moreover, most nitrogen compounds are mainly amides, nitriles, and nitrogen heterocyclic compounds (Cao et al., 2010). Some of the components identified in the aqueous phase are water, ammonia, methanol, acetonitrile, propane nitrile, pyrrole, pyridine, and acetamide. (Kaminsky and Kummer, 1989). In the aqueous phase, most components are nitrogen compounds and therefore the bio-oil can be utilized as fertilizer or production of fertilizers. (Azuara et al., 2010). In order to use the bio-oil as a fuel, the study of nitrogen-containing compounds could be attractive and to choose an adequate method to reduce the nitrogen in the bio-oil.

Bio-oil is basic due to the presence of ammonia and nitrogen-containing compounds and is unstable due to the presence of reactive compounds. One of the major drawbacks of the chemical composition of bio-oil is very similar to that of original biomass and it is extremely different from petroleum-derived fuels and chemicals (Maher and Bressler, 2007). Phenol with ketones and aldehydes groups and almost all the functional groups showed the extensive existence of oxygen. Abundant aldehyde and ketones make bio-oil hydrophilic and make it difficult to remove the water from bio-oil (Wang et al., 2004).

2.5.3.7 Need to improve quality of bio-oil

As an aforementioned discussion, the characteristics of bio-oil are high oxygen-containing components, high nitrogen-containing components, high water content, low calorific value compares to conventional fuels. Also, the yield of bio-oil produced by pyrolysis of sludge is low because sludge contains a large amount of ash. The heterogeneous nature of bio-oil may lead to instability, physical and chemical changes, which reduced the heating value of bio-oil and also leads to NO_x and SO₂ emission problems if the liquid is used as fuel, therefore, it is necessary to improve the quality and yield of sludge pyrolysis oil

Therefore, the approach for improving the energy value of pyrolytic bio-oil is required. Numerous studies have been undertaken to obtain high-grade bio-oil with low oxygen content and high calorific value using various upgrading processes. The most commonly used upgrading processes are hydrodeoxygenation (HDO), catalytic cracking, steam reforming, emulsification, supercritical fluids, esterification, etc. The process of catalytic cracking is a cheaper method than hydrodeoxygenation; however, their results are not effective as there is a high coke formation of (8-25 wt %) and the obtained fuel quality is poor. The upgrading method of HDO received special attention because of the significant increase in hydrocarbon fuel during conversion of low-grade pyrolysis oil (Zhang et al., 2007A; Toba et al., 2011; Joshi and Lawal, 2012). However, the complicated equipment, need for catalysts and high-pressure requirement for the reaction have made the method very complex and costly. Similarly, steam reforming, emulsification, supercritical fluids, and esterification have also some advantages and limitations. Somehow, these processes are too expensive, not cost-effective, and not suitable for large-scale production. Therefore, a new approach is sought after to reduce this cost (Abnisa and Daud, 2014).

These problems associated with bio-oil of MSS pyrolysis would be reduced if MSS is co-pyrolyzed with biomass (Ding and Jiang, 2013) and whose valorization by fast pyrolysis has been widely studied and has attained a considerable development stage (Bridgwater, 2012; Meier et al., 2013). Therefore, the present investigation on the co-pyrolysis process is more focused. However, this process is very simple and cost-effective, and especially important to produce high-grade fuel oil (Abnisa and Daud, 2014).

2.6 Co-pyrolysis

Co-pyrolysis is the most promising technique, which can meet the aforementioned criteria while reducing the volume of waste and environmental issues at the same time. In co-pyrolysis, due to the high heating value of biomass, the heating value of bio-oil from co-pyrolysis would be elevated so that bio-oil can supply enough energy for a self-heated run of co-pyrolysis reactor. Co-pyrolysis has received much attention in recent years because it provides an alternative way to dispose of and convert MSS and biomass to high calorific value feedstock and fuels. Recent investigations have shown that MSS and biomass co-pyrolysis achieve a synergistic effect with an increase in liquid yield products and improvement in the overall process efficiency.

The co-pyrolysis process involves more than one different material as feedstock. Many studies have shown that the co-pyrolysis of biomass has successfully improved the oil quantity and quality without any improvement in the system process. In contrast to catalytic cracking and HDO, co-pyrolysis has shown promise for future application in the industry because of its attractive performance/cost ratios. Previously, various studies have shown that co-pyrolysis of biomass with synthetic polymers has successfully improved the quality and quantity of liquid fuel without any additional modification of the system (Aboulkas et al., 2012; Martinez et al., 2014; Brebu et al., 2010; Zhang et al., 2016).

Pyrolysis of sewage sludge is an environmentally friendly process where organic contents of MSS are thermochemically decomposed into liquid (bio-oil) and solids (bio-char) at moderate temperature (400–600 °C) in an inert atmosphere (Bridgwater, 2003). Waste agriculture biomass is an important renewable energy resource because of its high volatile matter and low ash content. Considering the high ash content and density of MSS (Fonts et al., 2009A), co-pyrolysis of MSS with waste biomass have some advantages, such as reduction of floatation of biomass in pyrolysis reactor and improvement of pyrolysis airflow (Zhang et al., 2009). Moreover, the heating value of bio-oil from co-pyrolysis would be improved due to the high heating value of waste biomass.

Furthermore, the main benefit of the co-pyrolysis method is that the volume of waste can be reduced significantly as more waste is consumed as feedstock. Additional benefits are reducing the landfill sites needed, saving costs for waste treatment, and solving several environmental-related problems. Since the disposal of waste in landfills is undesirable (Garforth et al., 2004), this method could be proposed as an alternative waste management procedure for the future that will have a significant impact on waste reduction and may enhance energy security. In addition, from an economic point of view, co-pyrolysis is a promising option for a biomass conversion technique to produce pyrolysis oil. One of the studies investigated that the use of co-pyrolysis of biomass with waste biopolymer material is more cost-effective than pyrolysis of only biomass and it has potential for commercial development (Kuppens et al., 2010).

Many researchers have investigated and reported the co-pyrolysis characteristics of waste biomass with many other solid wastes with organic content, such as MSS, biomass agriculture, and plastics (Abnisa and Daud, 2014). The synergetic effect observed in the increase of activation energy is for the co-pyrolysis of sawdust and waste plastics (Zhang et al., 2016). The co-pyrolysis of biomass and lignite investigated and discovered the optimum temperature, 600 °C for synergetic effects, and at which enough free radicals and

hydrogen donors were generated (Zhang et al., 2007B). A bio-oil with higher stability is obtained in co-pyrolysis of pine wood chips and waste tire and also observed improvement in lower oxygen content and higher calorific value (Martinez et al., 2014).

2.6.1 Studies on Co-pyrolysis of Sludge and biomass

In the past several years, co-pyrolysis of MSS and waste biomass materials have put on more concentration. Table 2.9 shows the research work investigated by various researchers on co-pyrolysis of sewage sludge with various biomass. These studies are mainly focused on bio-oil production, pollutant emission, and heavy metal distribution in co-pyrolysis products (Samanya et al., 2012; Ren, 2012; Zhang et al., 2011). Though, some issues existing in the co-pyrolysis process of sewage sludge and biomass are conflicting. For example, one of the studies of bio-oil yield in fast pyrolysis of sewage sludge and rice waste, it is revealed that the bio-oil yield of co-pyrolysis is in the range of sewage sludge and rice waste pyrolysis alone, which showed that there is no obvious synergistic effect between sewage sludge and rice waste (Fairous et al., 2011). Encouraging NH_3 and HCN formation by co-pyrolysis of sludge and cotton stalk may also indicate synergistic effect occurred to some extent (Ren, 2012). The noticeable synergistic effect observed sewage sludge and rice straw co-pyrolysis by using thermogravimetry analysis (TGA) and differential thermogravimetry (DTG) (Zhang et al., (2009). Bio-oil produced in municipal sewage sludge pyrolysis is a complex mixture of organics including sulfur and nitrogen-containing compounds, which may lead to SO_2 and NO_x emission problems. These problems would be relieved if lignocellulosic biomass is co-pyrolyzed with sewage sludge (Ding and Jiang 2013). The synergetic effect between sewage sludge and wheat straw results in an increase in gas and bio-oil yield and a decrease in bio-char yield and the strongest interaction appeared at the biomass proportion of 60% wt (Wang et al., 2016). An increase in gas yield is also observed during co-pyrolysis of sewage sludge and rice husk and syngas content and gas lower heating value was significantly improved (Zhang et al., 2015). More importantly, little information is known about the energy balance which determines the economic feasibility of the co-pyrolysis technology. Thus, the systematic study about co-pyrolysis of sewage sludge and biomass is important for the practical application of co-pyrolysis technology.

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Table 2.9 Studies on co-pyrolysis of sewage sludge with various biomass

Feedstock	Temperature (°C)	Equipment	Type of study	Reference
Sewage sludge and rice straw	30-900	Thermal Analyzer	Kinetic study	Zhang et al., 2009
Sewage sludge and rice straw	30-800	Thermal analyzer	TG-DTG analysis	Shuang-Quan et al., 2009
Secondary sludge and corn straw	500-800	Tube furnace	Fractional distribution changes of heavy metals	Zhang et al., 2011
Sewage sludge and Mixed wood, rapeseed, wheat straw.	450	Batch reactor	Product yield and composition of bio-oil (upper phase)	Samanya et al., 2012
Sewage sludge with sawdust and rice husk.	300-550	Vertical Fixed Bed reactor	TG-DTG and Products Yield	Ding and Hong, 2013
Sewage sludge and pine sawdust	25-900	Thermal Analyzer	Kinetic study	Zhu et al., 2015
Sewage sludge and Poplar sawdust	500	Tube reactor	TG study, the composition of top phase bio-oil	Zuo et al., 2014
Sewage sludge and Pinewood sawdust	500	Conical spouted bed reactor	Products yield and analysis of products	Alvarez et al., 2015
Paper sludge and municipal solid waste	1000	Thermal Analyzer	Kinetic study	Fang et al., 2015
Secondary sewage sludge and rice husk	900	Fixed bed vacuum reactor	The yield of products, Gas, and Char analysis	Zhang et al., 2015
Sewage sludge and rice straw	500	Microwave device	TG analysis and Bio-char characterization	Huang et al. (2015)
Sewage sludge and Microalgae	425-500	Fixed bed reactor	Kinetic study and yield of products	Wang et al., 2016
Sewage sludge and manure	525	Stirred batch reactor	TG analysis, Yield, and characterization of products	Ruiz-Gomez et al., 2017
Sewage Sludge and hazelnut shell	-	Vacuum tube furnace	Kinetic study and product characterization	Xu et al., 2017
Sewage sludge and bagasse	700	Py-GC MS	TG Analysis, Characterization of bio-oil and gas	Lin et al., 2017
Oily sludge (from crude oil tanks) and rice husk	600	Fixed bed reactor	Bio-oil and gas product analysis	Lin et al., 2018B

Bio-oil produced in municipal sewage sludge pyrolysis is a complex mixture of organics including sulfur and nitrogen-containing compounds, which may lead to SO₂ and NO_x emission problems. These problems would be relieved if lignocellulosic biomass is co-pyrolyzed with sewage sludge (Ding and Jiang 2013). The synergetic effect between sewage sludge and wheat straw results in an increase in gas and bio-oil yield and a decrease in bio-char yield and the strongest interaction appeared at the biomass proportion of 60% wt (Wang et al., 2016). An increase in gas yield is also observed during co-pyrolysis of sewage sludge and rice husk and syngas content and gas lower heating value was significantly improved (Zhang et al., 2015). More importantly, little information is known about the energy balance which determines the economic feasibility of the co-pyrolysis technology. Thus, the systematic study about co-pyrolysis of sewage sludge and biomass is important for the practical application of co-pyrolysis technology.

Alvarez et al. (2015) studied the co-pyrolysis behavior of sewage sludge from wastewater treatment plants and pinewood sawdust to improve the composition of the bio-oil produced from the fast pyrolysis of sewage sludge. Fast pyrolysis of a mixture of sludge and pinewood sawdust (50-50 wt%) was carried out at 500°C in a conical bed spouted reactor. The particle size of the dried sludge and sawdust was between 0.5-3 mm and 1-2 mm, respectively. In each run, 50 g of the mixture had been fed for 50 min at the rate of 1 g/min. The mass loss of sawdust was higher than sludge because of the higher ash content of the sludge. Degradation of sludge started at 100°C and was completed at 575°C, whereas the biomass started at 175°C and finished at 500°C. Inorganic elements present in sludge such as Ca, Mg, and K would promote the degradation of cellulose and hemicelluloses from biomass, favoring the production of gas. The bio-oil formed in the pyrolysis consisted of oxygen-containing compounds and water, with a concentration of 48.6 wt% and 31.6 wt%, respectively. There were no sulfur-containing compounds present in the bio-oil, therefore no desulphurization methods were required for oil use as fuel. Nitrogen-containing compounds were produced in the decomposition of the protein derived from the dead bacteria present in the sludge. Synergetic effects were observed in the thermal analysis, which shifts the first degradation step to lower temperatures. This bio-oil may be used as raw materials in bio-refineries for the production of different fuels, chemicals, and H₂. The char produced from pyrolysis reaction is used in agriculture applications.

Ruiz-Gomez et al. (2017) studied the synergetic effects of co-pyrolysis of digested sludge and manure. Manure has lower ash content than sludge. The stirred batch reactor was used

to pyrolyze a mixture of sludge and manure by 50 wt% of each. The pyrolysis was performed at 525°C as the and the heating rate was 8°C/min. The pyrolysis of manure resulted in a higher yield of gas fraction and lower yield of bio-oil and solids (bio-char) than the sludge pyrolysis. The lower yields of CO₂ and CO and higher yield of H₂ and H₂S were observed for sludge pyrolysis than that of manure pyrolysis. Two phases of bio-oil, one is an organic phase, and another is aqueous phase, are observed and separated for characterization. Oil is mainly found in the organic phase and the aqueous phase contains mainly water. The major components in the oil phase from sludge pyrolysis were carboxylic acids. And phenols were the major compounds in the oil phase of manure. The total energy yield of sludge pyrolysis was higher than that achieved from the pyrolysis of manure, mostly due to the lower energy recovery of the aqueous phase. There is no noticeable synergy observed in the yields of products and liquid properties. However, the yield of organic components is a little higher than the calculated average. It is observed that in the organic phase, the fatty acid composition is decreased, and aliphatic nitriles increased in the co-pyrolysis liquid phase in comparison to the calculated average. Co-pyrolysis of sludge and manure can be considered as an alternative method for waste management.

Lin et al. (2017) studied co-pyrolysis characteristics of sewage sludge and sugar cane bagasse at various proportions of sludge (10, 30, and 50%) using TG-FTIR and Py-GC/MS. The initial and final temperature of co-pyrolysis is increased with the temperature. Sugarcane bagasse contains celluloses, hemicelluloses, and lignin. Bio-oil of sugar cane bagasse pyrolysis were mainly contained benzene and its derivatives, which mostly generated due to degradation of lignin. Sewage sludge contains mainly protein and lipid. The nitrogen fraction of sewage sludge was five times that of sugarcane bagasse, which was probably carried by protein. The TG and DTG analysis of bagasse, sludge, and their mixture were carried out under a heating rate of 20°C. The Pyrolysis process of mixture and bagasse was divided into four stages, including moisture removal (160°C), devolatilization (160-250°C), stabilization (250-560°C), and the inorganic decomposition (560-1000°C). The Pyrolysis process of sludge was divided into three stages. By TG analysis, the devolatilization finished before 700°C, this was selected as the operating temperature for Py-GC/MS experiment. The chemical composition of bio-oil is classified as C7# (components with carbon number less than or equal to 7), acetic acid, furfural, benzene derivatives, C7p (components with carbon atoms more than 7). Increasing sludge

ratio in co-pyrolysis, the contents of furfural, acetic acid, and C7# were reduced and the content of C7p enhanced.

Lin et al. (2018B) performed co-pyrolysis of oily sludge and rice husk in a fixed bed reactor to examine the effects of interactions on the products and improve the quality of bio-oil. Oily sludge was collected from the bottom of crude oil tanks solid waste central disposal company. Oily sludge is a complex mixture of heavy oil, water, and solids. Oily sludge and rice husk were mixed with blending ratios of 2:1, 1:1, and 1:2. In this experiment, a fixed bed reactor of quartz tube was used, and reactor temperature was increased up to 600°C and maintained for 20 min. The liquid yield of oily sludge was higher due to its high volatiles content and the residue yield of rice husk was higher due to its high ash content. The synergy in co-pyrolysis was observed in a reduction in the yield of bio-oil and an increase in the yield of bio-char. The reason for the synergy is the catalytic effect of biomass ash which promotes the secondary reactions of hydrocarbons, such as cracking and dehydrogenation. The major components in the sludge pyrolysis oil were hydrocarbons, such as alkanes, olefins, and aromatics, accounting for a total content of 91.7%. Oxygenates, ketones, phenols, furans, and organic acid, were major components found in rice husk pyrolysis oil. The total gas volume of rice husk pyrolysis generates more gas fractions than oily sludge. The oxygenated compounds are reduced in bio-oil due to the increase in the formation of CO and CO₂ in the decomposition of oxygenated functional groups. Therefore, the total volume of the gas product increased as the fraction of rice husk in the mixture increased. The pyrolysis of biomass can produce a considerable amount of water vapour, which provided a gasification agent and encouraged the water-gas shift reaction to produce more H₂ and CO. Also, the yields of H₂ from co-pyrolysis were higher than that from individual pyrolysis of sludge and rice husk, indicating that the synergetic effect enhanced the production of H₂. As the blending ratio of rice husk increased, the amounts of H₂S was decreased from 0.051 to 0.030 mol per kg sample, and the sulfur content in oil reduced from 1.73% to 1.22%. Synergy was observed by increasing the saturates by a maximum of 55% and aromatics by 86% while reducing resins to a minimum of 31% and asphaltenes by 68%. GC-MS results confirmed that the fraction of oxygenated components in the bio-oil was reduced by 46-93%.

Fang et al (2015) studied the pyrolysis characteristics of municipal solid waste, paper sludge, and their mixture through thermo-gravimetric analysis. Their kinetics, activation energy, pre-exponential, and the reaction model, was studied by Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. The various blends of paper sludge

were 10%, 20%, 50%, 70%, 90% were studied. The operating temperature was up to 1000 °C and the heating rate for the pyrolysis experiment was 30, 40, and 50 °C/min. The solid waste was a mixture of various components such as food waste, wood, and peel. Results showed that with the increase of paper sludge ratio, the mass loss peak was increasing. The initial temperature was increased slightly from 267.2°C to 306.2°C with the fraction of paper sludge increasing in the mixture. The pyrolysis characteristic index (D) is determined which signifies pyrolysis characteristics of materials and the higher value of D represents easier pyrolysis. Results show that for the proportion of paper sludge less than half, the pyrolysis performance was good. The activation energy of the municipal solid waste was higher than that of paper sludge. The minimum value activation energy obtained is 95.70 kJ/mol by the KAS method and 111.56 kJ/mol by FWO at the equal proportion of two materials.

Shuang-quan et al (2009) studied the co-pyrolysis characteristics of sewage sludge with rice straw. Pyrolysis experiments are carried out at a heating rate of 10°C/min. The TG-DTG curves of the mixture revealed that the maximum mass loss rate increase with the increasing proportion of the rice straw in the mixture. The sewage sludge pyrolysis is inhibited in presence of rice straw at a temperature less than 290 °C and the rate of decomposition is slow. The enhancement of sludge pyrolysis and rate of decomposition was observed at a temperature of more than 290°C. Results discovered that pyrolysis reaction time was reduced by adding rice straw to the mixture. And mass loss is also enhanced as the increased content of rice straw in sludge mixture. It also investigated that the Arrhenius equation with first-order pyrolysis reaction signifies the volatile matter release during pyrolysis satisfactorily.

Zhang et al (2011) studied the synergy for heavy metals distribution in co-pyrolysis of sewage sludge and corn straw. Inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze the heavy metal contents. This work concludes that the heavy metal concentration was increased during co-pyrolysis. The highest fraction of chromium, nickel, and lead was observed at 700 °C, and the highest fraction of Cadmium, Copper, and Zinc was observed at 500 °C.

Samanya et al (2012) studied and compared the effect of the addition of 40 wt% of each material such as mixed wood, rapeseed, and wheat straw to the sewage sludge pyrolysis for mainly bio-oil characteristics and properties. The pyrolysis experiments are performed in the cylindrical batch reactor of a quartz tube with a glass cover and the temperature was

raised to 450 °C and kept for 15 min and bio-oil is collected. The upper phase of bio-oil obtained by co-pyrolysis is analyzed for chemical composition and also analyzed for ultimate analysis, high heating value, moisture content, viscosity, pH, and acid number. Bio-oil oil from sewage sludge and rapeseed found the highest heating value among the three and decreases the viscosity. Its yield and hydrogen content is increased compared to the yield and hydrogen content of bio-oil produced from sewage sludge. The highest viscosity, significant improvement in carbon content, and reduction in nitrogen content are observed for bio-oil of 40% mixed wood and sludge.

Ding and Hong (2013) investigated the synergistic effect during co-pyrolysis of sewage sludge with waste biomass such as sawdust and rice husk. The thermogravimetric (TG) and derivative thermogravimetry (DTG) study of all three feedstocks was reported. The residual weights of sewage sludge, sawdust, and rice husk are 59.6, 17.0, and 28.3%, respectively. Sewage sludge and biomass show similar thermochemical characteristics and can be well co-pyrolyzed as they have similar TG behavior. The vertical batch reactor was used for pyrolysis experiments and different sludge ratios like 0, 10, 20, 30, 50, 70, and 100 % were used. The yield of products and effect of various sludge ratios on yield of products, synergistic effect was evaluated. There is no obvious synergy was reported during co-pyrolysis. The max mass rate of both biomasses is higher than that of sludge due to the higher volatile matter content of biomass than in sludge. The heat demand for sludge and biomass was evaluated. The heat demand for co-pyrolysis would be the sum of the heat demand of each portion of feedstock involved.

Zuo et al (2014) researched the effect of the addition of poplar sawdust in the pyrolysis of sewage sludge. The experiments of co-pyrolysis were conducted for a mixture that contains 0, 5, 10, 15, 20, and 25% poplar sawdust in a horizontal stainless-steel reactor at 500 °C. The condensed bio-oil was separated into two phases. The TG and DTG curves were reported for sludge, sawdust, and mixture (25% wt sawdust). The max %age of mass loss for mixture is higher than the predicted value of mass loss rate indicates synergistic reaction may occur during co-pyrolysis. The impact of the second material on pyrolysis was investigated for the yield of products and characterization of top phase oil. The maximum top phase oil yield, the largest amount of aliphatic, and the highest heating value are observed in the mixture which contains 15% poplar sawdust. Sewage sludge contains high content of ash, which plays a critical role as a catalyzer in this co-pyrolysis reaction. The synergistic reaction occurs during co-pyrolysis of sewage sludge and poplar sawdust.

Zhu et al (2015) studied the thermogravimetric analysis of sewage sludge, pine sawdust, and their blends in a nitrogen atmosphere at a heating rate of 10, 20, and 30 °C/min. The pine sawdust and sewage sludge blends are prepared in ratios of 25-75%, 50-50%, and 75-25% proportions. Three thermal stages were identified in pyrolysis pure sewage sludge and pine sawdust and as well as their blends. The co-pyrolysis improves the devolatilization properties of sewage sludge and with increasing proportions of pine sawdust, the initial degradation temperature was increased. In conclusion, no significant synergy is observed in pyrolytic characteristics which are calculated from that of pure materials. The Friedman equation and distributed activation energy model (DAEM) are used to evaluate kinetic parameters such as activation energy and frequency factor. Both the results are in good agreement with low deviation which supports the validity of DAEM results. Moreover, the yield of the solid residue, bio-char, is studied at three heating rates for all blending ratios of feedstock. It shows strong linear distributions between bio-char yield and the blending ratios.

Xu et al (2017) investigated municipal sewage sludge and hazelnut shell co-pyrolysis characteristics by using multiple heating rates (5, 10, 15, 20, 30 °C/min) and various mixing ratios (0, 5, 10, 15, 20, 30, and 100% hazelnut shell in mixture) in TG-DTG. The activation energy was estimated by using DAEM (Distributed activation energy model). The degradation behavior of mixtures was similar to sewage sludge rather than that of hazelnut shells. There are mainly four stages are observed for degradation. The accelerative interaction between two materials was observed between 450 to 900 °C while inhibitive interaction was observed between 260 to 400 °C. The physical and chemical characterization of solid residue generated after pyrolysis were analyzed with SEM (Scanning Electron Microscopy) and FTIR (Fourier transform infrared) spectra. Development of porous structure, nucleation, and crystallization was observed in bio-char samples. A significant increase in surface area in bio-char of co-pyrolysis was observed.

Huang et al (2015) investigated co-pyrolysis of sewage sludge and rice straw by applying microwave heating. Pyrolysis of sewage sludge conducted at a various power input of microwave which signifies only drying or overheating. Upon the addition of rice straw in sewage sludge, the performance of microwave heating was improved. Proximate and ultimate analysis, SEM analysis, surface characterization by BET (Brunauer-Emmett-Teller) method was analyzed for raw and pyrolyzed sewage sludge and rice straw. Thermogravimetric study of sewage sludge, rice straw, and 1:1 mixture was investigated at

a heating rate of 20 °C and summarized pyrolysis characteristics. Very slow rates of degradation were observed in TGA. The degradation of the mixture was low compared to the predicted value based on sewage sludge and rice straw. The controlled amount of straw addition is beneficial in the co-pyrolysis of raw materials to absorb microwave heating. The mixture of 20% rice straw with sludge was observed to absorb more microwave energy and the temperature is 500 °C.

Zhang et al. (2015) investigated experiments on co-pyrolysis of sewage sludge with rice husk in a vacuum fixed bed reactor to study the synergetic effects. Anaerobically digested sludge from the wastewater treatment plant is used for the study. Sewage sludge, rice husk, and its blend (1:1) are pyrolyzed at 900 °C for 2 h. Volatile products were pumped out, gases and solids (bio-char) were collected and analyzed. In this study, the synergetic effect was analyzed by evaluating the deviation between calculated and experimental values. Synergy is obtained in form of more char gasification during co-pyrolysis which leads to the reduction in solids yield and gas yield increase. The BET surface area of bio-char of mixture was very low (85.1%) than the predicted value. The deviation for hydrogen, carbon dioxide, and carbon monoxide fractions reported the synergetic effect. The fraction of CO and H₂ were higher and a fraction of CO₂ was lower than the predicted value. Alkali and alkaline metals of sewage sludge and rice husk might act as catalysts and advance gasification.

2.7 Sugarcane bagasse: Potential biomass for co-pyrolysis

India is one of the leading sugarcane (and sugar) producing countries in the world. The Indian sugar industry has witnessed tremendous growth in the past 60 years without any impediments. India currently ranks second in the cultivation area (5.11 million ha) and sugarcane production (303.83 million tonnes) next to Brazil. The major solid waste streams generated in the sugar manufacturing process include sugarcane trash, sugarcane bagasse (SCB), press mud cake (PMC) and SCB fly ash. Sugarcane bagasse (SCB) is the dry fibrous residue obtained after sugarcane crushing and juice extraction. In the crushing season 2018–19, SCB production was 91.15 million tonnes in India, respectively (Cooperative Sugar, 2019). It is almost 30% of sugarcane plant production. Its composition is 40-50% cellulose, 19-25% hemicellulose, 17-25% lignin and 2-4% ash (Abhilash & Singh, 2008).

The current SCB utilization approach in India is restricted to cogeneration (of steam & power) where SCB is used as a fuel source for boilers in sugar industries. But this is not fully used as a source of energy in sugar industries, because it creates the waste management problem at the industry site. Moreover, the efficiency of SCB in direct combustion is only 26% as well as airborne fly ash formed due to the burning of SCB in the boilers which is accountable for major health hazards. So, considering the valorization potential of SCB, cogeneration is not the best option (although mature). There is a limitation on the use of SCB for cogeneration due to the diminishing market price of electricity also. In the future, the economics of sugar industries will not only depend on sugar, ethanol, and cogeneration but will also depend on the optimal use of (waste) resources available within the industry. The current total installed capacity of these cogeneration plants in India is 9200 MW. Despite its use in boilers, a significant amount of SCB remains as waste. Therefore, there is a need to identify other valorization routes that can help in effective SCB management with a surplus economic gain. SCB can be used as a renewable source for high-density biofuels production through energy-efficient and cost-effective thermochemical conversion processes such as gasification, pyrolysis, etc. A preliminary review of the literature indicates that SCB can serve as a potential feedstock for the low-cost production of green chemicals and fuels. This is mainly attributed to its abundant availability making its supply constant and stable. Moreover, high-value co-product and biofuel production from SCB and other types of biomass waste is explored (Solomon, 2011).

Various researchers reported the proximate and ultimate analysis of SCB in literature to investigate its fuel properties and its potential to be used as fuels. (Varma & Mondal, 2017; Islam et al., 2010; Leal et al., 2013; Kumar et al., 2017). The range of the volatile matter and ash content was observed to be 76%-86% and 2%-5%, respectively. The data shows that the composition of SCB varies depending on its source and sugar processing. The average gross calorific value (GCV) of bagasse was found to be 16.7 MJ/kg and is comparable to that of firewood and lignite coal. The SCB has high energy content and is available abundantly in India. So, it has the potential to be utilized as feedstock for pyrolysis. (Varma & Mondal, 2017).

Table 2.10 summarizes some studies available on the pyrolysis of SCB in various researches. Different types of pyrolysis processes such as fast, slow, and vacuum pyrolysis for bio-fuel generation are studied. Many studies have investigated the effect of temperature on pyrolysis products yield and physic-chemical properties of bio-oil, bio-

char, and gas. The maximum yield of bio-oil observed in various studies is in the range of 40% to 45% and heating value in the range of 24 to 28 MJ/kg which demonstrates that the useful energy production from the sugarcane bagasse, a solid waste. Based on the proximate analysis of sugarcane bagasse, studies on bio-oil production by pyrolysis of sugarcane bagasse, and a large quantity of bagasse available, it has a vast potential to be used as a second material for co-pyrolysis with Municipal sewage sludge.

Table 2.10 Studies on pyrolysis of SCB reported in the literature

Type of reactor	Temperature (°C)	Heating rate (°C/min)	Key study	Reference
Induction Heating	400-800	100-500	The yield of products, Bio-oil properties	Tsai et al., 2006
Fixed bed tubular	400-550	25	The yield of products, Bio-oil properties	Parihar et al., 2007
Fixed bed	300-600	50	The yield of products, Bio-oil properties	Asadullah et al., 2007
Fluidized bed	400-500	100	The yield of products, Bio-oil properties	Islam et al., 2010
Quartz tube	350-530	9-23	The yield of products, Bio-char properties	Carrier et al., 2011
Batch Reactor	400-600	--	The yield of products, Bio-oil properties	Mantilla et al., 2014
Semi batch Reactor	350-650	10-50	The yield of products, Products analysis	Varma & Mondal, 2017

2.8 Co-pyrolysis of MSS and SCB

The synergy between two materials in co-pyrolysis is still in discussion and requires comprehensive study. The in-depth study on co-pyrolysis of MSS and SCB which include kinetics, product yield, and characterization is little reported. In this study, the co-pyrolysis of MSS and SCB have been carried out with the aim of assessing the feasibility of their combined pyrolysis. The thermal behavior of MSS and SCB and their blends are scientifically investigated with the objective to understand behavior and interactions in terms of thermodynamic and kinetic parameters. The co-pyrolysis experiments of MSS and SCB were carried out in a thermogravimetric analyzer and fixed bed batch reactor to study the synergetic effect. The synergies between these two feedstocks have been explored in the mechanism of pyrolysis, concerning both the yield of product fractions and the composition of the bio-oil. Due to the high ash content of sewage sludge, significant interactions are expected which lead the secondary reactions due to the catalytic effect. The secondary reactions involve bio-oil components, such as dehydration, cracking, and dehydrogenation (Ding and Jiang, 2013), and therefore the bio-oil yield is significantly affected (Samanya et al., 2012). The characterization of the solid residue, bio-char,

produced by co-pyrolysis was studied by FTIR and SEM analysis to determine the physical and chemical characterization. The activation energy of the co-pyrolysis was obtained by the Arrhenius model.

2.9 Kinetic study of pyrolysis/Co-pyrolysis

Fundamentally, understanding the thermal degradation in co-pyrolysis of MSS and SCB is very important. The kinetic study of co-pyrolysis is intrinsically related to the mechanism of degradation of feedstock. Therefore, it is very essential to study the TGA (thermogravimetric analysis) to understand the kinetic mechanism of the MSS and SCB mixture. Thermogravimetric Analysis is frequently used to evaluate the solid-phase thermal degradation and is also a useful technique to estimate the kinetic parameters such as Activation energy (E), pre-exponential factor (A), and order of reaction model (n). TGA is considered a common analysis technique to investigate thermal behavior and kinetics. TGA study involves measuring the amount of mass degraded versus the temperature at regular time intervals. The advantages of the TGA method are real-time sample mass measurements, high reproducibility, and well-defined temperature and gas-phase conditions (Mueller et al., 2015; Shen et al., 2018). There are many methods for determining the non-isothermal solid-state kinetic data from TGA (Słopiecka et al., 2012). The rate law expression which obeys the fundamental Arrhenius equation is used to study the kinetics of pyrolysis reaction. Arrhenius equation is model fitting and model-free methods. Model fitting methods involve the various models used to find the best fit and based on that the kinetic parameters are evaluated. These methods are widely used for solid-phase reactions due to the direct determination of kinetic parameters from a single TG measurement. In model-free methods, the kinetic parameters can be evaluated at a specific degree of conversion. The major advantage of these methods is fewer errors and simplicity with kinetic models (Opferman et al., 2002).

Various studies have been reported in past to evaluate the decomposition kinetics of biomass, plastic, sewage sludge, and other organic waste using TGA. Furthermore, many investigations are reported for co-pyrolysis of a mixture of biomass and plastic, sewage and biomass, etc. As per the various literature on TG studies, degradation of cellulosic biomass and solids is a series of a large number of reactions and is reported as first-order kinetics (Naqvi et al., 2019). The solid-state reactions are reported as



The solid-state kinetics have been described through the Arrhenius equation as (2.1)

$$k = A e^{\frac{-E}{RT}} \quad (2.1)$$

Where A is the pre-exponential (frequency) factor. E is the activation energy and R is the universal gas constant and T is the absolute temperature.

The various studies are reported on co-pyrolysis of sewage sludge with different biomass, e.g. lignocellulosic biomass, rice straw, bagasse, pine sawdust, etc. Lin et al., (2018A) evaluated the kinetic models for sewage sludge, sugarcane bagasse, and their mixtures by using the M-DAEM (Multiple normal distributed activation energy models). Change in activation energies was reported for the mixture of sewage sludge and bagasse at a heating rate of 20 °C per minute. The kinetic models are compared with experimental data which results in similar values of R² higher than 99%.

Co-pyrolysis behavior and kinetics of sewage sludge and pine sawdust blends under non-isothermal conditions have been studied by TGA using Friedman and Distributed activation energy model (DAEM). The average values of apparent activation energy for the three blends calculated by the Friedman method and DAEM were 152.39-175.39 and 148.05-172.72 kJ mol⁻¹, respectively. It was also observed that the apparent activation energy of sewage sludge does not change significantly in the presence of biomass, and the effect of adding sewage sludge with biomass was also very slight (Zhu et al, 2015).

Lin et al. (2016) studied Co-pyrolysis kinetics of a mixture of sewage sludge and oil shale thermal decomposition using TGA-FTIR analysis and compared with individual materials. From the results, it was found that the blending of both materials improves the pyrolysis performance. At 10% blending of sewage sludge with oil shale, activation energy was declined by about 11.11%. The kinetics and thermodynamic potential of co-pyrolysis of sewage sludge and rice husk were studied by using TGA following multiple reaction mechanisms. For two temperature regions (200-400 °C) and (400-600 °C), the descending sequence of R² for kinetics and thermodynamic parameters during the co-pyrolysis process was; diffusion > chemical reaction > phase interfacial reaction > nucleation > power law. The addition of rice husk in sewage sludge in co-pyrolysis is a promising and eco-friendly process to recover organic materials (Naqvi et al., 2019).

In the study of co-pyrolysis of sewage sludge and rice straw, it was found that the parameters are not just simple summation calculation but existing some synergistic or coupling effects to accelerate the release of volatile matter. The result of the kinetic analysis shows that first-order reaction together with Arrhenius law accounts for the

volatile matter release stages of sewage sludge, rice straw, and their blends quite satisfactorily. And the kinetic compensation effect was found (Zhang et al., 2009).

From the above, it can be suggested that the co-pyrolysis kinetics had gained a lot of importance in the last decades due to certain synergistic effects such as higher quantity and better quality of product, limited supply of certain feedstock, and improving the overall pyrolysis process.

2.10 Bio-char: Physicochemical Properties and applications

Pyrolysis is a thermal degradation of solid waste materials in an absence of oxygen and producing products such as bio-oil, syngas, and solid residue. There are many applications of the bio-oil produced through the pyrolysis of sludge as well as co-pyrolysis of sludge with waste biomass, the solid fraction called bio-char has also been found to have many useful applications. Bio-char signifies the porous carbonaceous solids produced by the pyrolysis of organic materials in an oxygen-deficient atmosphere and have suitable physical and chemical properties for safe and long-term storage of carbon in the environment (EBC 2012). The term bio-char is defined as the solid product of biomass pyrolysis is also applicable for sewage sludge. Nowadays, bio-char is considered as a multifunctional material that has applications in carbon sequestration, contaminant immobilization, GHG (Greenhouse gas) reduction, soil fertilization, and wastewater treatments (Ahmad et al., 2012; Awad et al., 2012; Bolan et al. 2012; Lehmann and Joseph 2009).

The bio-char provides an exceptional platform for the removal of contaminants and the chemical composition of bio-char depends on the type of feedstock and operating conditions. Bio-char containing mainly organic (mainly carbon) and inorganic fractions (Minerals such as Ca, Mg, K, and inorganic carbonates) depend on the type of feedstock. It is difficult to define the exact chemical composition of bio-char (Lehmann and Joseph 2009). International Bio-char Initiative (IBI) published various standards which include a working definition of bio-char and methods for the analysis of bio-char. Generally, the characterization of bio-char is investigated mainly to serve four purposes namely soil improvement, waste management, climate change mitigation, and energy production. The physicochemical properties of bio-char are discussed in the following sections.

2.10.1 Total organic carbon

One of the important properties of bio-char is its total carbon content or organic carbon content which is primarily stored in recalcitrant condensed aromatic rings with some reactive functional groups (Xu et al., 2012). The carbon content of bio-char is found in the range of 36-94%, depending upon the feedstock and temperature of pyrolysis (Keiluweit et al., 2010; Novak et al., 2009). The carbon content is observed in the range of 60-95% and 50-70% for lower temperature pyrolysis of wood and nutshells, respectively (Mukome and Parikh 2013). For lower temperature pyrolysis bio-char. Due to the high carbon content of bio-char, it has a significant potential to serve as a soil conditioner to improve the physicochemical and biological properties of soils. The water retention capacity of bio-char increases with an increase in organic carbon. About an 18% increase in the water holding capacity of soil with the use of bio-char (Glaser et al., 2002). The organic carbon content of bio-char is mainly dependent upon the type of feedstock and the pyrolysis operating conditions and about 50% of organic carbon of feedstock would be stored in bio-char (Sohi et al., 2010).

2.10.2 Carbon/Nitrogen ratio

One of the most important parameters for soil improvement is the C/N ratio which signifies the mineralization and nitrogen release in soils. The typical adequate value of the C/N ratio for soil amendments is 20:1 which is normally found in manures and composts. But the C/N ratio value of about 12:1 is many times a preferred value to increase the nitrogen pool in plants. The C/N value for bio-char varies widely in the range of 8 to 1500 (Enders et al., 2012; Keiluweit et al., 2010; Mutanda et al., 2011), which shows that many bio-chars are effectively used to increase nitrogen immobilization in soil. Although feedstock for pyrolysis and temperature are the most important parameters impacting the C/N ratio of bio-char.

2.10.3 Bio-char pH

The pH of bio-char is a measure of the acidity or alkalinity and one of the important properties of bio-char. The pH of mostly all bio-char is alkaline (more than 7) and the use of this bio-char increases the pH of the soil and affects the mobility of cations in the soil (Lehman and Joseph, 2009; VanZwieten et al., 2010). Bio-char pH is affected by the

pyrolysis process and temperature. The alkaline nature of bio-char is due to the presence of carbonates and chlorides of potassium and calcium, oxygen-containing compounds, etc. (Montes-Moran et al., 2004).

2.10.4 Cation Exchange Capacity (CEC)

CEC is an important measure of soil quality and productivity. It is the measure of exchangeable cations such as Ca^{+2} , Mg^{+2} , K^{+} , Na^{+} , etc. The CEC value of bio-char is dependent on the feedstock and temperature of pyrolysis. As the surface of bio-char is negatively charged, the amendments of soil by addition of bio-char have shown to increase the soil CEC. (Liang et al., 2006).

2.10.5 Potential Environmental Concern

Although bio-char is beneficial for cropping systems, soil improvement, and climates, the use of bio-char also leads to some disadvantages. Bio-char contains organic compounds which adversely effects on growth of crops and soil. There are several toxic compounds are generated during the production of pyrolysis. Many volatile components condensed on the surface bio-char as they cool which are generally considered undesirable and toxic but it is still not known the effect of these compounds on the quality of bio-char.

2.10.6 Surface Characterization

The potential application of bio-char in carbon sequestration, GHG (greenhouse gas) emission reduction, water retention, and sorption of contaminants are mainly dependent on the surface properties of bio-char. There have been many numbers of studies that investigated the physical and chemical properties of bio-char. They mainly studied the surface area, porosity, surface morphology, and presence of the functional group.

2.10.6.1 Surface area

The BET (Brunauer-Emmette-Teller) surface area is area per gram of sample and is typically measured by assuming monolayer physical sorption of a gas (N_2 and CO_2) onto the bio-char surface at the temperature of liquid nitrogen at 77 K. Various studies shows the bio-char has typically high surface area than the soil and there is a positive correlation

between the surface area of bio-char and pyrolysis temperature (Keiluweit et al., 2010; Kookana et al., 2011). The other parameters which may affect bio-char properties are heating rate, pressure, and retention time (Chun et al., 2004). In general, with pyrolysis temperature the surface area of bio-char is increases. But surface area reduction with temperature is also reported (Uchimiya et al., 2011). Demolition of ester and alkyl groups and exposure of the aromatic lignin core may be responsible for the increase in surface area (Chen and Chen, 2009). The range of value of the surface area for bio-char prepared from various feedstock like waste agriculture biomass, sewage sludge, etc. was between 2-5 to 400-500 m²/g.

2.10.6.2 Porosity

Porosity involves the regions of the bio-char particles that are not filled by solids. Bio-char porosity is mainly classified as micropore, macropores, and mesopores depending on the size of bio-char particles. As per IUPAC, pore size less than 2 nm is defined as micropores and more than 50 nm size is defined as macropores. The size between 2 to 50 nm is classified as mesopores. The high sorption capacity such as retention of water, gases, heavy metals, organics, and nutrients are due to the micropore size.

2.10.6.3 Morphology

Morphology is a bulk measure of the size, shape, and structure of the bio-char. This characteristic is normally obtained as an image of the bio-char surface and it depends on pyrolysis feedstock and operating temperature. SEM (Scanning Electron Microscopy) is used to characterize the surface morphology.

2.10.6.4 Functional groups present

The chemistry of the functional group present on the surface of bio-char is very important to predict and understand how the bio-char will react in the soil as well as other organic materials. The addition of bio-char to solid shows the increase in sorption of heavy metals (Johanson and Edger 2006), pesticides (Spokas, 2010), and PHAs (Zhang et al., 2010). However, to predict which bio-char is best suited for a binding specific class of components, the characterization of bio-char is very critical for the assessment of the sorption process.

To characterize the bio-char, Fourier Transform Infrared (FTIR) and Nuclear magnetic resonance (NMR) spectroscopies are used. The FTIR results for various bio-char shows the presence of various functional groups and the effect of temperature on their presence. The complete list of functional groups present is described in one of the studies of characterization of bio-char (Parikh et al., 2014). The impact of pyrolysis temperature on the change of various functional groups is also reported (Keiluweit et al., 2010; Peng et al., 2011). The results of spectroscopy would be important for understanding the mechanism for interaction of bio-char with soil, organic and inorganic compounds of soil, and wastewater. For example, bio-char with a significant contribution of carboxyl and hydroxyl group have a high sorption capacity for cations and metals. High aromatic bio-char is hydrophobic and has an affinity for various organic compounds. Therefore, with knowledge of the functional groups present, bio-char can potentially be selected for a variety of desired agronomic or environmental impacts.

2.11 Bio-char application for wastewater treatment as adsorbent

Carbonaceous materials like bio-char have been used for the removal of organic and inorganic components in soil and water. Activated carbon reported to be is prepared to increase microporosity and surface area from this kind of carbonaceous material. Bio-char was quite similar to activated carbon as it has been produced by pyrolysis with medium to high surface area (Cao et al., 2011). Additionally, bio-char composition showed O-containing carboxyl, hydroxyl, and phenolic surface group compounds which were highly responsible for effective interaction with soil and water contaminants (organic and inorganic). These multifunctional characteristics of bio-char showed the potential of bio-char to use as sorbent for organic and inorganic contaminants from soil and water. Here we mainly discuss the bio-char used for the removal of heavy metals and organic contaminants.

Various activation methods were applied to prepare activated bio-char which alters the chemistry of bio-char. HCl, HNO₃, KOH, NaOH, KMnO₄, etc. are applied to modify bio-char for different purposes (Wang et al., 2015; Cha et al., 2016; Wang et al., 2017). The chemically activated bio-char had a higher surface area, porous structure, functional group improvement, and improved adsorption capacity (Yang et al., 2019). Chemically activated bio-char using H₃PO₄ at a moderate temperature generated a higher surface area up to 1500 m²/g with a mesoporous structure. (Molina-Sabio et al., 1995; Patnukao and Pavasant,

2008; Arami-Niya et al., 2010). Moreover, enhancement in porosity of bio-char was reported in various studies of bio-char which was activated by using phosphoric acid. (Diao et al., 2002; Jagtoyen and Derbyshire, 1998; Suarez-Garcia et al., 2002; Vernersson et al., 2002). As per our knowledge, MSS-SCB co-pyrolysed activated bio-char and its application for the treatment of wastewater from pulp and paper industry mills were rarely reported.

As per the above discussion, bio-char is effective adsorbent used to remove or reduce various pollutants from wastewater due to their large surface area and plentiful functional groups on the surface. Thus, bio-char became extensively important to be used to reduce or remove pollutants from industrial and agricultural fields to improve the quality of the environment (Wang et al., 2017). Wastewater in process industries, commercial or agricultural processes is a universal challenge. Activated carbon was a preferred adsorbent to remove organics from wastewater due to its large surface area and chemical functional group present on the surface (Chern and Chien 2003). However, activated carbon was not fully applicable for wastewater treatment due to its high cost for preparation and regeneration (Ali and Gupta 2006). Demand for developing low-cost activated carbon is increasing. Due to the similar physico-chemical properties, carbonaceous adsorbent, bio-char, have gained more interest. Bio-char prepared from various solid wastes has great potential for the treatment of wastewater. There were various studies where bio-char was used for the treatment of wastewater from the industry, commercial, and agriculture sector. The major contaminants in industrial wastewater generated in various chemical industries are heavy metals and organic matter. A bio-char and chitosan mixture were an effective adsorbent for the removal of copper, lead, arsenic, cadmium, and other heavy metals in industrial wastewater (Hussain et al., 2017). Bio-char prepared by pyrolysis of sugarcane bagasse was applied to remove lead from wastewater (Poonam et al., 2018). Papermill sludge-produced bio-char was applied to remove As^{+5} and the maximum adsorptive capacity was 252.31 mg/g (Cho et al., 2017). Bio-char prepared from banana peels was studied to remove Pb^{+2} and found adsorption capacity of 359 mg/g and 193 mg/g (Zhou et al., 2017). Various nutrients from dairy-based effluent were adsorbed on bio-char prepared from agriculture waste biomass. 20-43% and 19-65% adsorption of ammonium and phosphate were observed, respectively (Ghezzehei et al., 2014).

Use of bio-char in municipal wastewater treatment observed in removal of ammonium by using the bio-char which was prepared from secondary sludge. The adsorption was controlled by chemisorption. (Tang et al., 2019). Bio-char either separate or combined with

a biofilter was used to recover nitrogen and phosphorous from municipal wastewater (Cole et al., 2017). Bio-char derived from municipal waste was used in the bio-filtration step. The reduction in COD and TSS has observed 90 and 89 percentages, respectively (Manyuchi et al., 2018). Bio-char prepared from sludge was used as an adsorbent with a catalyst to reduce total organic carbon by oxidation. Bio-char influenced the oxidation by forming hydroxyl radical and mineralized carbon fraction of wastewater contaminants (Chen et al., 2019). Thus far, most research on bio-char application in wastewater treatment were conducted at a laboratory scale, further research and implementation in commercial applications are needed.

Bio-char, a solid residue of the pyrolysis process, was an efficient and low-cost adsorbent that was prepared from a variety of waste biomass includes agriculture residues, sewage sludge, manures, municipal solid waste, and thus has been used in wastewater treatment. The present study addresses the chemical activation method (using phosphoric acid) for the activation of the residue (bio-char) generated from the co-pyrolysis of MSS and SCB. The resulting activated bio-char was characterized for surface area, total pore volume, and average diameter. Moreover, porosity and the functional group were analyzed with the use of SEM and FTIR, respectively. Further, activated bio-char was tested for removal of COD and color of secondary treated pulp and paper industry wastewater. Besides this, data were analyzed using Langmuir and Freundlich isotherm model to obtained equilibrium.

2.12 Composition of un-condensable gases from MSS pyrolysis

The complex composition of pyrolysis gases and heating values are displayed in Table 2. The main sludge pyrolysis gas components are CO₂, CO, H₂, and CH₄ with their sum being almost 90 vol. %. The rest of the pyrolysis gases are composed of hydrocarbons, nitrogen, and other minor compounds.

Table 2.11 Composition and heating value of pyrolysis gases from sewage sludge (Mosko et al., 2020)

Pyrolysis Temperature, °C	400	500	600	700	800
Gas Composition (vol %)					
CO ₂	62.3	49.5	38.1	29.1	23.6
H ₂	10.0	20.6	25.3	26.5	27.9
CO	8.24	8.59	12.6	18.4	24.5
CH ₄	7.81	11.2	12.7	12.2	10.7
N ₂	0.0930	0.0424	1.62	3.61	5.0
H/C	8.93	8.29	7.88	9.01	7.62
Others	2.70	1.81	1.86	1.21	0.73
HHV (MJ/m³)	17.0	17.8	19.1	20.1	18.2

2.13 Gas composition during the co-pyrolysis process

The change of the gas composition was reported at different wheat straw addition percentages during pyrolysis at 600 °C (Wang et al., 2016). It was investigated that uncondensable gases (vol%) produced during the pyrolysis of sewage sludge contain CO₂, CO, H₂, CH₄, and C₂H_m (i.e. C₂H₂, C₂H₄, C₂H₆) about 36.2, 26.1, 9.5, 14.1, and 14.0 vol. % respectively; while as to wheat straw pyrolysis, those were 33.5, 42.6, 6.9, 11.6, and 5.4 vol.% respectively. This comparison proves that wheat straw pyrolysis tends to produce more gas, because the CO₂, CO, H₂, CH₄, and C₂H_m volume contents from the pyrolysis of sewage sludge are less than wheat straw pyrolysis. The CO volume content of gas from wheat straw pyrolysis was higher than the pyrolysis of sewage sludge by 16.5 vol.%, while the volume content of CO₂ from wheat straw pyrolysis was lower than sewage sludge pyrolysis. These differences in gas component contents were explained on the basis of the chemical composition of materials. Experimental values were compared with theoretically calculated upon addition of wheat straw (percentage of 0 and 100 wt.%), the theoretically calculated gas compositions with the wheat straw addition percentages of 20, 40, 60, and 80 wt.% were determined, plotted and compared with experimental results. As observed for all the wheat straw addition percentages, the differences for the volume content of CO₂, CH₄ and C₂H_m between the theoretical calculation and experimental measurement were little. The synergetic effect of co-pyrolysis on CH₄ and C₂H_m was observed to be weak, whereas the synergetic effect on CO, CO₂, and H₂ producing was indeed observed. The authors investigated the existence of a synergetic effect on the gas producing during the co-pyrolysis process of sewage sludge and wheat straw. The synergetic effect was analyzed to be complicated and showed different impacts on each gas component. Generally, the synergetic effect in the co-pyrolysis of sewage sludge and wheat straw promotes the formation of CO₂ and H₂, inhibits the formation of CO, but takes little influence on the formations of CH₄ and C₂H_m.

CHAPTER 3

Kinetic Study for Co-pyrolysis of Municipal Sewage Sludge with Sugarcane Bagasse

3.1 Introduction

3.1.1 Management of municipal sewage sludge

In view of the higher growth rate of population, urbanization, and industrialization in India, the generation of sewage is expected to increase at a faster rate, which will, in turn, lead to a generation of massive quantities of municipal sewage sludge (MSS) from the sewage treatment plant (STP). The Ministry of Environment, Forest, and Climate Change of India reported generation of sewage water close to 61,948 million liters per day (MLD) with an equivalent amount of sludge from the Indian urban area in 2018 (MoEFCC, 2019). The quantity of dry sludge produced from conventional sewage treatment plants was reported to be 55 to 170 kg per million-liter treatment of sewage water (Karia and Christian, 2013). Accordingly, annual MSS generation purely from the urban areas of India is estimated to be nearly 4 million metric tonnes. The management of MSS is a difficult and expensive issue. Due to major environmental concerns such as huge space requirement and leachate contamination in soil, landfilling of MSS is not a preferred solution (Cao et al., 2010), while land application as a fertilizer leads to toxic metals accumulation in soil (Vasseur et al., 1999). Incineration had been investigated as an efficient route for the resourceful disposal of waste. However, a huge cost for pretreatment and pollution control is not a preferred option (Manara and Zabaniotou, 2012). Hence, increasing generation of MSS needs a technique providing the techno-economic feasible solution for its proper disposal.

3.1.2 Sugarcane bagasse - Potential biomass

Industrial biomass residue, e.g., sugarcane bagasse (SCB), a by-product generated from sugar manufacturing, is anticipated to be produced in huge quantities in India. In India, nearly 75-90 million tons of SCB produces annually from 377 million tons of sugarcane (Sugarcane statistics, 2020; Quereshi et al., 2020). SCB is mainly utilized as boiler fuel at sugar mills itself in cogeneration power plants during the 180 days of sugarcane crushing season in India with surplus quantities, typically 3-4% of the cane crushed, required to be stored in the offseason (Yadav et al., 2011; Umamaheswaran and Batra, 2008). Thus, there is a need to explore resource recovery from a surplus quantity of SCB.

3.1.3 Co-pyrolysis of MSS and SCB

To refer to the resource recovery potential of available massive quantities of MSS and SCB in India, the co-pyrolysis study of these both the materials evaluated for their thermal behavior to explore their useful potential, e.g., recovery of chemicals and replacement of fossil fuels. Pyrolysis is one of the thermal decomposition methods used to recover energy from sewage sludge and biomass. It has attracted lots of attention from researchers (Jahirul, 2012; Demirbas, 2005; Kim and Parker, 2008). It is a method that occurs in an oxygen-deficient environment for the decomposition of the organic mass of biomass (i.e., MSS and SCB), leading to a reduction in the volume of the biomass and stabilization of the organic mass. It produces high valued products, i.e. dark brown liquid (also known as bio-oil), char, and gaseous fuel (Bilgen, 2016; Henkel et al., 2016; Hossain and Davies, 2013). Different proportions of these products were investigated at various conditions, e.g., type of pyrolysis (slow or fast), the configuration of reactor (augur, batch, etc.), catalyst, medium (N₂, argon, etc.), feedstock, etc. (Li et al., 2004). Flash pyrolysis of sewage sludge studied at 500 °C to decompose the organic content (proteins, lipids, and carbohydrates) of the sewage sludge, yielded 43 % wt. bio-oil (Pokorna, 2009). The high energy density of bio-oil is exhibited as a potential fuel and its oxygenates content supports application as a fertilizer and resins (Inguanzo et al., 2002). Furthermore, pyrolysis of sludge demonstrated residue generation with a stabilized carbonaceous matrix (Caballero et al., 1997).

Nevertheless, the bio-oil obtained from only-MSS pyrolysis is a complex mixture of oxygenates, water, and hydrocarbons, which imparts heterogeneity, leading to instability.

Moreover, nitrogen and Sulphur-containing compounds in the bio-oil lead to the issue of NO_x and SO₂ emission in exhaust gases and limit its application as a fuel (Fonts et al., 2012). Thus, the up-gradation of bio-oil is needed by reducing oxygenates along with nitrogen and Sulphur-containing compounds (Tsai et al., 2007). Sewage sludge exhibited typical characteristics, i.e., high ash and low heating value, whereas biomass contains lower ash and high heating value (Fonts et al, 2009A). Certain advantages offer through co-pyrolysis reported for sewage and rice-straw, i.e., yield and elevated heating value of bio-oil (Zhang et al., 2009).

The TGA has been used extensively by various researchers for the evolution of kinetic parameters, mainly activation energy, regression coefficient, and pre-exponential factor (Naqvi et al., 2019; Liu et al., 2015; Zhai et al., 2012; Conesa et al., 1997). To address in-depth co-pyrolysis operation at a larger scale, the study of kinetic is required to be determined. Various authors had investigated significant synergistic effects using sewage sludge with different biomass residues in co-pyrolysis, e.g. lignocellulosic biomass, rice straw through TGA (Zhang et al., 2009; Alvarez et al., 2015). Change in activation energies reported for the mixture of sewage sludge and bagasse at a heating rate of 20 °C per minute (Lin et al., 2018A). Moreover, noteworthy synergetic interaction between two materials, i.e. rice bran (low heating value) and plastics (high heating value material) was investigated by TGA and studied the change in activation energy, residue generation, and decomposition rate (Rotliwala and Parikh, 2011). In line with this, a comprehensive study on co-pyrolysis of MSS and SCB through TGA is little reported.

3.1.4 Objective of this work

To overcome the issues associated with the pyrolysis of only-MSS, the objective of the study was to evaluate the influence of the addition of sugarcane bagasse in co-pyrolysis with sewage sludge. Thus, the co-pyrolysis behavior and synergistic effect of these two materials were studied with the help of the thermogravimetric method along with its kinetics. However, the yield and characterization of the products will be discussed in further chapter 4.

3.2 Materials and Methods

3.2.1 Raw Materials

The raw materials used in this study were Municipal Sewage Sludge (MSS) and Sugar cane bagasse (SCB). Municipal Sewage Sludge was collected from the sewage treatment plant (STP) located at Vadodara, India. The sewage sludge is collected after the secondary treatment in the wastewater treatment plant. SCB was kindly provided by a sugar factory, namely Shree Khedut Sahakari Khand Udyog Mandli Ltd., Bardoli, India. Both the materials were separated from physical impurities and sun-dried for 10 days to get them free from moisture. After that, the raw materials were placed in the hot air oven at 105 °C for 24 h to remove the moisture till 5% of moisture in the material. The dry MSS and SCB were crushed in a grinder to get a powder form.



Fig. 3.1 Municipal Sewage Sludge



Fig. 3.2 Sugarcane bagasse



Fig. 3.3 Crushed MSS



Fig. 3.4 Crushed SCB

The powder materials were sieved using a BSS standard sieve to collect the particle size being less than 150 μm and stored in a desiccator. Before using for analysis, the samples of MSS and SCB (1:1) were blended in a ball mill for 20 min to achieve homogeneity. Fig. 3.1, 3.2, 3.3, and 3.4 show the pictorial representation of raw materials. The experiments discussed in Chapters 4 and 5 were based on the utilization of the same raw materials as discussed now.

3.2.2 Proximate and Ultimate analysis: Characterization of raw material

The proximate analysis, elemental analysis, and calorific value of MSS and SCB were done externally. Proximate analysis was carried out according to the ASTM D 3172-07a, which presents the information on moisture content, volatile matter, fixed carbon, and ash content. The ultimate analysis (elemental analysis) was carried out by CHNS elemental analyzer (Model - Vario Macro cube Elementar) using ASTM D5291 and D5373. It provides information about the elemental composition of carbon, hydrogen, nitrogen, and sulfur percentages while oxygen percentage was determined by difference. The calorific value of raw materials was determined by digital bomb calorimeter model RSB-5A/6/7 and the method was IS 1448-7(2004).

3.2.3 Thermogravimetric Analysis

10 mg of MSS, SCB, and their mixture (1:1 mass ratio) with a specified size was performed on a thermogravimetric analyzer (Mettler Toledo TGA/DSC1). Mass loss with temperature was determined in the temperature range of 30 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ in presence of argon (30 mL/min). Each run was performed in duplicate and the maximum deviation was stated $\pm 5\%$. Considering the limitation of the laboratory-scale batch pyrolysis reactor, the heating rate was settled at 10 $^{\circ}\text{C}/\text{min}$ to carry out a thermogravimetric analysis. Effect of heating rate on pyrolysis of various biomass feedstock investigated in the literature. They have shown a very common phenomenon during pyrolysis (Rotliwala and Parikh, 2011; Othman et al., 2010). This phenomenon mainly included shifting of peak temperature, increment in mass loss; the smaller amount of residue remaining in the solid-phase product, and change in activation energy. Moreover, little influence on the yield of

pyrolysis products and their composition was reported by various authors at the heating rate of 5 °C/s to 10000 °C/s (Montoya et al., 2017; Wang et al., 2019).

3.3 Results and Discussion

3.3.1 Characterization of raw materials

The proximate and ultimate analysis of the MSS and SCB is listed in Table 3.1. In contrast to MSS, it is observed that SCB has diverse properties. The ash content of SCB (3.4%) is much lower than that of MSS (51%). Moreover, SCB showed volatile matter and fixed carbon in the tune of 88.2% and 8% whereas MSS consist of 44.7% and 4%, respectively. Both materials have less than 1% moisture on a dry basis. The results of the proximate analysis are in agreement with the previously reported results (Alvarez et al., 2015; Lin et al., 2019; Zhao et al., 2018; Wang et al., 2016; Ruiz-Gomez et al., 2017). The high ash content of MSS is attributed to improving conversion efficiency during co-pyrolysis due to the presence of trace metals including catalytic elements such as K, Ni, Co, and Cu (Wang et al., 2016; Magdziarz and Wilk, 2013; Hao et al., 2018).

Table 3.1 Chemical composition of MSS and SCB

Properties	MSS	SCB
Proximate analysis (%wt)		
Volatile Matter	44.70	88.20
Fixed Carbon	4.00	8.00
Moisture	0.30	0.40
Ash	51.0	3.40
Ultimate Analysis (%wt)		
Carbon	23.44	41.80
Hydrogen	3.30	4.80
Nitrogen ^a	2.64	0.71
Oxygen ^b	70.62	52.69
H/C	1.18	1.45
O/C	1.13	0.47
High Heating Value (MJ/kg)	13.92	16.79

^a Dry, ash-free basis. ^bBy difference.

However, high ash can offensively affect the heating value of the material (Ruiz-Gomez et al., 2017). Higher content of oxygenates highlighted in both the materials, i.e. oxygen in MSS and SCB observed 70.6% and 52.69%, respectively. Abnisa et al. (2014) reported that the presence of high oxygen content is one of the factors in decreased calorific value of the fuel. Thus, the presence of more oxygen in MSS signifies that the obtained heating value of MSS is less than that of SCB. The heating value of SCB is 17% higher than that of MSS. Potential for bio-oil generation signifies by the contribution of carbon in MSS and

SCB assessed in the tune 21.44% and 41.8% whereas hydrogen content was 3.3 % and 4.8%, respectively. The nitrogen content of the MSS (2.64%) is higher as compared to SCB (0.71%). A negligible amount of sulfur content is reported in MSS and SCB (Zhu et al., 2015; Naqvi et al., 2019).

3.3.2 Thermal degradation of MSS, SCB, and their mixture

The characteristics of TG and DTG curves (Fig. 3.5(a) and 3.5(b)) showed three stages of decomposition, when only-MSS was present, whereas decomposition of SCB occurred in two stages. As shown in Table 3.2 profile of TG curves stated degradation of MSS, SCB, and their mixture nearly to the same temperature, i.e., 220-230 °C. As shown in Fig.3.5 (a) loss of traces of moisture present in materials is attributed to insignificant weight loss in the primary stage of degradation. The reason for a similar trend had been advanced for the thermal degradation of MSS, SCB, and their mixture for the slightly higher rate of heating (20 °C per minute) than that of the present study due to depolymerization reactions (Lin et al., 2017).

As shown in Fig. 3.5 (b) DTG curve showed three major mass loss peaks for only-MSS degradation credited to its chemical composition in order of lipids, protein followed by polysaccharides. Accordingly, as shown in Table 3.2 mainly signifies three stages, i.e. devolatilization (230-380 °C), stabilization (380-650 °C), and inorganic decomposition (650-775 °C). The degradation of lipids, proteins, and polysaccharides occurred in the overlapping temperature profile range of 227-557 °C (Alvarez et al., 2015). TG curve of MSS showed a wide flat shape profile, whereas SCB was observed to be a gradual process. SCB degradation refers to two major mass loss overlapping peaks in the DTG curve. As shown in Table 3.2 the first and second peak represents hemicellulose (300 °C) and cellulose (475 °C) followed by a sluggish rate of degradation of lignin (above 580 °C), respectively.

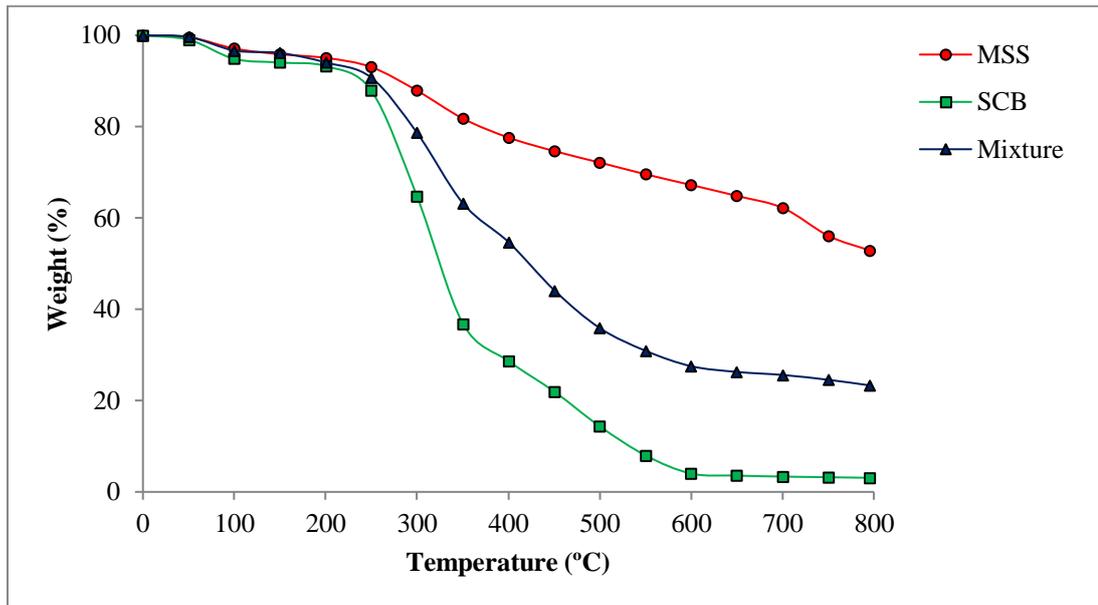
Table 3.2. Characteristics temperatures, residue generation, and maximum degradation rates of MSS, SCB, and their mixture

Material	1 st Stage		2 nd Stage		3 rd Stage		Residue generation wt%	Max % Degradation per min
	TR	PT	TR	PT	TR	PT		
MSS	230-380	325	380-650	475	650-775	750	52.86	2.7
SCB	200-375	300	380-580	475	--	--	3.08	5.2
MSS: SCB (50% wt)	220-370	320	370-625	410	625-750	700	23.31	4.2

TR: Temperature Range, °C; PT: Peak Temperature, °C

Thermogravimetry study of SCB under nitrogen at the different heating rates was earlier demonstrated in order of hemicelluloses, cellulose, and lignin (Gracia-Perez et al., 2001). Further to this, the small band was evident in TG and DTG curves at higher temperatures (650-750 °C) for only-MSS pyrolysis. This phenomenon might be attributed to the marginal decomposition in an inorganic matrix of ash content and resulting in the third stage. Similar reasoning had advanced for MSS thermal behavior (Zhu et al., 2015).

(a)



(b)

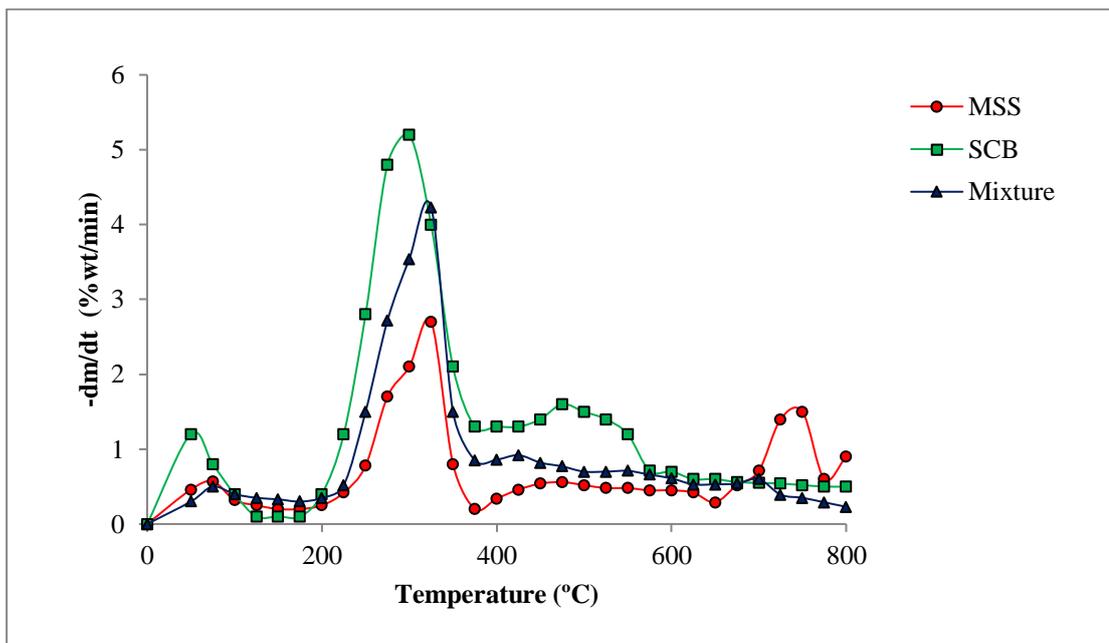


Fig. 3.5 The TGA (a) and DTG (b) curves for MSS, SCB, and Mixture

It can be seen from Table 3.2 that the maximum percentage degradation per minute increased by 55% for the mixtures as compared to that of only-MSS degradation (e.g., the maximum rate of mass loss for only-MSS was 2.7% and increased to 4.2% upon addition of SCB). Early-stage degradation of SCB resulting to metal-containing ash and catalytic effect of these metals might be responsible for higher devolatilization of MSS. Thus, the presence of SCB accelerates the decomposition rate of MSS. Moreover, the effect of SCB on higher devolatilization of MSS is depicted in Table 3.2. It shows that degradation of only MSS generated a larger quantity of residue, i.e., 52.86 wt % whereas; MSS-SCB co-processing produces less quantity of residue, i.e., 23.31 wt%. Thus, in contrast to only-MSS pyrolysis, co-processing offers a reduction in residue generation by 56%. During the primary stage degradation of SCB, resulting bio-oil might be encouraged MSS degradation leading to more volatile production from MSS itself. Also, it restricts the carbonization reactions that favor residue formation.

Thus, a reduction in residue generation was observed upon the addition of SCB in MSS. Similar reasoning had been advanced for lower residue formation in co-pyrolysis kinetic study of sewage sludge and bagasse at a heating rate of 20 °C per minute (Lin et al., 2018A). One of the researchers too had reported a reduction in residue formation for the co-pyrolysis mixture of MSS with rice straw and sawdust (Huang et al., 2017). Also, Table 3.2 shows that upon addition of SCB in MSS, co-processing mixture offers a shift of peak temperature (PT) to lower values by 2%, 13%, and 6% for first, the second, and third stages of degradation, respectively. Thus, upon the addition of SCB in MSS, co-pyrolysis offers a better synergistic effect in the second stage.

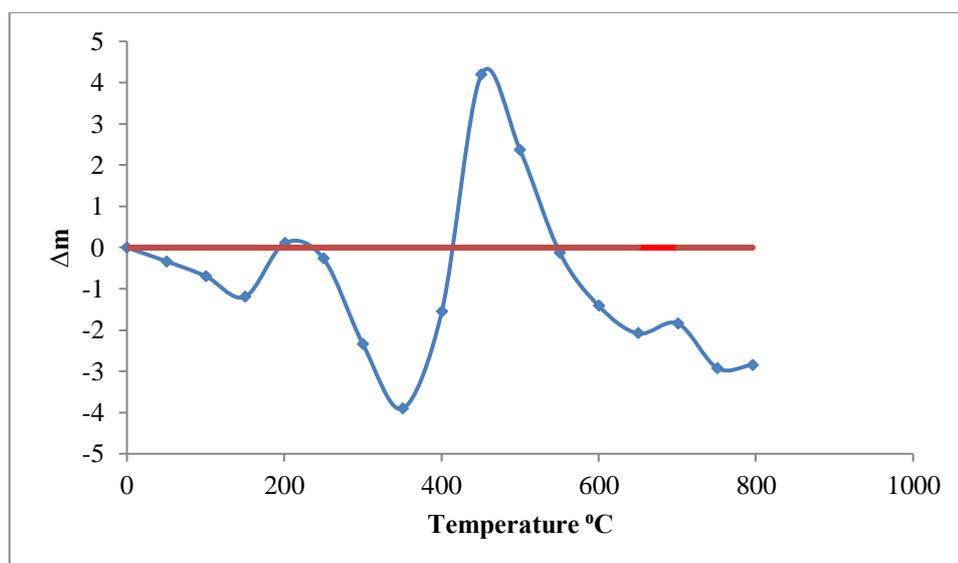


Fig. 3.6 Deviation in Δw for co-pyrolysis of MSS and SCB

Also, the synergistic effect or interaction between two materials was evaluated by calculating the weight loss difference, Δw as per the (3.1).

$$\Delta w = w_{mix} - (y_1 w_1 + y_2 w_2) \quad (3.1)$$

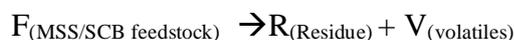
Where, w_{mix} is the mass loss of mixture of MSS and SCB (1:1) proportion, y_1 and y_2 are mass fraction of MSS and SCB in mixture respectively. w_1 and w_2 are mass loss of individual MSS and SCB respectively. Δw is described as the extent of synergistic effect or interaction in the co-pyrolysis of these two raw materials. Fig. 3.6 mentioned deviation in mass loss with change in temperature. The deviation in conversion for co-pyrolysis specifies synergy between two feedstocks. The negative interaction was observed during 200 - 350 °C while positive interaction occurred in the temperature range of 350 to 500 °C. The highest deviation in the value of Δw was observed during the temperature of 350 °C to 450 °C second stage of pyrolysis. Thus, a significant synergistic interaction could be achieved.

3.3.3 Kinetic Analysis

Thermal degradation of sewage sludge and biomass represents complex reactions and makes it difficult to achieve a precise model describing pyrolysis mechanisms. Thermogravimetry is the method providing ‘overall’ reaction kinetic, without referring to precise reactions. Thus, thermogravimetric analysis has been used extensively to obtain certain kinetic parameters (e.g. activation energy, etc.) without referring to individual reactions.

The kinetics of sewage sludge and biomass are generally reported to follow first-order reactions. Pyrolysis of high-ash sewage sludge was studied and reported to follow the first-order reaction model, which showed higher activation energy with better R^2 (Naqvi et al., 2019). Further to this, an earlier study represented the pyrolysis of sewage sludge with rice straw, paper sludge, oil shale, and pine sawdust by the first-order kinetics (Zhang et al., 2009; Parekh et al., 2009; Zhu et al., 2015; Fang et al, 2016; Lin et al., 2016). A comprehensive investigation reported the use of TG data for kinetics using iso-conversational model-free based on the Arrhenius (Shahbeig et al., 2020).

Considering the following reaction.



With the help of the TG/DTG profile, the determination method for activation energy had been advanced by various researchers (Parekh et al., 2009).

The kinetics of pyrolysis reaction is described by the Arrhenius equation (3.2).

$$\frac{dx}{dt} = f(x)Ae^{-E/RT} \quad (3.2)$$

x is the degree of conversion defined as (3.3),

$$x = \frac{C_0 - C}{C - C_f} \quad (3.3)$$

Where, C_0 , C and C_f is initial mass, mass at the time of degradation, and final mass at 800 °C

At constant heating rate (β), (3.2) is rewritten as (3.4).

$$-\ln(1 - x) = e^{-E/RT} \times \left(\frac{RA}{\beta E}\right) T^2 \quad (3.4)$$

Applying logarithm on both the sides in (3.4) results (3.5)

$$\ln[-\ln(1 - x)] = -E/RT + \ln\left[\left(\frac{RA}{\beta E}\right) T^2\right] \quad (3.5)$$

Slope of $\ln[-\ln(1 - x)]$ versus $1/T$ plot represents activation energy, E for one stage of MSS (Fig. 3.7). Similarly, it was determined for different stages of MSS, SCB, and MSS/SCB mixtures. Comprehensive values of all materials determined by this method in different stages are shown in Table 3.3.

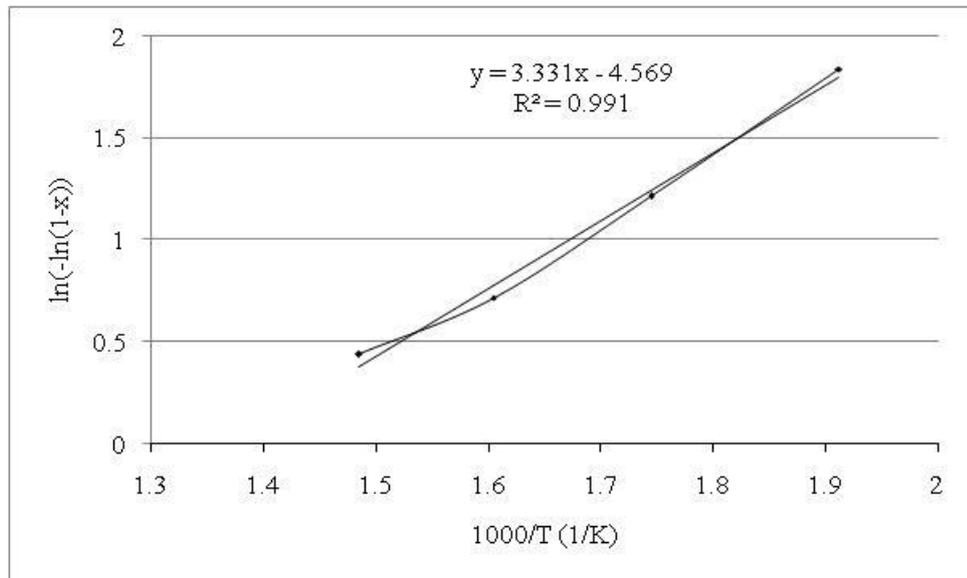


Fig. 3.7 Arrhenius plot for MSS degradation

Table 3.3 shows activation energy for MSS and SCB in the range of 27-52 kJ/mol and 29-46 kJ/mol, respectively. Whereas mixture confines 20-32 kJ/mol. It had been reported in

the literature that the activation energy of MSS varied over a wide range (30-180 kJ/mol) (Shao et al., 2008; He et al., 2020).

This study observed that the decomposition of MSS showed a significant increment in activation energy (52 kJ/mol) at a higher temperature. This can be explained based on decay of inorganic fraction and fixed carbon's combustion (600-800°C). A similar trend of higher activation energy was demonstrated for the sewage sludge obtained from the Giheung Respia treatment facility (Othman et al., 2010). Also, it was seen that the degradation of only-MSS and co-pyrolysis mixture offers three different values of activation energy in its overall temperature range due to the occurrence of degradation in three sub-intervals, whereas SCB showed only two values. It signifies the characteristics of MSS, SCB, and its mixtures. The study of the kinetics of sewage sludge and sugarcane bagasse co-pyrolysis using Coats and Redfern method demonstrated equivalent nature of sub-interval formulation and the value of activation energy of SCB, MSS and its blend (70% SCB & 30%MSS) confines 20.77-106.54 kJ/mol, 6.20-51.06 kJ/mol, and 17.15-82.77 kJ/mol, respectively (Hameed et al., 2018). It was noticed that the activation energy of the mixture was observed higher than those for individual MSS in the first and second stage, whereas reduced by 60% in the third stage. Thus, the addition of SCB in MSS in a 1:1 mass ratio showed variation in activation energy by -60% (mixture exhibited reduced activation energy in a third stage) to +36% (increased for first and second stage). Such a change in activation energy is attributed to the formation of char and bio-oil in a primary stage degradation of SCB and the catalytic effect of metal-containing ash. Thus, the decomposition profile of MSS accelerates upon the addition of SCB in co-pyrolysis.

Table 3.3 Kinetic parameter for degradation of MSS, SCB, and their mixture

Substance	Activation Energy kJ/mol		
	1 st stage	2 nd stage	3 rd stage
MSS	27.69	15.39	52.54
SCB	46.14	29.79	--
MSS: SCB (50% wt.)	32.82	20.89	20.61

3.4. Summary

The nature of TG and DTG curves showed that degradation only-MSS occurred in three stages represented by degradation of lipids, protein followed by polysaccharides, whereas SCB degradation in two stages indicated degradation of hemicellulose, cellulose followed by sluggish degradation of lignin. During the primary stage degradation of SCB, resulting bio-oil might be encouraged MSS degradation leading to more volatile production from

MSS itself. Also, it restricts the carbonization reactions that favor the residue formation. Thus, the co-pyrolysis mixture exhibited a reduction in residue generation by 56% than that of only-MSS degradation.

Also, degradation of SCB resulting to metal-containing ash and the catalytic effect of these metals might be responsible for higher devolatilization of MSS, leading to an increment in maximum percentage degradation per minute by 55% as compared to that of only-MSS degradation. The addition of SCB in MSS in a 1:1 mass ratio showed variation in activation energy by -60% (mixture exhibited reduced activation energy in a third stage) to +36% (increased for first and second stage). Such a change in activation energy is attributed to the formation of char and bio-oil in a primary stage degradation of SCB and the catalytic effect of metal-containing ash. Improvement in the highest rate of degradation, the shift of peak temperature to lower value, reduced quantity of residue, and alteration in activation energy for decomposition of the mixtures showed the existence of synergy in co-pyrolysis of MSS and SCB. Thus, the significant influence of SCB addition in co-pyrolysis with MSS was observed.

CHAPTER 4

Co-pyrolysis of Municipal Sewage Sludge and Sugarcane Bagasse: Yield of Products and Physico-chemical Characterization of Bio-oil

4.1 Introduction

Among the three products (liquid oil, gas, and char) from MSS pyrolysis, one of the potential products, i.e. liquid oil known as bio-oil is a dark brown liquid. The yield of MSS-derived bio-oil observed 50-60 wt%, is a complex mixture of water, oxygenates, hydrocarbons, nitrogen, and sulfur-containing compound. Thus, bio-oil exhibited heterogeneity in nature, and resulting to instability. Since nitrogen and sulfur-containing compounds in a bio-oil create an issue of NO_x and SO₂ emission in exhaust gases and limit its application as a fuel (Fonts et al., 2012). Thus, bio-oil needs to be upgraded by lowering oxygenates and also needs to reduce nitrogen and sulfur-containing compounds. The search for new upgraded alternative fuels and simultaneously reduces the negative environmental impact of MSS has led to the idea of studying co-pyrolysis of MSS with one of the solid residues (biomass) from sugar mill, namely sugarcane bagasse (SCB).

Co-pyrolysis of sewage sludge and lignocellulosic biomass (in 50% wt.) studied in a conical spouted bed reactor, showed a significant synergistic effect in terms of reduced oxygenates and nitrogen-containing products. Moreover, it was seen free of sulfur-containing compounds (Alvarez et al., 2015). Significant reduction in pyrolytic temperature and apparent activation energy investigated for catalytic co-pyrolysis of paper sludge and municipal solid waste with metal oxide, such as MgO, Al₂O₃, and ZnO (Fang et al., 2016). Co-pyrolysis of sewage sludge too was reported with oil shale showed improvement in gas generation, in particular methane (Lin et al., 2016). A

comprehensive study on the co-pyrolysis behavior of MSS and SCB mixture in terms of yield of products and its characterization is little reported.

4.1.1 Objective of the work

In view of the vast availability of these two types of waste materials: (i) MSS (ii) SCB in India, the aim was to show the effect of co-pyrolysis upon addition of SCB with MSS on biooil produced by performing experiments in a batch reactor at a slow heating rate.

4.2 Experimental

4.2.1 Pyrolysis in batch reactor

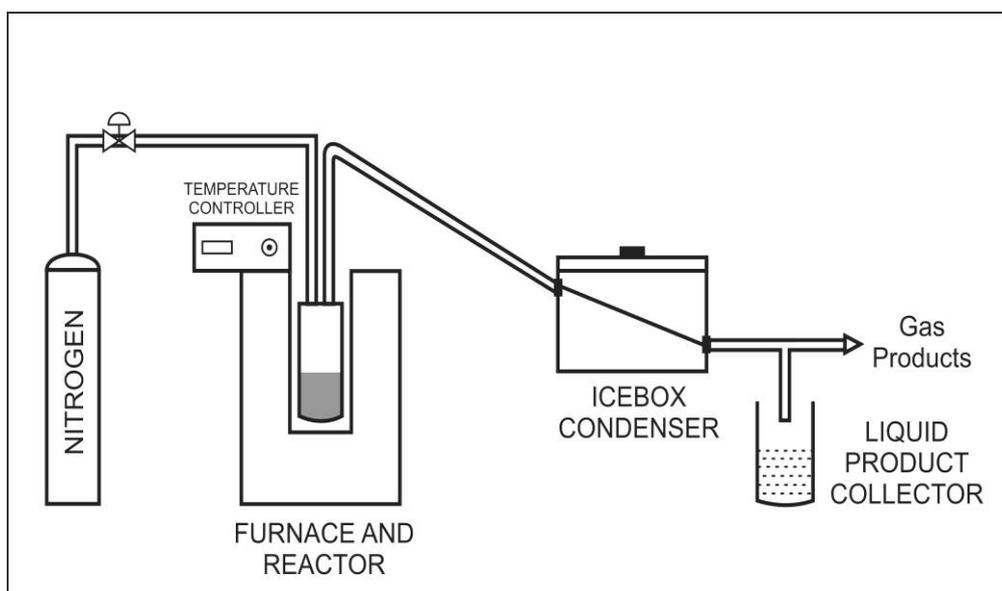


Fig. 4.1 Schematic diagram for pyrolysis/Co-pyrolysis process

Pyrolysis and co-pyrolysis experiments are performed in a laboratory-scale stainless steel batch reactor (50 mm ID X 190 mm length). 100 g of raw materials were taken in a reactor (Fig.4.1) and it was placed in a muffle furnace maintaining 500 °C at 10 °C/min. Air left in the reactor was purged with flowing nitrogen. The solid residue left behind in each run was measured by weighing the reactor before and after each experimental run. The volume of gas produced was measured through the displacement of water and cross-verified by subtracting the weight of liquid and residue from the sample feed, and the error was within $\pm 5\%$. The liquid product was collected in a glass impinge bottle placed in an ice bath. The

solid residue in the reactor was cooled down and stored in plastic containers. Several experiments are performed to collect the required quantity of bio-oil.

4.2.2 Physico-chemical Analysis of bio-oil

The bio-oil produced in pyrolysis and co-pyrolysis experiments was characterized for its physical and chemical properties. The physical properties such as density, viscosity, water content, pH, and acid value were determined. The chemical composition of bio-oil was investigated by using Gas chromatography-Mass spectroscopy (GC-MS). The instruments and methods used during the analysis of the bio-oil samples are prescribed below.

The density of bio-oil is measured as per ASTM D 405 using a density measurement bottle called a pycnometer. The dry flask and stopper are weighed on an analytical balance and the exact volume of the pycnometer is measured by filling it full with water. The full pycnometer with bio-oil sample is weighed on an analytical balance. The temperature is measured. The kinematic viscosity of bio-oil samples is measured using the ASTM D445 and Oswald's viscometer. This method is used to find the viscosity of petroleum products such as kerosene, fuel oils, diesel, gas oil, etc. In this method, the fixed volume of bio-oil is allowed to flow under gravity in the capillary of a calibrated viscometer, and the time for the flow is measured. Kinematic viscosity is calculated based on time value. The pH of bio-oil samples is measured by Systronics digital pH meter model 335 with the electrode. The acid number was measured using a Mettler Toledo G20 compact titrator according to ASTM D664-04. The water content of bio-oil is measured by digital automatic Karl Fischer moisture analyzer Veego Matic-D model (Shown in Fig.4.2) using ASTM D1744.



Fig. 4.2 Karl Fischer titrator

In this method, Karl Fischer reagent was used and it reacts selectively and quantitatively with water of bio-oil. The reagent contains iodine, sulfur dioxide, a base, and alcohol (solvent). In the titration method, a solvent is placed in the flask, and a titrant is used to remove all water from the solvent. Next, the bio-oil sample was added and the titration was carried out. The moisture content of the sample was calculated from the titration volume (mL). The endpoint was detected using the constant current polarization voltage method. The elemental analysis of bio-oil samples was carried in CHNS analyzer-Model Vario Macro cube Elementar using method ASTM D5291 and D5373). It provides information about the elemental composition of carbon, hydrogen, nitrogen, and sulfur percentages while oxygen percentage was determined by difference. The heating value of bio-oil was measured by digital bomb calorimeter model RSB-5A/6/7 and the method was IS 1448-7(2004). GC-MS analysis was carried out on Perkin Elmer Autosystem XL GC with Turbomass. The column used is Pe-5 MS with 30 m length, 0.025 mm diameter, and 0.25 μ thickness. The oven temperature is raised to 75 $^{\circ}$ C and held for 5 min and increased up to 780 $^{\circ}$ C with a hold time of 15 min at the rate of 10 $^{\circ}$ C/min. Helium was used as a carrier gas at a rate of 1 mL/min in a split ratio of 30:1. The injector temperature was held at 210 $^{\circ}$ C with a volume of 4 μ L. The compounds were identified using the NIST mass spectra library. The samples were diluted with hexane to the ratio of 1:100.

4.3 Results and Discussion

4.3.1 Product yield

In this study, SCB was used as a co-feed with MSS to improve the quality and quantity of bio-oil. Pyrolysis of MSS, SCB, and MSS: SCB blends were performed in a batch reactor at a temperature of 500 $^{\circ}$ C. Products obtained in the co-pyrolysis of MSS and SCB have been grouped into three parts i.e. liquid (bio-oil), solids (bio-char), and gas. Mass of bio-oil and bio-char are measured. The mass of gas is obtained by the mass balance of products and feedstock. Product yields are calculated based on the (4.1)

$$\% \text{ yield bio-oil} = \frac{\text{Mass bio-oil}}{\text{Mass feedstock}} \times 100 \quad (4.1)$$

Similarly, the bio-char yield was calculated. The pyrolysis of feedstocks with different SCB weight ratios (0%, 20%, 40%, 50%, 60%, 80%, and 100%) with MSS was performed

and the effect of a second material (SCB) on MSS pyrolysis was studied. The distribution of products (yield wt%) during co-pyrolysis for various blends of MSS and SCB at 500 °C are shown in Table 4.1 and Fig. 4.3.

Table 4.1 Product yield by co-pyrolysis of MSS and SCB (wt.%)

Feed (% SCB with MSS)	Yield of Products, wt%				
	Bio-oil		Bio-oil	Char	Gas
	Organic phase	Aqueous phase			
0	7.40	13.60	21.0	57.0	22.0
20	7.65	14.20	25.8	50.9	23.3
40	9.50	16.45	32.9	43.0	24.1
50	15.80	25.60	41.4	32.8	25.8
60	11.15	18.80	35.2	38.5	26.3
80	12.05	20.00	32.0	40.4	27.6
100	15.30	22.70	38.0	35.1	26.9

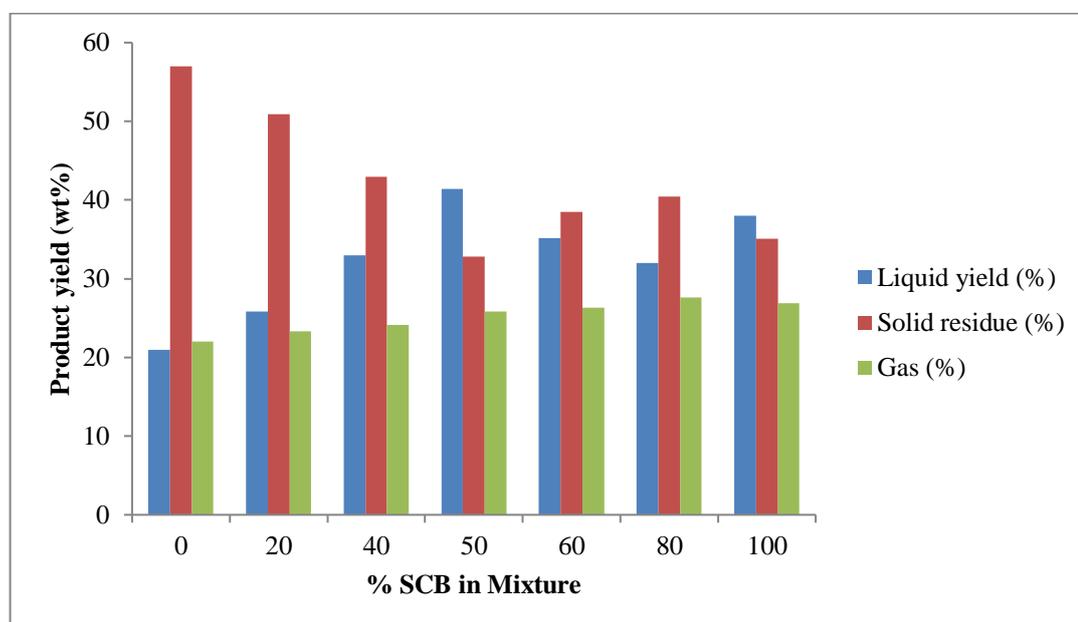


Fig. 4.3 The yields of products of co-pyrolysis at various % of SCB in MSS

The yield (weight%) of pyrolysis products was 21% for bio-oil, 57% for bio-char, and 22% for gas when MSS alone was pyrolyzed, whereas the yields of bio-oil, bio-char, and gas obtained from SCB pyrolysis are 38%, 35.1%, and 26.9% respectively. It is also observed that the yield of bio-oil is lower, and the yield of bio-char was higher in the case of pyrolysis of only MSS compared to only SCB pyrolysis. Similar results were observed in the co-pyrolysis of sewage sludge and biomass and it is due to the high ash contents of MSS (Fonts et al., 2009A; Ding and Jiang, 2013).

In co-pyrolysis of MSS and SCB, the weight % yield of products varied with the % of SCB added in MSS. As shown in Table 4.1, in contrast to merely MSS pyrolysis, upon addition of SCB in MSS, the bio-oil and gas yield was increased by 100% (from 21 to 41.4%) and

14% (22 to 25.8%) respectively whereas the yield of char (residue) decreased by 42% when two materials are mixed at equal proportion. MSS-SCB co-pyrolysis produces less quantity of residue, Early stage of degradation of SCB, produced bio-oils interact with MSS leading to increased production of volatiles and carbonization (to residue formation) of the bio-products is suppressed. Similar reasoning had been advanced to explain lower residue formation in co-pyrolysis kinetic study of sewage sludge and bagasse using multiple normal distributed activation energy models (Lin et al., 2018A).

In this study, the yield of bio-oil produced in only MSS pyrolysis is lower compare to other studies of MSS pyrolysis. As reported in the various studies on pyrolysis of MSS, the maximum yield of bio-oil is obtained at 42%, 42.6%, and 11.24%. (Kim and Parker, 2008; Park et al., 2010; Zuo et al., 2014). The yield of bio-oil depends on the composition of sewage sludge. SCB contains more volatiles than MSS leads to more yield of bio-oil. Thus, as SCB combined with MSS, more pyrolysis oil was generated. Researchers have found that the ash components of sewage sludge could promote devolatilization reaction (Park et al. 2010; Park et al. 2008). The ash content of MSS in the present study is high. In co-pyrolysis, SCB is mixed with MSS, vapor devolatilized from SCB and MSS particles had more opportunity to come into contact with ash components. Thus, the crack reaction catalyzed by the ash component is enhanced. Similar results were obtained during co-pyrolysis of sewage sludge and sawdust (Zuo et al., 2014).

Bio-oil contains two phases, the organic phase and an aqueous phase. The obtained bio-oil was observed with no clear separation of phases. Both the phases are separated by using simple distillation. Table 4.1 shows the yield of both phases. The aqueous phase was the major liquid phase in all the runs.

4.3.2 Synergistic effect in yield of bio-oil of co-pyrolysis

Moreover, to investigate whether interactions existed between MSS and SCB, the difference in yield was defined. It signifies the difference in yield of the products obtained as a result of co-pyrolysis mass and the calculated yield of the products obtained as a result of individual pyrolysis of MSS and SCB. The extent of the synergistic effect was observed. The calculated yield (CY) of co-pyrolysis mass was derived from (4.2).

$$CY = 0.5 (M + S) \quad (4.2)$$

Where M and S are the yield of product obtained by individual pyrolysis of MSS and SCB. Thus, a difference of yield, Y described as (4.3).

Table 4.2 Comparison of bio-oil yield (experimental and theoretical yield)

Feed (% SCB with MSS)	Actual Yield of Bio-oil, wt%	Theoretical Yield of Bio-oil, wt%	% Change in Bio-oil yield
0	21.0	--	--
20	25.8	24.4	5.7
40	32.9	27.8	18.3
50	41.4	29.5	40.3
60	35.2	31.2	12.8
80	32.0	34.6	-7.5
100	38.0	--	--

$$Y = AY - CY \tag{4.3}$$

Where AY is the actual yield obtained by performing co-pyrolysis experiments

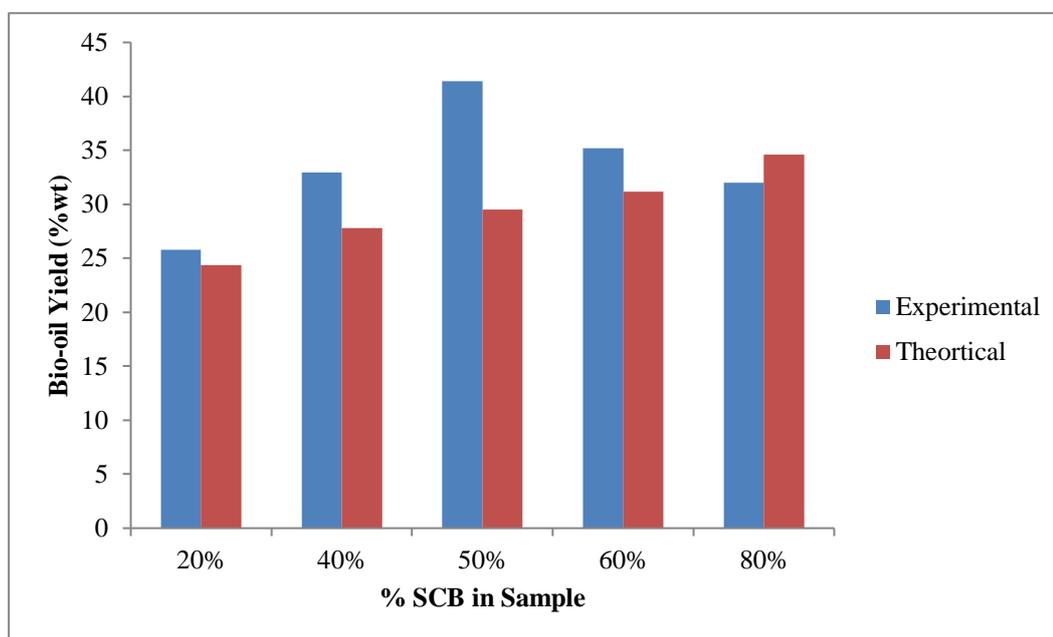


Fig. 4.4 Comparison of bio-oil yield (experimental) and theoretical yield (Calculated based on the yields for the individual feedstock).

Fig. 4.4 and Table 4.2 shows the comparison of the experimental yield of bio-oil and calculated yield. It is observed that the experimental value of bio-oil yield is higher than the calculated value of bio-oil yield for all blends except the 20:80 (MSS: SCB) blend. The increase in the synergistic effect which is described as “Y” is observed maximum for a blend of equal proportion of MSS and SCB. Fig. 4.5 shows the comparison of experimental yield and calculated yield of bio-oil, bio-char and gas products during co-pyrolysis of MSS and SCB blend of equal proportions (50-50 wt%). It can be seen that the extent of synergistic effect (Y), during the co-pyrolysis indicates an increase of about 40% and 5% in bio-oil and gas yield and a decrease of 28% in char yield. The char yield is approximate of the same order as the theoretical value. The reason for the synergistic effect

is the early stage of degradation of SCB, which produced bio-oils that interact with MSS leading to increased production of volatiles, and carbonization (to residue formation) of the bio-products is suppressed. The alkali metals present in the bio-char produced during early-stage degradation of SCB act as a catalyst that promotes the devolatilization of MSS.

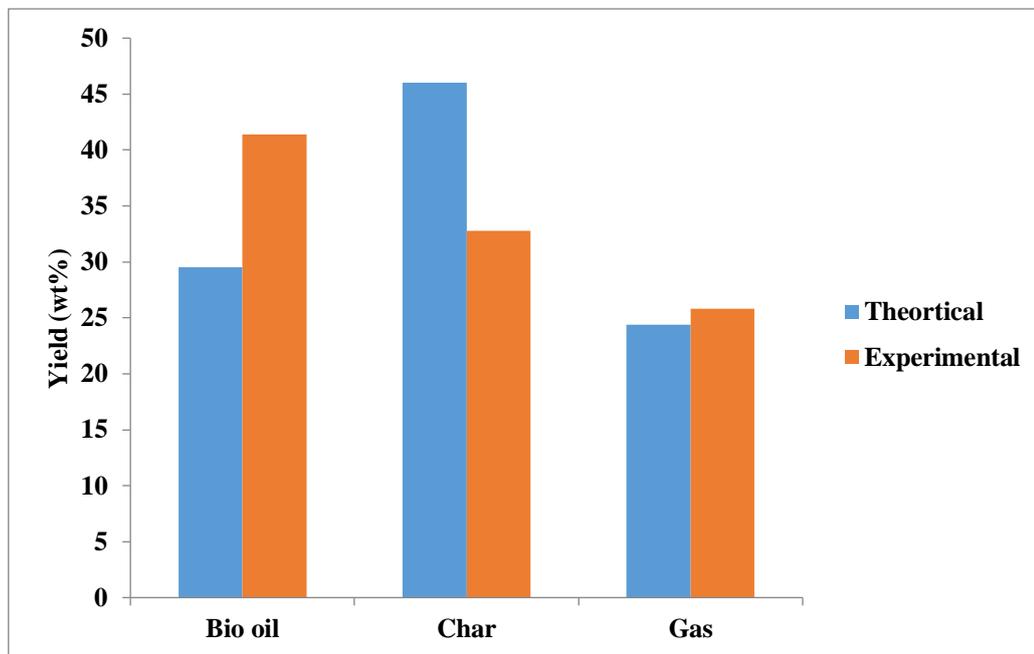


Fig. 4.5 Comparison of experimental and theoretical yield of products during co-pyrolysis of MSS and SCB.

4.3.3 Physico-Chemical properties of the bio-oil

4.3.3.1 Elemental Analysis of bio-oil

The elemental analysis of bio-oil was accomplished to predict the effect of SCB on MSS during pyrolysis. Table 4.3 showed the quantitative representation of carbon, hydrogen, nitrogen, sulfur, and oxygen in bio-oil produced by pyrolysis of individual MSS and SCB, and co-pyrolysis were determined.

Table 4.3 Elemental analysis of bio-oil of co-pyrolysis

Bio-oil	Ultimate Analysis (wt%)					HHV MJ/kg	H/C	O/C
	C	H	N	O*	S			
MSS	62.33	8.13	7.57	20.97	1.00	24.4	1.60	0.25
SCB	59.20	7.32	5.50	27.98	--	19.3	1.41	0.35
MSS: SCB (1:1)	61.10	7.80	6.20	24.90	--	20.4	1.50	0.30

The HHV of the bio-oil reported 60 % of fuel oil. Bio-oils have a high carbon and hydrogen content despite their lower concentration in the feedstock. Merely MSS-derived bio-oil contains 7.57 weight % nitrogen. Upon addition of SCB in MSS, co-pyrolyzed bio-

oil was observed with reduced nitrogen and free of sulfur. Thus, such an upgraded bio-oil reduced the emission of NO_x and SO_x in exhaust gases. Fuel classification is mostly based on the atomic ratio. The high heating value (HHV) of bio-oil derived from MSS, SCB, and that of mixture observed 24.4 MJ/kg, 19.3 MJ/kg, and 20.4 MJ/kg.

4.3.3.2 Physical Properties of bio-oil

Table 4.4 summarizes the pH value, acid value, density, viscosity and water content for each of the three bio-oil. MSS-derived bio-oil exhibited alkaline nature, whereas, SCB shows acidic nature. Thus, pH of co-pyrolysis derived bio-oil increases. Accordingly, the acid value of bio-oil increases. Moreover, water content is slightly increased. In contrast to this, density and viscosity are marginally reduced. Such a property of bio-oil favors its use as a transport fuel. Thus, application of co-pyrolysis technique upgraded bio-oil properties.

Table 4.4: Physical Properties of bio-oil

	Density (kg/m ³)	Viscosity (cSt at 40°C)	pH	Acid value (mg KOH/g)	Water Content %
MSS	1217	20.2	7.4	60.5	45.3
SCB	1108	15.1	2.85	110.2	47.4
MSS: SCB (1:1)	1187	19.3	3.71	104.2	52.1

4.3.4 Chemical composition of bio-oil (GC-MS Analysis)

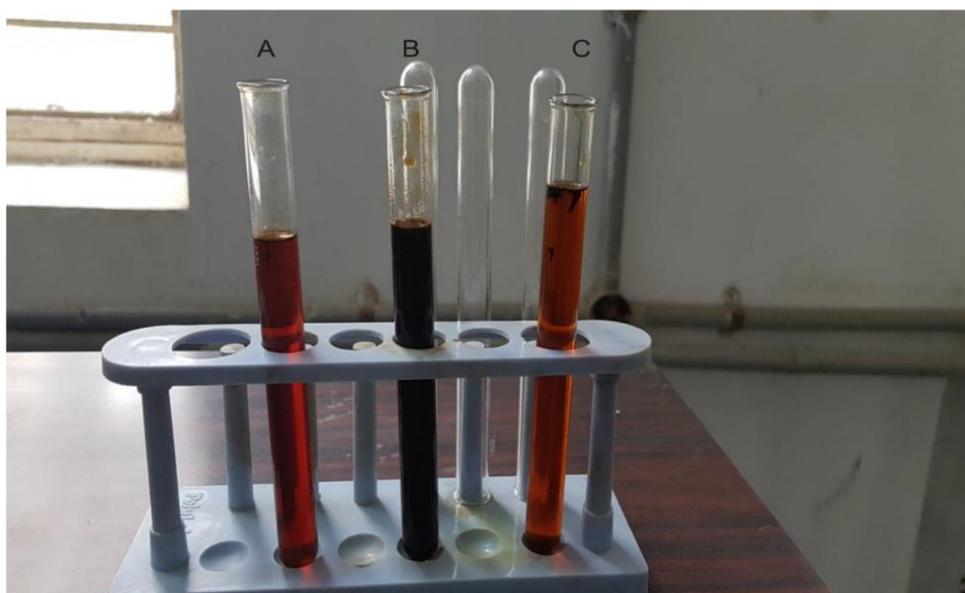
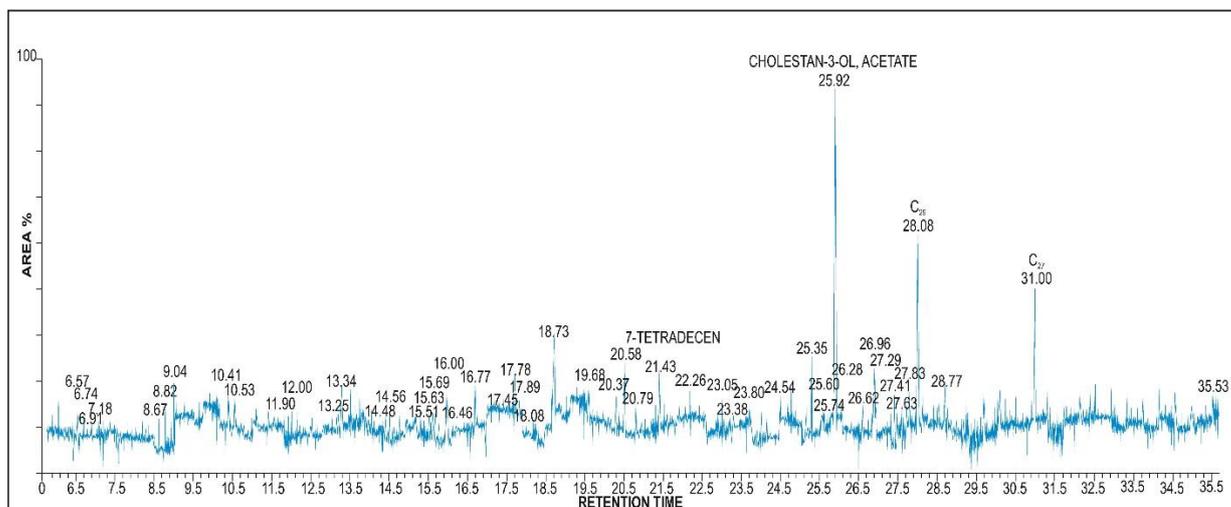


Fig. 4.6 Bio-oils produced from pyrolysis of (A) SCB (B) MSS and (C) blend of MSS: SCB (1:1)

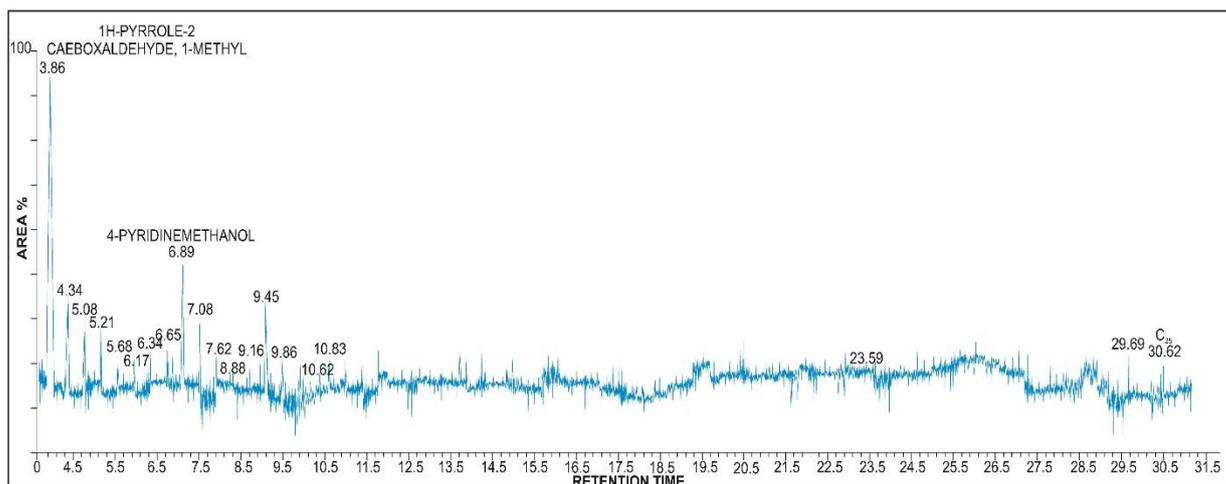
Fig. 4.6 showed physical appearance of bio-oil derived from MSS, SCB and their mixture. Organic and aqueous phases were observed in a miscible form, which was separated by

simple distillation. The chemical composition of bio-oil is essential to establish their potential utilization as fuel or other applications and therefore, it was analyzed

(a)



(b)



(c)

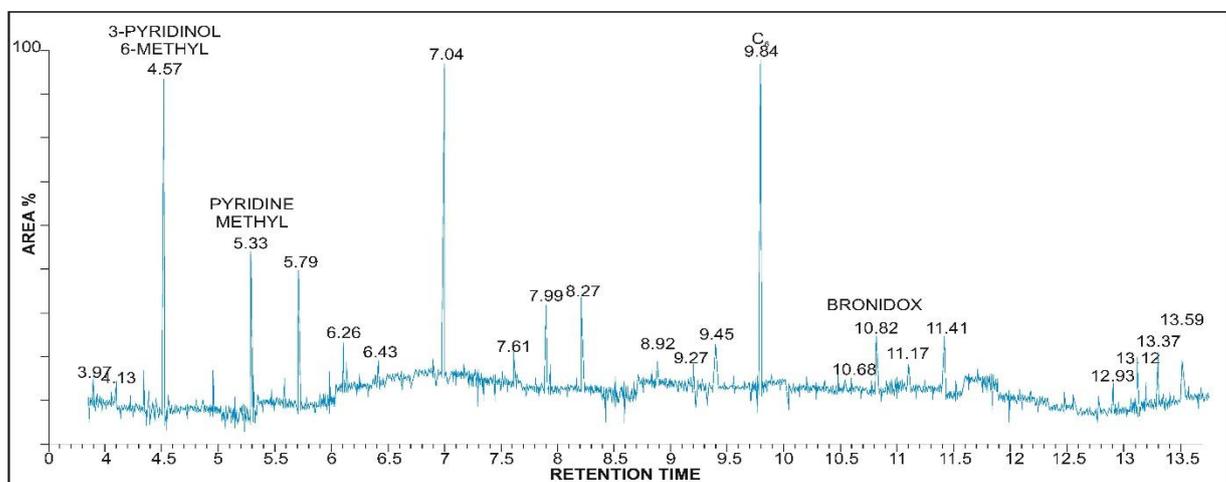


Fig. 4.7 Gas chromatograph of bio-oil of (a) MSS (b) SCB, and (c) Mixture

by using Gas chromatography-Mass spectrometry (GC-MS). Quantification of various compounds were determined in terms of % area. Pyrolytic oils were reported to be complex mixtures consisting of organic compounds with a wide range of chemical functionalities.

Fig. 4.7 (a), (b), and (c) indicated the chromatograms of bio-oil derived from pyrolysis of MSS, SCB, and their mixture. Table 4.5 showed the various compounds identified in the bio-oil samples. Moreover, Table 4.6 (a) and (b) represented the classification of identified compounds. These compounds were classified as oxygenates, nitrogenates, sulfur, hydrocarbon and steroids. Further to this, oxygen-containing compounds were classified based on the functional groups such as carboxylic acids, alcohols, phenols, esters, ethers, aldehydes, ketones and epoxy. Nitrogen-containing compounds were mainly amines, amides, nitriles, pyridines, pyrazines, pyrroles and N-heterocyclic.

The high percentage of water demonstrated in biomass and MSS-derived bio-oil is due to the presence of moisture. Moreover, dehydration and secondary reactions occurred during the pyrolysis resulting to water formation. (Alvarez et al., 2015). A significant reduction in sulfur containing compounds was seen upon co-pyrolysis. Moreover, nitrogen-containing compounds, hydrocarbons, and steroids were too reduced marginally. Various material combinations, e.g. lignocellulosic materials, rice straw, oil shale, etc. with sewage sludge reported that co-pyrolysis significantly reduces sulfur and nitrogen-containing compounds in a different reactor configuration. (Alvarez et al., 2015; Lin et al., 2016). Gaseous phase secondary reaction of hydrocarbons with oxygenates believe to lower the proportionate amount of hydrocarbon in a co-pyrolyzed resulting bio-oil. During co-pyrolysis, volatiles of SCB released at a lower temperature is believed to be reacted with MSS resulting to formed synergy (Aboyade et al., 2013). It was also reported that co-pyrolysis attracts desulfurization due to the hydrogen donor property of SCB, which encourages the release of sulfur compounds in the form of H_2S (Sonobe et al., 2008; Jones et al., 2005). Similar results were also investigated for co-pyrolysis of high sulfur coal and different biomass where enhanced desulfurization was observed (Cordero et al., 2004; Blesa et al., 2003). The presence of alkali and alkali metals attributed to fixed sulfur compounds in the form of CaS and $CaSO_4$, leading to a reduced concentration in the resulting bio-oil (Blesa et al., 2001; Haykiri-Acma and Yaman, 2007). Also, certain sulfur compounds of MSS may remain unreacted in char (Alvarez et al., 2015).

Table 4.5 The detailed composition (% area) of bio-oils

Bio-oil of MSS		Bio-oil of SCB		Bio-oil of MSS:SCB (1:1)	
Compounds	% Area	Compounds	% Area	Compounds	% Area
Oxygenates					
Fatty Acids/Carboxylic acids					
Acetic acid, Undec-2-Enylester	0.64	Tetradecanoic acid	0.59	3-Methyl-2-Furoic acid	2.24
Acetic acid, 2-Methyl-2-Phenyl-, hydrazide	0.45	Acetic acid	1.24	Acetic acid	1.86
Dodecanoic acid	0.58	--	--	Pentadecanoic acid	1.28
Pentadecanoic acid	0.78	--	--	--	--
Alcohols					
1,3-Butanediol	0.38	Nicotinyl alcohol	2.20	Z-2-dodecenol	0.57
Nonmethylen glycol	0.72	4-Pyridinemethanol	1.84	2-Furanmethanol	1.48
2-Nonanol	1.20	Benzeneethanol, 2-methoxy	0.63	2-Nitro-1-Phenyl-ethanol	1.34
4-Methylphenyl Methanol	0.92	--	--	2-Nonanol	0.87
Z-2-dodecenol	0.57	--	--	--	--
Aldehydes					
Formaldehyde	1.68	Formaldehyde, methyl (2-propenyl) hydrazone	1.44	1H-pyrrole-2-carboxaldehyde, 1-methyl-	1.54
n-Heptaldehyde	1.21	n-Heptaldehyde	0.80	2-Furaldehyde, 5-methyl-	0.36
--	--	--	--	n-Heptaldehyde	0.79
Ethers					
(4-Methylphenyl methanol, tert-,butylether	0.26	--	--	--	--
1-Methoxy-3-hexene	0.46	--	--	--	--
2-Ethoxy-2-methoxypropane	0.52	--	--	--	--
Phenols					
E-2-hexadecacen-1-ol	2.34	4-ethyl-2-methoxy phenol	3.46	Phenol	4.56
Phenol	3.12	Phenol	2.84	4-Methyl phenol	5.42
2-methoxy-4-(1-propenyl)-phenol	1.78	4- Amino phenol	2.32	2-Methoxyphenol	3.89
1,2-Benzenediol	3.26	4-Ethylphenol	2.78	4-Ethylphenol	2.38
4-Methyl-1,2-benzenediol	2.46	2-Ethylphenol	1.83	1,2-Benzenediol	0.73
4-Ethylcatechol	2.16	Phenol, 4-ethyl-2-methoxy	1.76	--	--
--	--	Phenol, 2-methyl-	2.64	--	--
--	--	Phenol, 2-methoxy-	1.69	--	--
Ketones					
Acetone	1.56	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	3.29	2H-Pyran-2-one, 3,4,5,6-Tetramethyl	1.78
1-Hydroxy-2-butanone	0.38	3-Methyl-1,2 cyclopentanedione	0.95	1-Hydroxy-2-butanone	0.76
2-Phenyl-6-methyl- 1,4-benzopyrone	0.64	--	--	Acetone	1.20
Esters					
Acetic acid, undec-2-enylester	1.72	Phathalic acid, nonyl oct-3-yl ester	2.68	--	--
Dichloroacetic acid, undec-2-enyl ester	0.52	--	--	--	--
Oxiranes/Epoxides					
Triepoxydecane	2.54	--	--	--	--
Furan					

Co-pyrolysis of Municipal Sewage Sludge and Sugarcane Bagasse: Yield of Products and Physico-chemical Characterization of Bio-oil

--	--	Furan, 2,5-dimethyl-	2.16	2-(2-propenyl) furan	1.98
--	--	Benzofuran, 2,3-dihydro-	0.68	Benzofuran, 2,3-dihydro-	1.60
Nitrogen-containing compounds					
Amides					
Pyridine-3-carboxamide, 6(1H)-oxo-n-(1-phenylethyl)	0.74	Pyrazinamide	1.05	Dodecanamide	1.57
Hexadecanamide	1.34	--	--	--	--
Dodecanamide	0.86	--	--	--	--
Amines					
N-benzoyltyramine	0.53	2-methoxy Benzenamine	0.56	4-methoxy Benzenamine (4 Methoxy Aniline)	0.24
1-methyl-1-phenyl hydrazine	0.37	--	--	Aniline	1.08
2,6-Xylidine	0.27	--	--	--	--
Methyldiallylamine	1.05	--	--	--	--
Nitriles					
Hexanenitrile	1.52	--	--	1H-pyrrole-3-carbonitrile	1.67
Acetonitrile	1.36	--	--	2-Methyl-(1H) pyrrole-3-carbonitrile	0.63
Hexadecanenitrile	0.42	--	--	--	--
Pyridines					
Pyridine-3-carboxamide, 6(1H)-oxo-n-(1-phenylethyl)	3.20	--	--	Pyridine, 4-methyl	3.10
Pyridine, 3-methyl-	1.10	--	--	--	--
Pyrazines					
2,3-Dimethylpyrazine	1.08	--	--	2,3-Dimethyl pyrazine,	0.34
--	--	--	--	Ethenyl Pyrazine	0.40
Pyrroles					
1H-pyrrole-2,5-dione	1.94	1H-Pyrrole-2-carboxaldehyde, 1-methyl	1.84	1,2,5-Trimethylpyrrole	0.73
(2H) pyrrole-2-carbonitrile, 5-amino-3,4-dihydro	0.64	--	--	1H-Pyrrole-3-carbonitrile	2.48
2-Pyrrolidinone	0.36	--	--	--	--
(N- heterocyclic)					
Aziridine	0.43	Pyrazole	0.32	--	--
Sulfur-Containing compounds					
phenyl-thiocarvone	2.12	--	--	--	--
1-Methyl-4-(methylthiol) benzene	1.26	--	--	--	--
Hydrocarbons (H/C)					
7-Tetradecene	2.38	--	--	Heneicosyl Cyclopentane	0.56
6-Tridecene, (z)	1.28	--	--	Methylbenzene	0.77
6-Dodecene, (z)	0.88	--	--	Ethyl bromide	0.23
Halogenated H/c					
7-Heptadecene, 17-chloro	1.52	--	--	3-Cyclohexenecarbonyl chloride	1.42
--	--	--	--	Ethyl bromide	0.84
--	--	--	--	Bronopol	1.32
Steroids – cholestene					
Cholest-5-ene,3, beta.-chloro	1.94	--	--	--	--
3-choloro-5-cholestene	2.58	--	--	--	--

Cholestane, 3-thiocyanato-, (3.alpha., 5.alpha.)	0.37	--	--	--	--
--	------	----	----	----	----

Table 4.6 (a) Chemical composition (Area %) of bio-oil produced by pyrolysis of MSS, SCB, and mixture.

Compounds	MSS	Biomass	MSS: SCB (1:1)
Oxygenates			
Fatty Acids/Carboxylic acids	2.45	1.83	5.38
Alcohols	3.79	4.67	4.26
Aldehydes	2.89	2.24	2.69
Ethers	1.24	--	--
Phenols	15.11	19.32	16.98
Ketones	2.58	4.24	3.74
Esters	2.24	2.68	--
Oxiranes/Epoxides	2.54	--	--
Furan	--	2.84	3.58
Total	32.84	37.82	36.63
Nitrogen-Containing compounds			
Amides	2.94	1.05	1.57
Amines	2.22	0.56	1.32
Nitriles	3.30	--	2.30
Pyridines	4.30	--	3.10
Pyrazines	1.08	--	0.74
pyrroles	2.94	1.84	3.21
(N- heterocyclic)	0.43 (Aziridine)	0.32 (Pyrazole)	--
Total	17.21	3.77	12.24
Sulfur-Containing compounds	3.38	--	--
H/C	4.54	--	1.56
Halogenated H/c	1.52	--	3.58
Steroids - cholestene	4.89	--	--

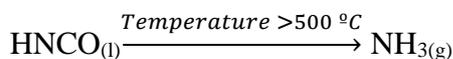
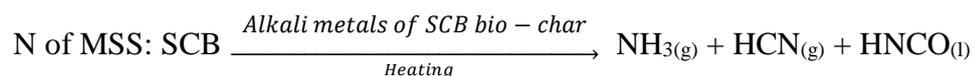
Table 4.6 (b) Classification of Chemical compounds (Area %) of bio-oil produced by pyrolysis of MSS, SCB, and mixture.

Group of compounds	MSS	SCB	MSS:SCB (1:1)
Oxygenates	32.84	37.82	36.63
Nitrogen compounds	17.21	3.77	12.24
Sulfur compounds	3.38	--	--
Hydrocarbons	4.54	--	1.56
Steroids(Cholestens)	4.89	--	--

It was observed that nitrogen-containing compounds, hydrocarbons, and steroids were too reduced marginally. Synergy in nitrogen compounds was investigated in the co-pyrolysis of sludge and biomass. The formation of gases such as NH₃ and HCN was observed at various stages of decomposition during the pyrolysis. The conversion of nitrogenous compounds to HCN and NH₃ in the gases product of pyrolysis increases with the addition of SCB in MSS leading to the reduction of nitrogen-containing compounds in bio-oil. The yield and conversion to HCN and NH₃ were observed to be increase in presence of cotton stalk with sludge (Ren, 2013). The high volatile and mineral matter contents in SCB, at

earlier degradation, may promote the formation of nitrogen-containing species (HCN, NH₃).

As observed in the chemical composition of bio-oil, N-heterocycles, pyrrole, and pyridine were formed during the pyrolysis of MSS in significant concentrations. The breakdown of these compounds at high temperatures resulted to high levels of HCN (Keyhani and Yaylayan, 1996). NO_x formation was enhanced at a later on stage (>500 °C). Another possible explanation was attributed to cellulose, hemicellulose, and lignin which imparted positive effects on the nitrogen conversion pathway of amino acids (Ren et al., 2011). The improved formation of Hydrogen cyanide (HCN) and Isocyanic acid (HNCO) reported in upon addition of biomass with MSS. (Ren, 2013). At temperatures above 500 °C, the decomposition reactions of nitrogen-containing liquid compounds are responsible for NH₃ presence in the gases fraction (Tian et al., 2013). The following reaction mechanisms were supported by authors for the reduction of nitrogen-containing compounds in co-pyrolysis bio-oil.



Thus, in contrast to bio-oil of MSS, reduction in various nitrogenates such as amines, amides, nitriles, pyridine, and pyrazines was observed in bio-oil derived from co-pyrolysis. Various material combinations, e.g. lignocellulosic materials, rice straw, oil shale, etc with sewage sludge reported that co-pyrolysis significantly reduce sulfur and nitrogen-containing compounds in a different reactor configuration (Alvarez et al., 2015; Lin et al., 2016). Gaseous phase secondary reaction of hydrocarbons with oxygenates believe to lower the proportionate amount of hydrocarbon in a co-pyrolyzed resulting bio-oil. Phenolic compounds were the major organic compounds present in the bio-oil of MSS, SCB, and their mixture.

Table 4.7 demonstrated number of carbon atoms presence in bio-oils. The components are classified as carbon atoms 6-12 (C₆₋₁₂, lighter compounds), carbon atoms 13-22 (C₁₃₋₂₂, Moderately high molecular weight compounds) hydrocarbons, and C₂₃ which contains carbon atom number higher than 23 (High molecular weight compounds). It was seen that bio-oil of SCB contains mainly C₆₋₁₂ compounds whereas, bio-oil of MSS pyrolysis

contains C₆₋₁₂, C₁₃₋₂₂, and C₂₃ compounds. The yield of C₂₃ compounds was more dominated in MSS bio-oil. Upon addition of SCB in MSS, the concentration of C₆₋₁₂ compounds was observed to increase, and a significant reduction in C₁₃₋₂₂ and C₂₃ compounds indicated the increased formation of the lighter fraction at the cost of a heavier one.

Table 4.7 Bio-oil composition (Relative % Area)

Class	MSS	SCB	MSS-SCB (1:1)
C ₆₋₁₂	10.0	30.0	35
C ₁₃₋₂₂	9.5	--	--
C ₂₃	36.7	1.8	--

4.3.5 Applications of various compounds in bio-oil

Miscibility of pyrolysis-derived bio-oil was reported very poor and therefore has limited application as commercial fuel (Ben et al., 2016). However, valuable compounds separated from bio-oil have been extensively used in various fields based on the properties of bio-oil. Bronidox can be used as Bactericide, fungicide, stabilizer, and surfactant. Also, widely used in cosmetics, perfumes, lotions, toothpaste, and as a preservative for shampoos. Bronopol is used as a microbicide or microbiostat in conditioning or humidifying systems, cooling water systems, paper mills, absorbent clays, and metal aliphatic halogen-nitro compounds. MSS bio-oil contains steroids and their derivatives (cholestene compounds) abundantly which are widely used in cosmetics and skincare products, especially hair dye. They are also used in drugs for liver diseases. MSS bio-oil also contains Oxiranes (epoxides) compounds, which is used as a fumigant, antifreeze, and ethylene glycol. 4-Methoxy Aniline condenses readily with aldehydes and ketones. It is used as a reagent to test for the presence of oxidation products in fats and oils (used in the American oil chemist's society) and also used in food quality testing. Phenol and its derivatives are used to manufacture Phenolic resins, which can be used as adhesives and coatings, circuit boards, molded products, etc. The composition bio-oil of co-pyrolysis demonstrated that bio-oil was appropriate to be used as fuel, and for the production of various chemicals (Effendi et al., 2008; Lehto et al., 2014; Gayubo et al., 2010).

4.4 Summary

The present study demonstrated the production of bio-oils from MSS, SCB, and their blends by using the batch pyrolysis process. The synergistic effect observed in co-pyrolysis

of MSS with SCB leads to enhanced bio-oil yield. In contrast to merely MSS pyrolysis, upon addition of SCB in MSS, the yield of bio-oil and gas increased by 100% and 14%, respectively, whereas the yield of char (residue) decreased by 42%. GC-MS analyses revealed that a significant reduction in sulfur-containing compounds, and steroids were seen upon co-pyrolysis. Moreover, nitrogen-containing compounds, and hydrocarbons were too reduced marginally. Physical properties such as pH, viscosity, and density favor the use of bio-oil as a transport fuel. Upon co-pyrolysis, significant improvement in higher heating value was not observed. Moreover, reduction in oxygenates was not referred. Alternatively, bio-oil may prove as a potential material to provide organic chemicals, mainly phenolic compounds.

CHAPTER 5

Co-pyrolysis Based Activated Bio-char: Characterization and Its Utilization for Secondary Treated Pulp and Paper Industry Wastewater

5.1 Introduction

5.1.1 Pulp and paper industry wastewater scenario

A massive quantity of freshwater, (an average 230 m³ per ton of paper consumed) in the pulp and paper industry leads to the generation of an enormous quantity of wastewater (Buyukkamaci and Koken, 2010). Production of pulp and paper is considered as one of the largest polluting after the manufacturing process of steel, leather, oil, textile and cement (Savant et al., 2006). In India, one-ton production of paper consumed 60 m³ freshwater, resulting in 50 m³ of wastewater (Thompson et al., 2001) with high Total organic carbon (TOC), COD, Adsorbable organic halides (AOX), colour with low biodegradability index (less than 0.4) (Pokhrel and Viraraghavan, 2004). These are attributed to the presence of various toxic components like phenolic compounds, lignin and its derivatives, fatty acids, tannin, resin acids, sulphur compounds etc. (Garg et al., 2007; Ali and Sreekrishnan, 2001). Thus, pulp and paper wastewater is considered poisonous to aquatic life, surrounding agriculture and human beings and calls the need for the treatment of wastewater.

The conventional wastewater treatment for pulp and paper industry wastewater widely reported includes sedimentation, aerobic and anaerobic treatment, ultra-filtration, coagulation, flocculation, electrolysis, ozonation, photo-catalysis, and adsorption

(Bhattacharjee et al., 2007; Wong et al., 2006; Kishimoto et al., 2010; Amor et al., 2019; Kamali and Khodaparast, 2015). Pollutant reduction through conventional treatment reported by various authors for suspended solids, total solid, colour, BOD, COD, adsorbable organic halides in the range of 75-80%, 70-80%, 80-90%, 65-70%, 65-70% and 40-50%, respectively (Thompson et al., 2001; Bhattacharjee et al., 2007; De Los et al., 2009; Junna and Ruonala, 1991; Peerbhoi et al., 2003; Ashrafi et al., 2015). An enormous quantum of treated wastewater after conventional treatment was observed to be matching the permissible norms of the state pollution control board and thus, most of the industries are discharging their treated wastewater into the natural body (river). Consequently, the idea of the present study originated to explore the potential of such treated wastewater to utilize in the manufacturing process of pulp and paper industry itself by providing additional treatment of adsorption for the removal of COD and colour, which were analyzed the major hurdle to consider treated wastewater for recycling.

5.1.2 Various biomass derived adsorbents for the treatment of wastewater

It was reported that COD and colour of pulp and paper wastewater are strongly imparted due to lignin and its derivatives (Dilek and Gokcay, 1994). Also, it was reported that biological degradation of lignin bearing compounds becomes difficult (Livernoche et al., 1983; Archibald et al., 1995). Adsorption treatment is considered an attractive method among various treatment methods for the removal of organic pollutants in wastewater. Nevertheless, the high cost of commercially available activated carbon was observed to be a constraint for its applicability. Therefore, more attention towards the production of relatively inexpensive activated carbon from renewable sources is highly demanded in wastewater treatment applications. Studies on the production of activated carbon from various biomass waste and agriculture residue along with its adsorption characteristics were reported in the literature. Biomass waste and agriculture residue such as rice husk (Georgieva et al., 2015), sugar cane bagasse (SCB) (Onal et al., 2007), apricot shell (Karagozoglul et al., 2007), maize bran (Hasan et al., 2008), rose waste biomass (Iqbal et al., 2013), sunflower waste (Jain et al., 2009), Litchi peel (Yi et al., 2017), coconut shells (Singh et al., 2008), oil pal fibre (Tan et al., 2007), date stones (Hameed et al., 2009A), palm empty fruit bunch (Hameed et al., 2009B), and sewage sludge (Agrafioti et al., 2013) reported being used for the production of activated carbon through chemical and/or physical activation methods.

5.1.3 Bio-char activation methods

Activation of bio-char using chemical and/or physical activation methods reduce the pore size of resulting bio-char, leading to improvement in carbon structure and adsorption efficiency (Sudaryanto et al., 2006). Physical activation occurred in two steps including carbonization and partial gasification using CO₂, steam, or air at a high temperature (about 1000 °C) whereas, the chemical activation method happened in one step at a lower temperature (i.e., 700 °C) than that of physical activation. Moreover, the chemical activation provides better performance than that of physical activation in terms of yield of activated bio-char, surface area and pore development in carbon structure, which improve the adsorption capacity and reduce the reaction time. (Sudaryanto et al., 2006; Yahya et al., 2015). The most commonly used chemical activation agents are H₃PO₄, NaOH, KOH, Na₂CO₃, and K₂CO₃ and ZnCl₂ (Rosas et al., 2014). Alkali such as KOH able to generate a very high surface area (> 2000 m² /g) and significant micropore structure with a drawback of low carbon yield and harmful effects on the environment (Rashidi and Yusup, 2017). Conversely, activation through phosphoric acid (H₃PO₄) produces a reasonable surface area of about 1500 m²/g including mesopores (Molina-Sabio et al., 1995; Patnukao and Pavasant, 2008; Arami-Niya et al., 2010; Xu et al., 2014).

During the adsorption, H₃PO₄ act as a catalyst, helping to protect the pore structure. Thus, it prevents excessive burn-off of carbon structure resulting in higher yield (Xu et al., 2014). Also, less harmful in view of environmental points. Thus, the use of H₃PO₄ as an activation agent proved to be well known (Zuo et al., 2009). Chemical activation using phosphoric acid is widely reported by various authors for the enrichment of porosity of bio-char (Diao et al., 2002; Jagtoyen et al., 1998; Suarez-Garcia et al., 2002; Vernersson et al., 2002).

5.1.4 Source of co-pyrolyzed Bio-char

Considering the enormous availability of sugarcane bagasse (SCB) (50 million metric tons per annum) (Yadav and Singh, 2011), and municipal sewage sludge (MSS) (4 million tonnes per annum in urban areas) (Karia and Christian, 2013) available in India leading to the idea of utilization of these two materials as a feedstock for co-pyrolysis process. To enrich the value addition of the co-pyrolysis product, mainly bio-char, this study was carried out for the utilization of bio-char (after chemical activation) for secondary treated

wastewater of pulp and paper industry. Chemical activation of bio-char obtained from MSS and SCB co-pyrolysis and its utilization for secondary treated wastewater from pulp and paper mills was rarely reported.

5.1.5 Objective of this work

The present study addresses the chemical activation using phosphoric acid for the activation of the bio-char generated from the co-pyrolysis of MSS-SCB (50% mass). The resulting activated bio-char was characterized for surface area, total pore volume and average diameter. Moreover, porosity and the functional group were analyzed with the use of SEM and FTIR, respectively. Further, activated bio-char was utilized for the removal of COD and colour of pulp and paper industry wastewater obtained from the conventional secondary treatment process to explore the recycling potential in the pulp and paper manufacturing process itself. Besides this, data were analyzed using Langmuir and Freundlich isotherm model to obtained equilibrium.

5.2 Experimental

5.2.1 Sampling of secondary treated wastewater from pulp and paper industry

Pulp and paper industry effluent after the biological treatment was collected from J.K. Paper Ltd, Gujarat, India. The key processes of this industry included pulping, cleaning, bleaching, washing and drying. The samples were stored at ≤ 5 °C to avoid any change in their physicochemical characteristics. Different parameters of wastewater were analyzed as per standard procedures prescribed in APHA (Baird and Bridgewater, 2017).

5.2.2 Preparation of activated bio-char

The raw materials for co-pyrolysis were MSS and SCB which were described in chapter 3 and the method for co-pyrolysis was discussed in chapter 4. Bio-char (Solid residue) of the co-pyrolysis was cooled down and stored in containers. The detailed method of bio-char activation using phosphoric acid as activating agent is shown in Fig. 5.1. The specified quantity of bio-char was cleaned with hot distilled water to eliminate dusty impurity, oven-dried at 105 °C, ground and sieved to particle size 0.2-0.3 mm. Bio-char sample was

activated by using chemical activation method using 40 wt% phosphoric acid (strength 85%).

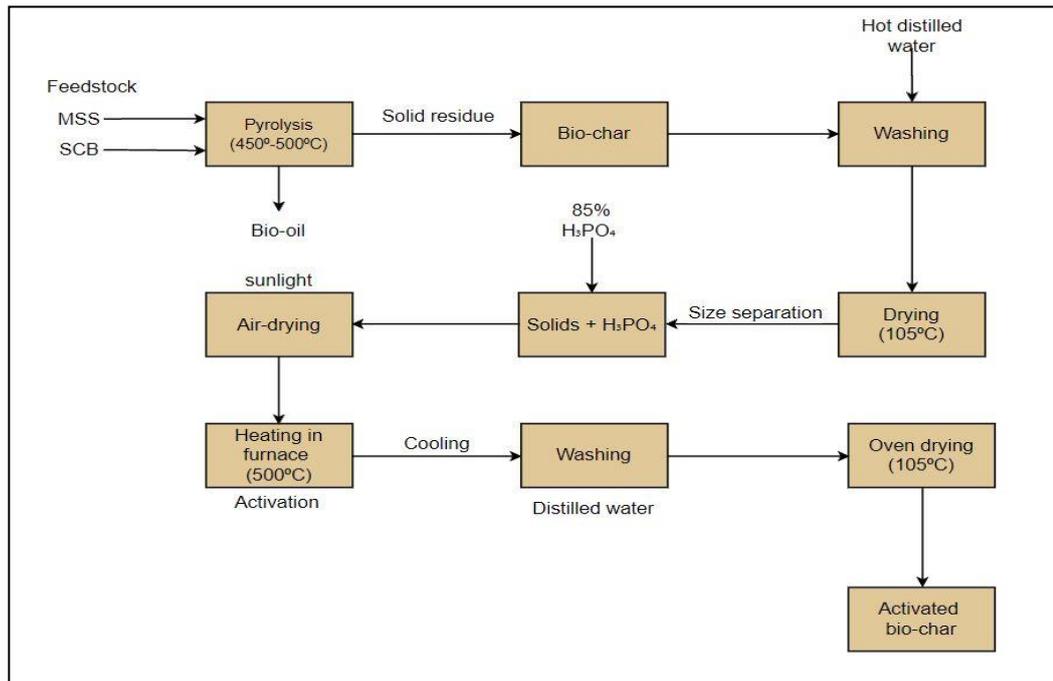


Fig. 5.1 Chemical activation of co-pyrolyzed bio-char

In a typical process, 40 g of bio-char was soaked in 24 ml of 40 wt% concentrated phosphoric acid and the acid-solid mixture was kept for 10 h with occasional stirring at an interval of 2 h to permit dispersion of acid into the bio-char sample. Consequently, this precursor was sun-dried for 3 days. Then after, activation of impregnated bio-char was carried out in a muffle furnace at the temperature of 500 °C for a duration of 5 h in a flowing inert medium of nitrogen gas. A similar method was reported earlier at a flow rate of nitrogen 150 mL/m for a heating rate of 10 °C/min (Ahmad and Hameed, 2009). Further, the sample was cooled and rinsed frequently with hot distilled water at 70 °C till the pH of the washing solution reached neutral. Finally, the oven-dried sample at 105 °C for 24 h was stored in an airtight container. Fig. 5.2 shows the image of a sample of activated bio-char.

The yield of activated bio-char was calculated as per the (5.1).

$$Yield (\%) = \frac{M_b}{M_0} \times 100 \quad (5.1)$$

Where M_b is the mass of the activated bio-char sample (dry) and M_0 is the mass of precursor (dry).



Fig. 5.2 Activated bio-char

5.2.3 Treatment of secondary treated pulp and paper industry wastewater using activated bio-char

Batch adsorption experiments for removal of COD and colour in secondary treated wastewater were performed at room temperature (30 °C). Sample wastewater was taken in different volumetric flasks of 250 mL using an average shakers speed of 120-130 rpm as shown in Fig. 5.3. The effect of various operating parameters was investigated by changing one parameter and maintaining other parameters constant. Dilute 0.1 N NaOH and 0.1 N HCl were used to maintain the required pH for the adsorption process. The initial COD and colour of a wastewater sample is 234 mg/L and 51 Pt/Co respectively. In each experiment, 100 mL of wastewater sample was treated with an adsorbent dose (0.03 g/L to 0.16 g/L), contact time (1-24 h) and pH (2-12). At elapse of each set, the treated wastewater sample was filtered through 0.45 μm filter paper and analysed for COD and colour.



Fig. 5.3 Laboratory set-up for treatment of wastewater

The effect of pH was studied by using varying pH between 2 to 12 keeping an adsorbent dose 0.14 g/L and contact duration of 24 h. Thereafter, all experiments were conducted using optimum pH. To determine the effect of different doses of adsorbent, the wastewater was treated with various doses, i.e. 0.03 g/L to 0.16 g/L of bio-char for the duration of 24 h. The effect of contact time was studied by treating wastewater with 0.14 g/L of adsorbent for varying periods (1-24 h). The sample of treated water after each set of experiments was analyzed by using Lovibond Spectrodirect Spectrophotometer for COD and colour.

The adsorption amount at equilibrium, q_{eq} , and the reduction percentage were calculated from (5.2) and (5.3), respectively:

$$q_{eq} = \frac{(C_0 - C_e)V}{m} \quad (5.2)$$

$$\% \text{ reduction} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (5.3)$$

Where, C_0 and C_e are the liquid-phase concentrations of adsorbate at initial and at equilibrium, respectively; V (mL) is the volume of solution and m (g) is the mass of dry adsorbent (bio-char) used.

5.2.4 Characterization of Activated bio-char

FT-IR Spectroscopy (Alpha FT-IR spectrometer Brucker) was carried out for the determination of the functional groups that exist in bio-char. The surface characterization mainly surface area, total pore volume, and average pore diameter of the activated bio-char were carried out in Nova Touch LX2 gas sorption analyzer, Quantachrome Instruments by Brunauer-Emmett-Teller (BET) method. Surface morphology and the presence of porosity of activated bio-char were studied using scanning electron microscopy (SEM) analysis (Model Nova NanoSEM 450).

5.3 Adsorption isotherms

The adsorption isotherms are the equilibrium relationship between the concentration in the liquid phase and the concentration in the adsorbent surface at a given temperature. Various types of adsorption isotherms such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich were used to study the adsorption process. In this study, Langmuir and Freundlich's isotherms were studied to investigate the mechanism of the adsorption

process, surface properties, adsorption affinities of COD and colour on activated bio-char. The equilibrium data of adsorption are very important for the design of the adsorption system.

The Freundlich isotherm was efficient on multilayer and also, for the heterogeneous surface, is expressed by the (5.4).

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_e \quad (5.4)$$

Where, q_{eq} and C_{eq} is the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively. Freundlich parameters i.e. K_F and n were determined by plotting a graph of $\log q_{eq}$ versus $\log C_{eq}$. The significance of K_F and n are the adsorption capacity of solid surface and favorability for adsorption, respectively. The slope $1/n$ signifies the intensity of adsorption or heterogeneity of the surface. The value of $1/n$ nearer to zero indicates a more heterogeneous surface (Haghseresht and Lu, 1998).

Langmuir adsorption was very useful for predicting adsorption capacities and also interpreting into mass transfer relationships. The isotherm is written as (5.5).

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m} C_{eq} + \frac{1}{K_L q_m} \quad (5.5)$$

Where, q_m and K_L were the Langmuir constants, which measure monolayer (maximum) adsorption capacity (in mg/g) and energy of adsorption (in g/L), respectively. These constants were determined by plotting C_{eq}/q_{eq} versus C_{eq} .

5.4 Results and discussion

5.4.1 Characteristics of secondary treated wastewater of pulp and paper industry

Table 5.1 shows the typical characteristics of secondary treated wastewater (after biological treatment) sample analyzed according to methods prescribed in APHA (Baird and Bridgewater, 2017). It shows COD and colour of secondary treated wastewater observed 234 mg/L and 51 Pt/Co, respectively. Due to the COD and colour of wastewater, the recycling of wastewater in the process was not feasible. The treated wastewater can be recycled for reuse in the pulp and paper industry if COD and colour of wastewater is reduced or removed through a wastewater treatment.

Table 5.1 Characteristics of secondary treated wastewater of pulp and paper industry

Parameters	Unit	Value
pH	-	6-8
Temperature	°C	27 °C
BOD	mg/L	39
COD	mg/L	234
Colour	Pt-Co	51
Conductivity	µS/cm	1.932
TDS	mg/L	1054
Chloride	mg/L	280
Sulphate	mg/L	60
Ammonical Nitrogen	mg/L	1.2
Oil and Grease	mg/L	0.4

5.4.2 Characterization of Activated bio-char

5.4.2.1 BET Analysis

Table 5.2 shows the results generated in the analysis of BET surface area, pore volume and pore diameter. The BET surface area before and after activation was analyzed and found to be 5.60 m²/g and 273.89 m²/g, respectively. Thus, significant improvement (50 times) in BET surface area indicated that phosphoric acid is considered to be acted effectively for developing the pores onto bio-char. It also observed that total pore volume and average pore diameter for bio-char was 0.022 cm³/g and 17.9 nm, respectively, while for activated bio-char was 0.226 cm³/g and 3.31 nm. Thus, it was analyzed that total pore volume increases, and average pore diameter decrease to the tune of 10 times and 5 times, respectively, upon activation. Pore size classification suggested by IUPAC (International Union of Pure and Applied Chemistry) are defined as micropores, mesopores and macropores for the pore size <2 nm, 2-50 nm and >50 nm respectively (IUPAC, 1972). The activated carbon of this study is in the mesopore region.

Table 5.2 Comparison of surface characteristics for co-pyrolysis bio-char samples.

Bio-char samples	Surface Area, m ² /g	Pore volume, cm ³ /g	Pore diameter, nm
Before activation	5.6	0.022	17.9
Activated Bio-char	273.89	0.226	3.31

5.4.2.2 SEM Analysis

The scanning electron microscopy (SEM) photo micro-graph of the activated bio-char at 1,000 magnification is depicted in Fig. 5.4 (a) and (b). It showed that the resulting activated bio-char imparts irregular shape and heterogeneous pore structure. Also, many large pores in a honeycomb shape were observed on the surface of the activated carbon.

Such a structure believes to be effective for the accumulation of the contaminants of the solution. Thus, the surface structure characteristics of activated bio-char determine its potential to act as a good adsorbent.

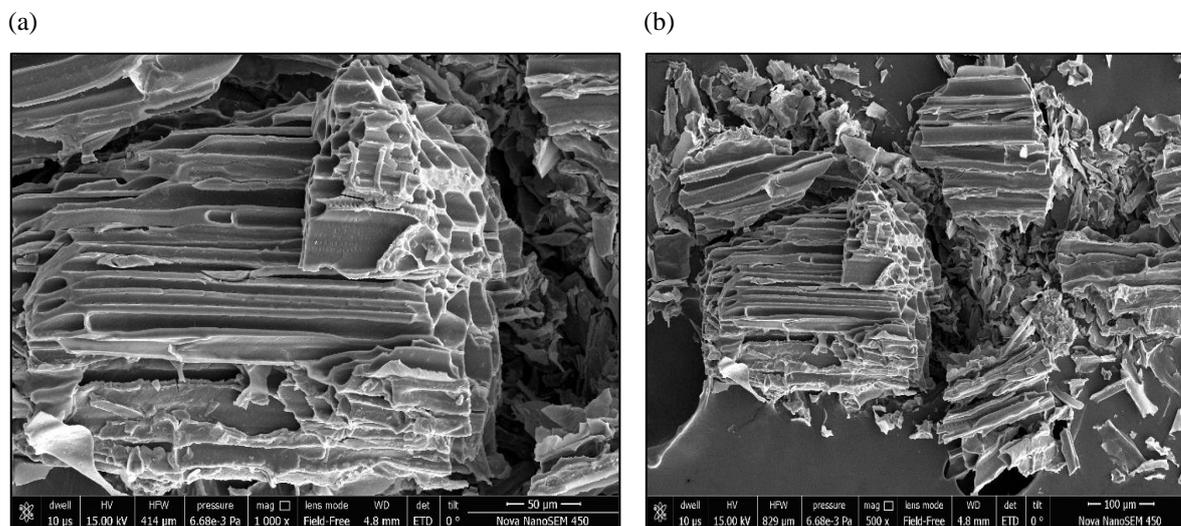


Fig. 5.4 (a) and (b) SEM images of co-pyrolysis based activated bio-char (magnification = 1000×)

5.4.2.3 FTIR Analysis

Fig.5.5 presented the FTIR spectra of activated bio-char, which showed different bands and denotes abundant functional groups. Broadbands near 3828 cm^{-1} , 3769 cm^{-1} and 3456 cm^{-1} recognized the presence of hydroxyl (-OH) group in activated bio-char. It was reported that spectral band in the range of $3200\text{--}3750\text{ cm}^{-1}$ for alcohols and phenols may be attributed to adsorbed water (Chen et al., 2002). The bands near 2943 cm^{-1} and 2384 cm^{-1} indicate the presence of aliphatic C-H and carbonyl C=O stretching from ketones and aldehydes or carboxylic groups, respectively. Whereas band of 1594 cm^{-1} indicated due to C=C stretching vibration of the aromatic rings or C=O stretch carboxylic acid existed in bio-char. Bands near 1434 and 1036 cm^{-1} represents N-H bending and C=O groups reported earlier (Fan et al., 2016). In the low-wave number region, the shoulder peak at 887 cm^{-1} could be attributed to the out of plane bending absorption of C-H in the aromatic ring (Sun et al., 2012). Band of 674 cm^{-1} characterizes C-O-H twist broad. The overall study of FTIR spectra revealed that the surface of the bio-char after activation became rich in functional groups such as hydroxyl groups, carboxylic acid and carbonyl groups. These functional groups with such a characteristic provide active sites for the removal of COD and colour by chemical adsorption (Guo and Lua, 2003; Zhang et al., 2019; Luo et al., 2019).

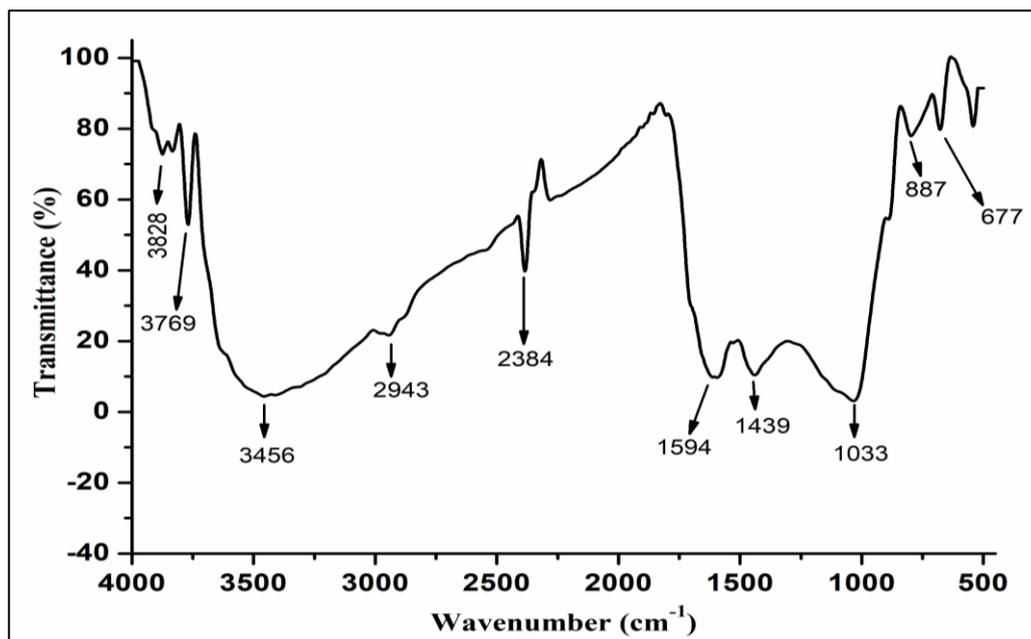


Fig. 5.5 FTIR spectra of activated bio-char

5.4.3 Treatment of secondary treated pulp and paper industry wastewater

5.4.3.1 Determination of optimum pH

Table 5.3 depicted the effect of pH for the removal of COD and colour at an experimentally optimized adsorption dose of 0.14 g/L for a duration of 24 h at the temperature of 30 °C. The percentage removal of COD and colour was determined based on (5.3). It was clearly shown that the percentage reduction of COD was 85.04% at pH 3, whereas 30.34 % at pH 12. Also, the percentage reduction of colour was 98.03 % at pH 3 and 31.37 % at pH 12. Moreover, COD and colour were analysed at pH 2 and observed a reduction in COD and colour by 73.07% and 86.27%, respectively. Thus, pH 3 was considered the optimum pH for the removal of COD and colour.

Table 5.3 Effect of different pH on COD and colour removal from wastewater.

pH	COD		Colour	
	C_{eq} (mg/L)	% Removal	C_{eq} , Pt-Co	% Removal
2	63	73.07	7	86.27
3	35	85.04	1	98.03
5	88	62.39	23	54.90
7	151	35.47	35	31.37
8	147	37.17	34.5	32.35
10	152	35.04	34	33.33
11	158	32.47	35	31.37
12	163	30.34	35	31.37

Other experiments were performed by fixing pH 3 for various adsorbent doses and contact duration. The pH is an important factor in the adsorption mechanism. Higher adsorption capacity at lower pH is due to the fact that increment the concentration of hydrogen (H_3O^+) ion and negatively charged adsorption surface is neutralized by acidic solution. At higher pH, excess hydroxide ion (OH^-) may be produced ionic repulsion between the negatively charged active sites of the adsorbent (Ahmad and Hameed, 2009).

5.4.3.2 Effect of activated bio-char doses

Fig.5.6 showed the percentage removal of COD and colour versus activated bio-char doses (0.3-0.14 g/L) at constant pH 3 for a duration of 24 h. It was observed that percentage reduction in the COD found to be 11.11, 29.91, 38.46, 53.84, 82.47 and 84.04 % for bio-char dose of 0.03, 0.05, 0.08, 0.10, 0.12 and 0.14 g/L respectively. Also, large percentage reduction in the colour was occurred to be 26.27, 45.09, 58.82, 80.1 and 97 % for bio-char doses of 0.03, 0.05, 0.08, 0.10, 0.12 and 0.14 g/L, respectively. Higher percentage removal was occurred by increasing bio-char doses, which attributed to the availability of more pores and sorption active site of adsorbent.

It was observed that COD and colour removal remained almost the same on further increments in doses of bio-char. Thus, the dosage of 0.14 g/L of bio-char has concluded the state of equilibrium. A similar trend of adsorbent saturation was investigated for the treatment of wastewater from pulp and paper mills and cotton textile mills with the use of bagasse fly ash and bamboo-based activated carbon, respectively (Srivastava et al., 2005; Ahmad and Hameed, 2009).

Fig. 5.7 depicted the effect of contact duration for the removal of COD and colour using activated bio-char at constant pH 3 and adsorbent doses of 0.14 g/L. The percentage removal of COD and colour was determined based on (5.3). It is clearly seen from Fig. 5.7 that increasing the contact duration increases the removal of COD and colour. It was observed that initially (1-5 h) the COD and colour were removed at a faster rate and after 5 h of contact time for adsorption, there is no effective change in the rate of removal of COD and colour. It was also observed that maximum COD removal occurred in 20 h of duration. Then after, slight changes in COD removal were observed. In line with this, a similar trend of colour removal was observed, i.e. 20 h. Thus, 20 h of contact duration is considered as for maximum removal of COD and colour.

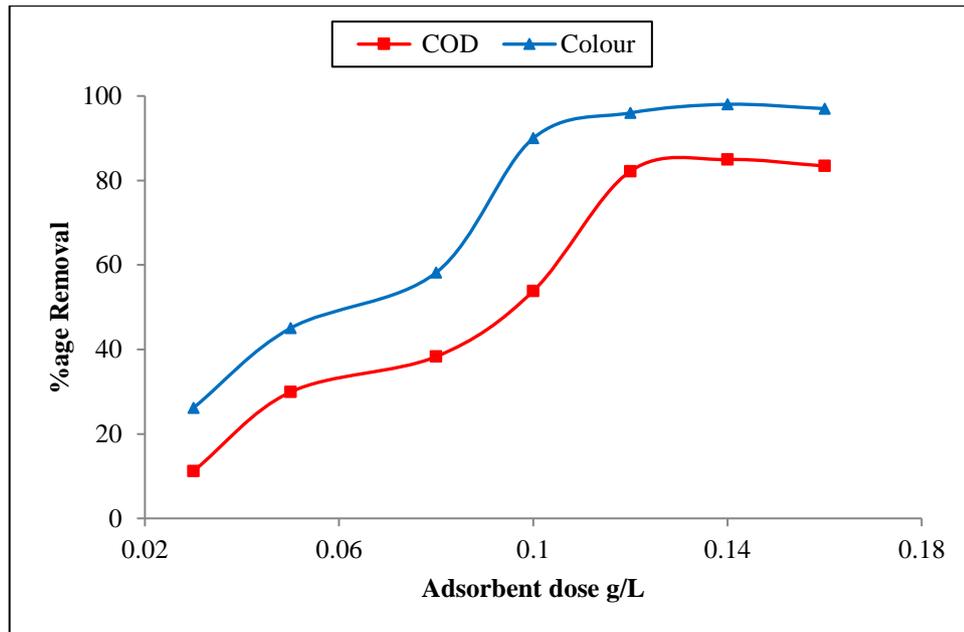


Fig. 5.6 Effect on COD and colour removal for a different dose of activated bio-char at pH 3 and contact duration 24 h

5.4.3.3 Effect of contact duration

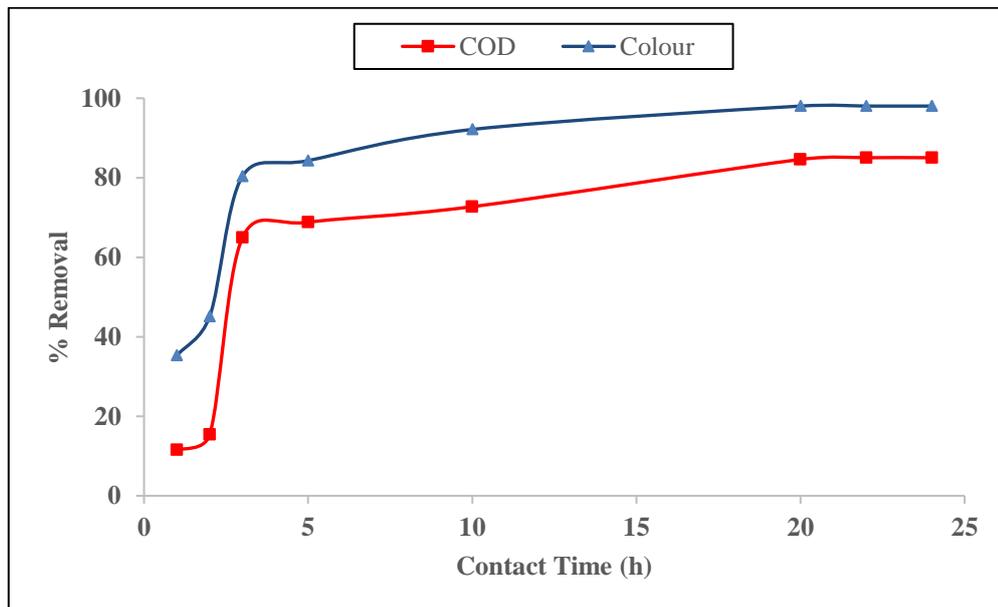


Fig. 5.7 Effect on COD and colour removal of various contact duration at pH 3 and adsorbent dosage 0.14g/L. Initially, higher removal of COD and colour was observed due to the fact that at the beginning of the sorption process, all the reaction sites are vacant and hence the extent of removal was high. After that, there was a transitional phase in which the rate of uptake was slow with uptake reaching almost constant value. Probably, during a contact time of 1-5 h, the contaminants are adsorbed at the exterior surface of activated bio-char and after

saturation condition, the molecules are diffused through pores of activated bio-char into the interior parts. This process may take a longer time. As it can be seen in Fig. 5.7, monolayer generated on outer layer of adsorbent in the initial period. The curved section shows the effect of monolayer adsorption and mass transfer. The nearly straight-line section at a longer period of contact time explains the diffusion of particles in the interior surface of the adsorbent. The optimum contact time for COD and colour removal from wastewater is 5 h. Similar reasoning was explained for COD and colour removal for textile industry wastewater using bamboo-based activated carbon (Ahmad and Hameed, 2009).

5.4.4 Adsorption isotherms

Fig. 5.8 and 5.9 represented Freundlich and Langmuir isotherm plots for the removal of COD and colour by activated bio-char. Values of the correlation coefficient, R^2 was derived in the range of 0.81 to 0.98 for both the isotherm models signifies the suitability of all experimental data. As earlier discussed, the K_F and n are the Freundlich constants that showed the adsorption capacity of the adsorbent and favorability towards the adsorption process, respectively. The factor “ $1/n$ ” gives an indication of the favorability of adsorption. The value of slope in a graph ($1/n$) derived was lesser than 0.5 representing that the adsorbate was easily adsorbed on the surface of bio-char. Researchers had reported that the value of slope below 0.5 showed a higher affinity towards adsorption, whereas values larger than 2 indicated unfavorable adsorption (Shi et al., 2014).

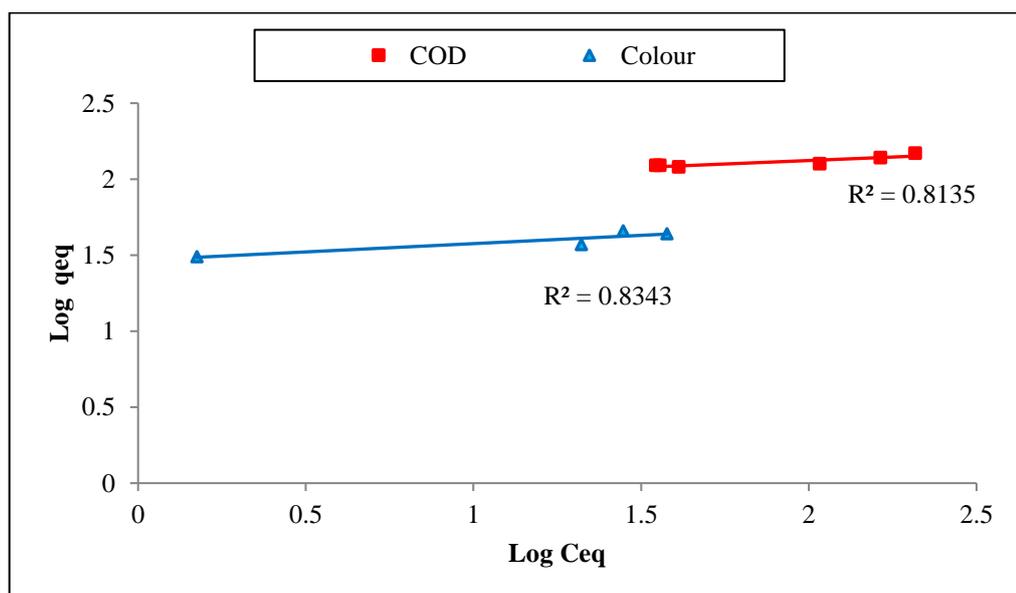


Fig. 5.8 Freundlich isotherm plot for removal of COD and colour

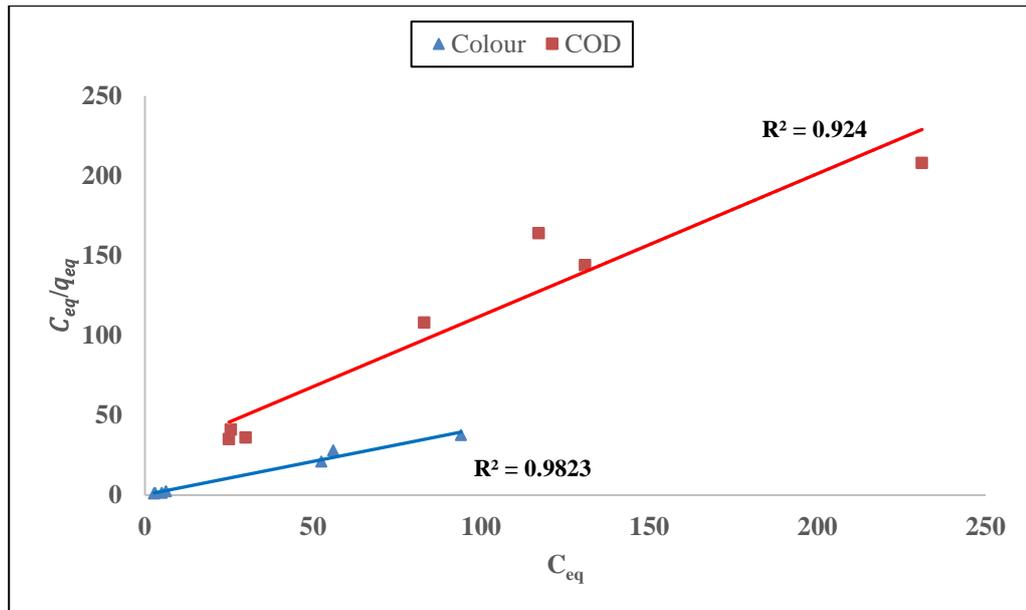


Fig 5.9 Langmuir Isotherm plot for removal of COD and colour

Table 5.4 indicates the various parameters for COD and colour removal using activated bio-char from pulp and paper industry wastewater. A dimensionless parameter of Langmuir isotherm is called separation factor, R_L , is defined as the following (5.6).

$$R_L = \frac{1}{1+K_L C_0} \quad (5.6)$$

Where K_L is the Langmuir constant (L/mg) and C_0 is the initial concentration of COD and colour in solution (mg/L). The value of R_L indicates the shape of the Langmuir isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Moyo et al., 2016). As shown in Table 5.4 the value of R_L is less than 1 and it suggests that the adsorption process was favorable. The very low value of R_L suggests a higher affinity of activated bio-char adsorbent for the removal of COD and colour.

Table 5.4 Langmuir and Freundlich parameters for COD and colour removal using activated bio-char

Langmuir parameters			Freundlich Parameters		
Parameters	COD removal	Colour removal	Parameters	COD removal	Colour removal
q_m	1.124	2.39	K_L	86.89	29.24
K_L	0.037	2.019	$1/n$	0.019	0.109
R^2	0.982	0.924	R^2	0.834	0.813
R_L	0.1	0.01	-	-	-

5.5 Summary

Bio-char produced from co-pyrolysis of MSS and SCB and chemically activated by using phosphoric acid is a promising adsorbent to reduce the COD and colour from secondary

treated (after biological treatment) pulp and paper industry wastewater. It is an effective adsorbent with significant improvement (50 times) in BET surface area, 10 times in pore volume and 5 times reduction in pore size (was found to be mesoporous). Honeycomb shape in SEM image and existence of functional groups such as hydroxyl groups, carboxylic acid and carbonyl group in FTIR spectra attributed to such a significant improvement.

COD and colour were reduced by 68.8% and 86.31%, respectively at an optimized pH 3 with an activated bio-char of 0.14 g/L in a duration dose of 5 h. Langmuir and Freundlich isotherm model indicated strong affinity on the surface of activated bio-char towards adsorption of COD and colour imparting constituents of pulp and paper industry wastewater. Moreover, both the isotherm was observed best suited to obtained equilibrium.

CHAPTER 6

Conclusions and Future Scope

6.1 Conclusions

This study affirms that the co-pyrolysis, thermal technology, is a suitable option for handling the enormous quantity of available solids waste i.e. MSS and SCB, and can be converted into bio-oil and biochar. This study presented detailed information about the co-pyrolysis kinetics of MSS and SCB using TGA and DTG. It also suggested a synergistic effect in the thermal behavior of co-pyrolysis and the yield of products mainly bio-oil. To enrich the value addition of the co-pyrolysis product, mainly bio-char, this study was carried out for the utilization of bio-char (after chemical activation) for secondary treated wastewater of the pulp and paper industry. The followings are the conclusions of this study.

1. The raw materials, MSS and SCB, are characterized by proximate and ultimate analysis which shows the high ash content of ash in MSS and significant content of nitrogen and oxygen content in MSS and SCB. The thermal behavior of MSS, SCB, and its blend (1:1) was analyzed by TG and DTG. The nature of TG and DTG curves showed that degradation of MSS occurred in three stages represented by degradation of lipids, protein followed by polysaccharides, whereas SCB degradation in two stages indicated degradation of hemicellulose, cellulose followed by sluggish degradation of lignin. During the primary stage degradation of SCB, resulting bio-oil might be encouraged MSS degradation leading to more volatile production from MSS itself. Also, it restricts the carbonization reactions which favors the residue formation. Thus, the co-pyrolysis mixture exhibited a reduction in residue generation by 56% than that of only MSS degradation.

2. Also, degradation of SCB resulting to metal-containing ash and the catalytic effect of these metals might be responsible for higher devolatilization of MSS, leading to an increment in maximum percentage degradation per minute by 55% as compared to that of only MSS degradation. The addition of SCB in MSS in a 1:1 mass ratio showed variation in activation energy by -60% (mixture exhibited reduced activation energy in a third stage) to +36% (increased for first and second stage). Such a change in activation energy is attributed to the formation of char and bio-oil in a primary stage degradation of SCB and the catalytic effect of metal-containing ash. Improvement in the highest rate of degradation, the shift of peak temperature to lower value, reduced quantity of residue, and alteration in activation energy for decomposition of the mixtures showed the existence of synergy in co-pyrolysis of MSS and SCB. Thus, the significant influence of SCB addition in co-pyrolysis with MSS was observed.
3. The present study demonstrates the preparation of bio-oils from MSS, SCB, and their blends by using the batch pyrolysis process. The synergistic effect observed in co-pyrolysis of MSS with SCB led to enhanced bio-oil yield. In contrast to merely MSS pyrolysis, upon addition of SCB in MSS, the yield of bio-oil and gas increased by 100% and 14%, respectively, whereas the yield of char (residue) decreased by 42%.
4. GC-MS analyses revealed that a significant reduction in sulfur-containing compounds and steroids were seen upon co-pyrolysis. Moreover, nitrogen-containing compounds, and hydrocarbons were too reduced marginally. Physical properties such as pH, viscosity, and density favor the use of bio-oil as a transport fuel. Upon co-pyrolysis, significant improvement in higher heating value was not observed. Moreover, reduction in oxygenates was not referred. Alternatively, bio-oil may prove as a potential material to provide organic chemicals, mainly phenolic compounds.
5. Biochar produced from co-pyrolysis of MSS and SCB and chemically activated by using phosphoric acid is a promising adsorbent to reduce the COD and colour from secondary treated (after biological treatment) pulp and paper industry wastewater. It is an effective adsorbent with significant improvement (50 times) in BET surface area, 10 times in pore volume, and 5 times reduction in pore size (was found to be mesoporous). Honeycomb shape in SEM image and existence of functional groups such as hydroxyl groups,

carboxylic acid, and carbonyl group in FTIR spectra attributed to such a significant improvement.

6. COD and colour were reduced by 68.8% and 86.31%, respectively at an optimized pH 3 with an activated bio-char dose of 0.14 g/L in a duration of 5 h. Langmuir and Freundlich's isotherm model indicated strong affinity on the surface of activated bio-char towards adsorption of COD and colour imparting constituents of pulp and paper industry wastewater. Moreover, both the isotherm was observed best suited to obtained equilibrium.

6.2 Future scope of this study

1. Various authors reported improvement in hydrogen production of un-condensable gases during co-pyrolysis. Thus, study on un-condensable gases during co-pyrolysis of MSS and SCB would be the future scope of work.
2. Due to presence of high molecular weight hydrocarbons and oxygenated compounds in the bio-oil limits its application as a fuel. In this context, catalytic pyrolysis is another attainable route to upgrade bio-oil quality. Among different catalysts (i.e., zeolites) studied for pyrolysis, activated bio-char (ACB) become eco-friendly alternatives. The beneficial features of ACB derived from MSS-SCB co-pyrolysis comprise the comparatively large surface area, porosity, enriched surface functional groups, and presence of a high amount of metal species that can improve the catalytic activity. Thus, the application of activated bio-char as a catalyst for up-gradation of co-pyrolyzed bio-oil will be the future scope of the study.
3. GC-MS study showed that bio-oil comprises of various compounds, which would provide value addition of bio-oil. Thus, the downstream application of bio-oil for various purposes such as cosmetics, pharmaceuticals, etc. will be explored.
4. A comprehensive techno-economic feasibility study report for the pilot-scale co-pyrolysis process is to be explored.

References

- Abhilash, P. C., & Singh, N. (2008). Influence of the application of sugarcane bagasse on lindane (γ -HCH) mobility through soil column: implication for biotreatment. *Bioresource technology*, *99*(18), 8961-8966.
- Abnisa, F., & Daud, W. M. A. W. (2014). A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Conversion and Management*, *87*, 71-85.
- Aboulkas, A., Makayssi, T., Bilali, L., Nadifiyine, M., & Benchanaa, M. (2012). Co-pyrolysis of oil shale and high density polyethylene: structural characterization of the oil. *Fuel processing technology*, *96*, 203-208.
- Aboyade, A. O., Gorgens, J. F., Carrier, M., Meyer, E. L., & Knoetze, J. H. (2013). Thermogravimetric study of the pyrolysis characteristics and kinetics of coal blends with corn and sugarcane residues. *Fuel Processing Technology*, *106*, 310-320.
- Agarwal, M., Tardio, J., & Mohan, S. V. (2015). Pyrolysis of activated sludge: energy analysis and its technical feasibility. *Bioresource technology*, *178*, 70-75.
- Agrafioti, E., Bouras, G., Kalderis, D., & Diamadopoulos, E. (2013). Bio-char production by sewage sludge pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *102*, 72-78.
- Aguado, R., Olazar, M., Gaisán, B., Prieto, R., & Bilbao, J. (2002). Kinetic study of polyolefin pyrolysis in a conical spouted bed reactor. *Industrial & engineering chemistry research*, *41*(18), 4559-4566.
- Ahmad, A. A., & Hameed, B. H. (2009). Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon. *Journal of hazardous materials*, *172*(2-3), 1538-1543.
- Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J. K., Yang, J. E., & Ok, Y. S. (2012). Effects of pyrolysis temperature on soybean stover-and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresource technology*, *118*, 536-544.
- Ali, I., & Gupta, V. K. (2006). Advances in water treatment by adsorption technology. *Nature protocols*, *1*(6), 2661-2667.
- Ali, M., & Sreekrishnan, T.R. (2001). Aquatic toxicity from pulp and paper mill effluents: A review. *Advances in environmental research*, *5*, 175-196.
- Alvarez, J., Amutio, M., Lopez, G., Bilbao, J., & Olazar, M. (2015). Fast co-pyrolysis of sewage sludge and lignocellulosic biomass in a conical spouted bed reactor. *Fuel*, *159*, 810-818.
- Amor, C., Marchao, L., Lucas, M.S., & Peres, J.A. (2019). Application of advanced oxidation processes for the treatment of recalcitrant agro-industrial wastewater: A review. *Water*, *11*, 205.
- Arami-Niya, A., Daud, W.W., & Mjalli, F. (2010). Production of palm shell-based activated carbon with more homogeneous pore size distribution. *Journal of Applied Sciences*, *10*, 3361-3366.
- Arazo, R. O., Genuino, D. A. D., de Luna, M. D. G., & Capareda, S. C. (2017). Bio-oil production from dry sewage sludge by fast pyrolysis in an electrically-heated fluidized bed reactor. *Sustainable Environment Research*, *27*(1), 7-14.
- Archibald, F., & Roy-Arcand, L. (1995). Photo degradation of high molecular weight kraft bleachery effluent organochlorine and colour. *Water research*, *29*, 661-669.
- Asadullah, M., Rahman, M. A., Ali, M. M., Rahman, M. S., Motin, M. A., Sultan, M. B., & Alam, M. R. (2007). Production of bio-oil from fixed bed pyrolysis of bagasse. *Fuel*, *86*(16), 2514-2520.
- Ashrafi, O., Yerushalmi, L., & Haghghat, F. (2015). Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of environmental management*, *158*, 146-157.
- Atienza-Martínez, M., Mastral, J. F., Ábrego, J., Ceamanos, J., & Gea, G. (2015). Sewage sludge torrefaction in an auger reactor. *Energy & Fuels*, *29*(1), 160-170.
- Awad, Y. M., Blagodatskaya, E., Ok, Y. S., & Kuzyakov, Y. (2012). Effects of polyacrylamide, biopolymer, and biochar on decomposition of soil organic matter and plant residues as determined by ^{14}C and enzyme activities. *European Journal of Soil Biology*, *48*, 1-10.
- Bahadur, N. P., Boocock, D. G., & Konar, S. K. (1995). Liquid hydrocarbons from catalytic pyrolysis of sewage sludge lipid and canola oil: evaluation of fuel properties. *Energy & fuels*, *9*(2), 248-256.
- Baird, R., & Bridgewater, L. (2017). Standard methods for the examination of water and wastewater. 23rd edition. Washington DC. *American Public Health Association*.
- Ben, H., Yoo, C.G., Hao, N., Adhikari, S., & Ragauskas, A.J. (2016). Review of NMR characterization of pyrolysis oils. *Energy Fuels*, *30*, 6863-6880.

- Bharathiraja, B., Yogendran, D., Ranjith Kumar, R., Chakravarthy, M., & Palani, S. (2014). Biofuels from sewage sludge-A review. *International Journal of ChemTech Research*, 6(9), 4417-4427.
- Bhattacharjee, S., Datta, S., & Bhattacharjee, C. (2007). Improvement of wastewater quality parameters by sedimentation followed by tertiary treatments. *Desalination*, 212, 92-102.
- Bilgen, S. (2016). Correlation for estimation of the chemical availability (exergy) from ultimate analysis of pyrolytic oils obtained from fast pyrolysis of biomass. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 38(9), 1286-1292.
- Bioenergy, I. E. A. (2010). IEA Bioenergy Task 34: Pyrolysis. *Online available at* <http://www.pyne.co.uk>, Accessed 13 September 2011
- Blesa, M. J., Fierro, V., Miranda, J. L., Moliner, R., & Palacios, J. M. (2001). Effect of the Pyrolysis Process on the Physicochemical and Mechanical Properties of Smokeless Fuel Briquettes. *Fuel Processing Technology*, 74, 1-17.
- Blesa, M. J., Miranda, J. L., Moliner, R., Izquierdo, M. T., & Palacios, J. M. (2003). Low-temperature co-pyrolysis of a low-rank coal and biomass to prepare smokeless fuel briquettes. *Journal of Analytical and Applied Pyrolysis*, 70, 665-677.
- Bolan, N. S., Kunhikrishnan, A., Choppala, G. K., Thangarajan, R., & Chung, J. W. (2012). Stabilization of carbon in composts and biochars in relation to carbon sequestration and soil fertility. *Science of the Total Environment*, 424, 264-270.
- Bondarczuk, K., Markowicz, A., & Piotrowska-Seget, Z. (2016). The urgent need for risk assessment on the antibiotic resistance spread via sewage sludge land application. *Environment international*, 87, 49-55.
- Brebu, M., Ucar, S., Vasile, C., & Yanik, J. (2010). Co-pyrolysis of pine cone with synthetic polymers. *Fuel*, 89(8), 1911-1918.
- Bridgwater T. (2007). Biomass pyrolysis, *Biomass Bioenergy*, 31.
- Bridgwater, A. V. (2003). Renewable fuels and chemicals by thermal processing of biomass. *Chemical engineering journal*, 91(2-3), 87-102.
- Bridgwater, A. V. (2004). Biomass fast pyrolysis. *Thermal science*, 8(2), 21-50.
- Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and bioenergy*, 38, 68-94.
- Bridgwater, A. V., Meier, D., & Radlein, D. (1999A). An overview of fast pyrolysis of biomass. *Organic geochemistry*, 30(12), 1479-1493.
- Bridgwater, A., Czernik, S., Diebold, J., Meier, D., Oasmaa, A., Peacocke, C., Piskorz, J. & Radlein, D. (1999B). Fast pyrolysis of biomass: a handbook. United Kingdom.
- Bridgwater, A.V. (2005). Fast pyrolysis of biomass: A handbook. *CRL Press, Newbury*.
- Bridle, T.T., Campbell, H.W., Sachdev, A., Marvan, I. (1983). Thermal conversion of sewage sludge to liquid and solid fuels, In Proceedings : Canadian Chemical Engineering Conference 1983.
- Buyukkamaci, N., & Koken, E. (2010). Economic evaluation of alternative wastewater treatment plant options for pulp and paper industry. *Science to the total environment*, 408, 6070-6078.
- Caballero, J. A., Front, R., Marcilla, A., & Conesa, J. A. (1997). Characterization of sewage sludges by primary and secondary pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 40, 433-450.
- Cao, J. P., Zhao, X. Y., Morishita, K., Wei, X. Y., & Takarada, T. (2010). Fractionation and identification of organic nitrogen species from bio-oil produced by fast pyrolysis of sewage sludge. *Bioresource technology*, 101(19), 7648-7652.
- Cao, J.P. (2011). Production and Chemical Utilization of Bio-oil by Fast Pyrolysis of Sewage Sludge. *A dissertation, Graduate School of Engineering, Gunma University*.
- Cao, X., Ma, L., Liang, Y., Gao, B., & Harris, W. (2011). Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environmental science & technology*, 45(11), 4884-4889.
- Capareda, S. (2013). Introduction to biomass energy conversions. 1st ed., CRC Press.
- Carrier, M., Hugo, T., Gorgens, J., & Knoetze, H. (2011). Comparison of slow and vacuum pyrolysis of sugar cane bagasse. *Journal of analytical and applied pyrolysis*, 90(1), 18-26.
- Cha, J. S., Park, S. H., Jung, S. C., Ryu, C., Jeon, J. K., Shin, M. C., & Park, Y. K. (2016). Production and utilization of biochar: A review. *Journal of Industrial and Engineering Chemistry*, 40, 1-15.
- Chen, B., & Chen, Z. (2009). Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, 76(1), 127-133.
- Chen, C., Yan, X., Xu, Y., Yoza, B. A., Wang, X., Kou, Y., Ye, H., Wang, Q., & Li, Q. X. (2019). Activated petroleum waste sludge biochar for efficient catalytic ozonation of refinery wastewater. *Science of the Total Environment*, 651, 2631-2640.

- Chen, X., Jeyaseelan, S., & Graham, N. (2002). Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Management*, 22(7), 755-760.
- Chern, J. M., & Chien, Y. W. (2003). Competitive adsorption of benzoic acid and p-nitrophenol onto activated carbon: isotherm and breakthrough curves. *Water Research*, 37(10), 2347-2356.
- Cho, D. W., Kwon, G., Yoon, K., Tsang, Y. F., Ok, Y. S., Kwon, E. E., & Song, H. (2017). Simultaneous production of syngas and magnetic biochar via pyrolysis of paper mill sludge using CO₂ as reaction medium. *Energy conversion and management*, 145, 1-9.
- Chun, Y., Sheng, G., Chiou, C. T., & Xing, B. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental science & technology*, 38(17), 4649-4655.
- Cole, A. J., Paul, N. A., De Nys, R., & Roberts, D. A. (2017). Good for sewage treatment and good for agriculture: Algal based compost and biochar. *Journal of environmental management*, 200, 105-113.
- Conesa, J.A., Marcilla, A., Prats, D., & Rodríguez-Pastor, M. (1997). Kinetic Study of the Pyrolysis of Sewage Sludge. *Waste Management & Research*, 15(3), 293-305.
- Cordero, T., Rodríguez-Mirasol, J., Pastrana, J., & Rodríguez, J. J. (2004). Improved solid fuels from co-pyrolysis of a high-sulphur content coal and different lignocellulosic wastes. *Fuel*, 83, 1585-1590.
- CPCB, 2015. Inventorization of sewage treatment plant. Available at. https://nrcd.nic.in/writereaddata/FileUpload/NewItem_210_Inventorization_of_Sewage-Treatment_Plant.pdf. Accessed 14 July 2017).
- De Los, S.R.W., Poznyak, T., Chairez, I., & Cordova, R.I. (2009). Remediation of lignin and its derivatives from pulp and paper industry wastewater by the combination of chemical precipitation and ozonation. *Journal of hazardous materials*, 169, 428-434.
- Degremont, G. (1979). *Water Technical Manual*, Fourth Edition.
- Demirbas, A. (2005). Pyrolysis of ground beech wood in irregular heating rate conditions. *Journal of Analytical and Applied Pyrolysis*, 73(1), 39-43.
- Diao, Y., Walawender, W. P., & Fan, L. T. (2002). Activated carbons prepared from phosphoric acid activation of grain sorghum. *Bioresource technology*, 81(1), 45-52.
- Dilek, F.B., Gokcay, C.F. (1994). Treatment of effluents from hemp-based pulp and paper industry: I - waste characterization and physico-chemical treatability. *Water science & technology*, 29(9), 161-163.
- Ding, H. S., & Jiang, H. (2013). Self-heating co-pyrolysis of excessive activated sludge with waste biomass: energy balance and sludge reduction. *Bioresource technology*, 133, 16-22.
- Disposal and Recycling Routes for Sewage Sludge (2002), European Commission. Office for Official Publications of the European Communities. ISBN: 92-894-1801-X.
- Dominguez, A., Menéndez, J. A., & Pis, J. J. (2006A). Hydrogen rich fuel gas production from the pyrolysis of wet sewage sludge at high temperature. *Journal of analytical and applied pyrolysis*, 77(2), 127-132.
- Domínguez, A., Menéndez, J. A., Inguanzo, M., & Pis, J. J. (2005). Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge. *Fuel Processing Technology*, 86(9), 1007-1020.
- Domínguez, A., Menéndez, J. A., Inguanzo, M., & Pis, J. J. (2006B). Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating. *Bioresource technology*, 97(10), 1185-1193.
- Dominguez, A., Menendez, J. A., Inguanzo, M., Bernad, P. L., & Pis, J. J. (2003). Gas chromatographic-mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges. *Journal of chromatography A*, 1012(2), 193-206.
- Doshi, V. A., Vuthaluru, H. B., & Bastow, T. (2005). Investigations into the control of odour and viscosity of biomass oil derived from pyrolysis of sewage sludge. *Fuel processing technology*, 86(8), 885-897.
- Effendi, A., Gerhauser, H., & Bridgwater, A. V. (2008). Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renewable and sustainable energy reviews*, 12(8), 2092-2116.
- Enders, A., Hanley, K., Whitman, T., Joseph, S., & Lehmann, J. (2012). Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresource technology*, 114, 644-653.
- European Biochar Foundation (EBC) (2012). European Biochar Certificate—Guidelines for a Sustainable Production of Biochar. *European Biochar Foundation, Arbaz, Switzerland*, <http://www.european-biochar.org/en/download> (accessed 14 August 2017).
- Fairous, S., Rusnah, S., & Maryam, H. (2011). Bio-fuel source from combination feed of sewage sludge and rice waste. In: *2011 International Conference on Environment Science and Engineering, Singapore*, pp. 68–72.

- Fan, S., Tang, J., Wang, Y., Li, H., Zhang, H., Tang, J., Wang, Z., & Li, X. (2016). Biochar prepared from co-pyrolysis of municipal sewage sludge and tea waste for the adsorption of methylene blue from aqueous solutions: kinetics, isotherm, thermodynamic and mechanism. *Journal of Molecular Liquids*, 220, 432-441.
- Fang, S., Yu, Z., Lin, Y., Hu, S., Liao, Y., & Ma, X. (2015). Thermogravimetric analysis of the co-pyrolysis of paper sludge and municipal solid waste. *Energy conversion and management*, 101, 626-631.
- Fang, S., Yu, Z., Lin, Y., Lin, Y., Fan, Y., Liao, Y., & Ma, X., (2016). Effects of additives on the copyrolysis of municipal solid waste and paper sludge by using thermogravimetric analysis. *Bioresource Technology*, 209, 265–272.
- Font, R., Fullana, A., & Conesa, J. A. (2001) Analysis of the pyrolysis and combustion of different sewage sludges by TG, *Journal of Analytical and Applied Pyrolysis*, 1, 927-941.
- Fonts, I., Azuara, M., Gea, G., & Murillo, M. B. (2009A). Study of the pyrolysis liquids obtained from different sewage sludge. *Journal of analytical and applied pyrolysis*, 85(1-2), 184-191.
- Fonts, I., Azuara, M., Lázaro, L., Gea, G., & Murillo, M. B. (2009(B)). Gas chromatography study of sewage sludge pyrolysis liquids obtained at different operational conditions in a fluidized bed. *Industrial & engineering chemistry research*, 48(12), 5907-5915.
- Fonts, I., Gea, G., Azuara, M., Ábrego, J., & Arauzo, J. (2012). Sewage sludge pyrolysis for liquid production: a review. *Renewable and sustainable energy reviews*, 16(5), 2781-2805.
- Fonts, I., Juan, A., Gea, G., Murillo, M. B., & Arauzo, J. (2009C). Sewage sludge pyrolysis in a fluidized bed, 2: influence of operating conditions on some physicochemical properties of the liquid product. *Industrial & engineering chemistry research*, 48(4), 2179-2187.
- Fonts, I., Juan, A., Gea, G., Murillo, M. B., & Sanchez, J. L. (2008). Sewage sludge pyrolysis in fluidized bed, 1: influence of operational conditions on the product distribution. *Industrial & engineering chemistry research*, 47(15), 5376-5385.
- Fonts, I., Kuoppala, E., & Oasmaa, A. (2009D). Physicochemical properties of product liquid from pyrolysis of sewage sludge. *Energy & Fuels*, 23(8), 4121-4128.
- Forster, C. F. (2003). *Wastewater treatment and technology*. Thomas Telford, UK.
- Fullana, A., Contreras, J. A., Striebich, R. C., & Sidhu, S. S. (2005). Multidimensional GC/MS analysis of pyrolytic oils. *Journal of analytical and applied pyrolysis*, 74(1-2), 315-326.
- Fytli, D., & Zabaniotou, A. (2008). Utilization of sewage sludge in EU application of old and new methods-A review. *Renewable and sustainable energy reviews*, 12(1), 116-140.
- Gao, N., Li, J., Qi, B., Li, A., Duan, Y., & Wang, Z. (2014). Thermal analysis and products distribution of dried sewage sludge pyrolysis. *Journal of analytical and applied pyrolysis*, 105, 43-48.
- García-Pérez, M., Chaala, A., Yang, J., & Roy, C. (2001). Co-pyrolysis of sugarcane bagasse with petroleum residue. Part I: thermogravimetric analysis. *Fuel*, 80(9), 1245-1258.
- Garforth, A. A., Ali, S., Hernández-Martínez, J., & Akah, A. (2004). Feedstock recycling of polymer wastes. *Current Opinion in Solid State and Materials Science*, 8(6), 419-425.
- Garg, A., Mishra, I.M., & Chand, S. (2007). Catalytic wet oxidation of the pretreated synthetic pulp and paper mill effluent under moderate conditions. *Chemosphere*, 66, 1799-1805.
- Gayubo, A. G., Valle, B., Aguayo, A. T., Olazar, M., & Bilbao, J. (2010). Olefin production by catalytic transformation of crude bio-oil in a two-step process. *Industrial & Engineering Chemistry Research*, 49(1), 123-131.
- Georgieva, V.G., Tavlieva, M.P., Genieva, S.D., & Vlaev, L.T. (2015). Adsorption kinetics of Cr (VI) ions from aqueous solutions onto black rice husk ash. *Journal of molecular liquids*, 208, 219-226.
- Ghezzehei, T. A., Sarkhot, D. V., & Berhe, A. A. (2014). Biochar can be used to capture essential nutrients from dairy wastewater and improve soil physico-chemical properties. *Solid Earth*, 5(2), 953-962.
- Gil-Lalaguna, N., Fonts, I., Gea, G., Murillo, M. B., & Lazaro, L. (2010). Reduction of water content in sewage sludge pyrolysis liquid by selective online condensation of the vapors. *Energy & fuels*, 24(12), 6555-6564.
- Girovich, M. J. (1996). *Biosolids treatment and management: Processes for beneficial use*. CRC Press, New York, ISBN - 082479706X, 9780824797065.
- Glaser, B., Lehmann, J., & Zech, W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. *Biology and fertility of soils*, 35(4), 219-230.
- Guo, J., & Lua, A. C. (2003). Textural and chemical properties of adsorbent prepared from palm shell by phosphoric acid activation. *Materials chemistry and physics*, 80(1), 114-119.
- Haghsersht, F., & Lu, G. Q. (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. *Energy & Fuels*, 12(6), 1100-1107.

- Hameed, B.H., Salman, J.M., & Ahmad, A.L. (2009A). Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones, *Journal of hazardous materials*, 163, 121-126.
- Hameed, B.H., Tan, I.A.W., & Ahmad, A.L. (2009B) Preparation of oil palm empty fruit bunch based activated carbon for removal of 2,4,6-trichlorophenol: optimization using response surface methodology. *Journal of hazardous materials*, 164, 1316-1324.
- Hameed, Z., Aman, Z., Naqvi, S. R., Tariq, R., Ali, I., & Makki, A. A. (2018). Kinetic and thermodynamic analyses of sugar cane bagasse and sewage sludge co-pyrolysis process. *Energy & Fuels*, 32(9), 9551-9558.
- Hao, Z., Yang, B., & Jahng, D. (2018). Combustion characteristics of biodried sewage sludge. *Waste Management*, 72, 296-305.
- Harrison, E. Z., Oakes, S. R., Hysell, M., & Hay, A. (2006). Organic chemicals in sewage sludges. *Science of the total environment*, 367(2-3), 481-497.
- Hasan, S.H., Singh, K.K, Prakash, O., Talat, M., & Ho, Y.S. (2008). Removal of Cr (VI) from aqueous solutions using agricultural waste 'maize bran'. *Journal of hazardous materials*, 152, 356-365.
- Haykiri-Acma, H., & Yaman, S. (2007). Synergy in devolatilization characteristics of lignite and hazelnut shell during co-pyrolysis. *Fuel*, 86, 373-380.
- He, C., Tang, C., Liu, W., Dai, L., & Qiu, R. (2020). Co-pyrolysis of sewage sludge and hydrochar with coals: Pyrolytic behaviors and kinetics analysis using TG-FTIR and a discrete distributed activation energy model. *Energy Conversion and Management*, 203, 112226.
- He, P. (2008). China: Management of sewage sludge in urban areas. *Global Atlas of Excreta, Wastewater, Sludge, and Biosolids Management: Moving toward the Sustainable and Welcome Uses of a Global Resource*, 246-256.
- Henkel, C., Muley, P., Abdollahi, K.K., Marculescu, C., & Boldor, D. (2016). Pyrolysis of energy cane bagasse and invasive Chinese tallow tree (*Triadica sebifera* L.) biomass in an inductively heated reactor. *Energy Conversion and Management*. 109, 175-183.
- Horne, P. A., & Williams, P. T. (1996). Influence of temperature on the products from the flash pyrolysis of biomass. *Fuel*, 75(9), 1051-1059.
- Hornung, A., Apfelbacher, A., & Sagi, S. (2011). Intermediate pyrolysis: A sustainable biomass-to-energy concept-biothermal valorisation of biomass (BtVB) process. *Journal of Scientific and Industrial Research*, 70, 664-667.
- Hossain, A. K., & Davies, P. A. (2013). Pyrolysis liquids and gases as alternative fuels in internal combustion engines—A review. *Renewable and Sustainable Energy Reviews*, 21, 165-189.
- Huang, H. J., Yang, T., Lai, F. Y., & Wu, G. Q. (2017). Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar. *Journal of Analytical and Applied Pyrolysis*, 125, 61-68.
- Huang, Y. F., Shih, C. H., Chiueh, P. T., & Lo, S. L. (2015). Microwave co-pyrolysis of sewage sludge and rice straw. *Energy*, 87, 638-644.
- Hussain, A., Maitra, J., & Khan, K. A. (2017). Development of biochar and chitosan blend for heavy metals uptake from synthetic and industrial wastewater. *Applied Water Science*, 7(8), 4525-4537.
- Inguanzo, M., Dominguez, A., Menéndez, J. A., Blanco, C. G., & Pis, J. J. (2002). On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. *Journal of Analytical and Applied Pyrolysis*, 63(1), 209-222.
- Iqbal, M.J., Cecil, F., Ahmad, K., Iqbal, M., Mushtaq, M., Naeem, M.A., & Bokhari, T.H. (2013). Kinetic study of Cr(III) and Cr(VI) biosorption using *Rosa damascena* phytomass: A rose waste biomass. *Asian Journal of Chemistry*, 25, 2099-2103.
- Islam, M. R., Haniu, H., Islam, M. N., & Uddin, M. S. (2010). Thermochemical conversion of sugarcane bagasse into bio-crude oils by fluidized-bed pyrolysis technology. *Journal of Thermal Science and Technology*, 5(1), 11-23.
- IUPAC (1972). IUPAC manual of symbols and terminology, Pure Appl. Chem. 31 (1972) 587.
- Jagtoyen, M., & Derbyshire, F. (1998). Activated carbons from yellow poplar and white oak by H₃PO₄ activation. *Carbon*, 36(7-8), 1085-1097.
- Jahirul, M. I., Rasul, M. G., Chowdhury, A. A., & Ashwath, N. (2012). Biofuels production through biomass pyrolysis—a technological review. *Energies*, 5(12), 4952-5001.
- Jain, M., Garg, V.K., & Kadirvelu, K. (2009). Equilibrium and kinetic studies for sequestration of Cr (VI) from simulated wastewater using sunflower waste biomass. *Journal of hazardous materials*, 171, 328-334.
- Jindarom, C., Meeyoo, V., Rirksomboon, T., & Rangsunvigit, P. (2007). Thermochemical decomposition of sewage sludge in CO₂ and N₂ atmosphere. *Chemosphere*, 67(8), 1477-1484.

- Johnason, D. C., & Edgar, B. (2006). *From Lucy to Language: Revised, Updated and Expanded*. Simon and Schuster, New York.
- Jones, J. M., Kubacki, M., Kubica, K., Ross, A. B., & Williams, A. (2005). Devolatilisation characteristics of coal and biomass blends. *Journal of Analytical and Applied Pyrolysis*, *74*(1-2), 502–511.
- Joshi, N., & Lawal, A. (2012). Hydrodeoxygenation of pyrolysis oil in a microreactor. *Chemical Engineering Science*, *74*, 1-8.
- Junna, J., & Ruonala, S. (1991). Trends and guidelines in water pollution control in the Finnish pulp and paper industry. *Tappi journal*, *74*, 105-111.
- Kamali, M., & Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and environmental safety*, *114*, 326-342.
- Kaminsky, W., & Kummer, A. B. (1989). Fluidized bed pyrolysis of digested sewage sludge. *Journal of Analytical and Applied Pyrolysis*, *16*(1), 27-35.
- Kamyotra, J. S., & Bhardwaj, R. M. (2011). Municipal wastewater management in India. *India infrastructure report*, 299.
- Karaca, C., Sözen, S., Orhon, D., & Okutan, H. (2018). High temperature pyrolysis of sewage sludge as a sustainable process for energy recovery. *Waste management*, *78*, 217-226.
- Karagozoglu, B., Tasdemir, M., Demirbas, E., & Kobya, M. (2007). The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: kinetic and equilibrium studies. *Journal of hazardous materials*, *147*, 297-306.
- Karayildirim, T., Yanik, J., Yuksel, M., & Bockhorn, H. (2006). Characterisation of products from pyrolysis of waste sludges. *Fuel*, *85*(10-11), 1498-1508.
- Karia, G. L., & Christian, R. A. (2013). *Wastewater treatment: Concepts and design approach*. PHI Learning Pvt. Ltd., New Delhi, 371.
- Kasakura, T., Imoto, Y., & Mori, T. (1993). Overview and system analysis of various sewage sludge drying processes. *Drying Technology*, *11*(5), 871-900.
- Keiluweit, M., Nico, P. S., Johnson, M. G., & Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environmental science & technology*, *44*(4), 1247-1253.
- Keyhani, A., & Yaylayan, V. A. (1996). Pyrolysis/GC/MS analysis of N-(1-Deoxy-D-fructos-1-yl)-L-phenylalanine: Identification of novel pyridine and naphthalene derivatives. *Journal of Agricultural and Food Chemistry*, *44*(1), 223-229.
- Khiari, B., Marias, F., Zagrouba, F., & Vaxelaire, J. (2004). Analytical study of the pyrolysis process in a wastewater treatment pilot station. *Desalination*, *167*, 39-47.
- Kim, Y., & Parker, W. (2008). A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. *Bioresource technology*, *99*(5), 1409-1416.
- Kishimoto, N., Nakagawa, T., Okada, H., & Mizutani, H. (2010). Treatment of paper and pulp mill wastewater by ozonation combined with electrolysis. *Journal of water and environment technology*, *8*, 99-109.
- Kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E., & Singh, B. (2011). Biochar application to soil: agronomic and environmental benefits and unintended consequences. *Advances in agronomy*, *112*, 103-143.
- Kumar, D., Soomro, S. A., Mahar, H. U., Aziz, S., Unar, I. N., Memon, A. R., Malik, A., & Hussain, S. (2017). Co-firing of Brown Coal & Bagasse for Sulfur Reduction. *Technical Journal*, *22*(2).
- Kuppens, T., Cornelissen, T., Carleer, R., Yperman, J., Schreurs, S., Jans, M., & Thewys, T. (2010). Economic assessment of flash co-pyrolysis of short rotation coppice and biopolymer waste streams. *Journal of environmental management*, *91*(12), 2736-2747.
- Laternus, F., Von Arnold, K., & Grøn, C. (2007). Organic contaminants from sewage sludge applied to agricultural soils. False alarm regarding possible problems for food safety? (8 pp). *Environmental Science and Pollution Research*, *14*(1), 53-60.
- Leal, M. R. L., Galdos, M. V., Scarpore, F. V., Seabra, J. E., Walter, A., & Oliveira, C. O. (2013). Sugarcane straw availability, quality, recovery and energy use: a literature review. *Biomass and Bioenergy*, *53*, 11-19.
- Lehmann, J., & Joseph, S. (2009). *Biochar for environmental management: science and technology*. London, United Kingdom: Earthscan.
- Lehto, J., Oasmaa, A., Solantausta, Y., Kyto, M., & Chiaramonti, D. (2014). Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. *Applied energy*, *116*, 178–190.
- Li, S., Xu, S., Liu, S., Yang, C., & Lu, Q. (2004). Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Processing Technology*, *85*, 201-1211.

- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J. O., Thies, J., Luizao, F. J., Petersen, J., & Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, 70(5), 1719-1730.
- Lin, B., Huang, Q., & Chi, Y. (2018B). Co-pyrolysis of oily sludge and rice husk for improving pyrolysis oil quality. *Fuel Processing Technology*, 177, 275-282.
- Lin, Y., Chen, Z., Dai, M., Fang, S., Liao, Y., Yu, Z., & Ma, X. (2018A). Co-pyrolysis kinetics of sewage sludge and bagasse using multiple normal distributed activation energy model (M-DAEM). *Bioresource technology*, 259, 173-180.
- Lin, Y., Liao, Y., Yu, Z., Fang, S., & Ma, X. (2017). A study on co-pyrolysis of bagasse and sewage sludge using TG-FTIR and Py-GC/MS. *Energy Conversion and Management*, 151, 190-198.
- Lin, Y., Liao, Y., Yu, Z., Fang, S., Lin, Y., Fan, Y., Peng, X., & Ma, X. (2016). Co-pyrolysis kinetics of sewage sludge and oil shale thermal decomposition using TGA-FTIR analysis. *Energy Conversion and Management*. 118. 345-352.
- Lin, Y., Tian, Y., Xia, Y., Fang, S., Liao, Y., Yu, Z., & Ma, X. (2019). General distributed activation energy model (G-DAEM) on co-pyrolysis kinetics of bagasse and sewage sludge. *Bioresource technology*, 273, 545-555.
- Liu, G., Song, H., & Wu, J. (2015). Thermogravimetric study and kinetic analysis of dried industrial sludge pyrolysis. *Waste Management*, 41, 128-133.
- Livernoche, D., Jurasek, L., Desrochers, M., Dorica, J., & Veliky, I.A. (1983). Removal of colour from kraft mill wastewaters with cultures of white-rot fungi and with immobilized mycelium of *Coriolus Versicolor*. *Biotechnology and bioengineering*, 25(8), 2055-2065.
- Luo, C., Zhang, D., Lun, Z., Zhao, C., Wang, H., Pan, Z., Li, Y., Zhang, J., & Jia, S. (2019). Displacement behaviors of adsorbed coalbed methane on coals by injection of SO₂/CO₂ binary mixture. *Fuel*, 247, 356-367.
- Magdziarz, A., & Wilk, M. (2013). Thermal characteristics of the combustion process of biomass and sewage sludge. *Journal of thermal analysis and calorimetry*, 114(2), 519-529.
- Maher, K. D., & Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource technology*, 98(12), 2351-2368.
- Manara, P., & Zabaniotou, A. (2012). Towards sewage sludge-based biofuels via thermochemical conversion—A review. *Renewable and Sustainable Energy Reviews*, 16(5), 2566-2582.
- Mantilla, S. V., Gauthier-Maradei, P., Gil, P. Á., & Cárdenas, S. T. (2014). Comparative study of bio-oil production from sugarcane bagasse and palm empty fruit bunch: Yield optimization and bio-oil characterization. *Journal of Analytical and Applied Pyrolysis*, 108, 284-294.
- Manyuchi, M. M., Mbohwa, C., & Muzenda, E. (2018). Potential to use municipal waste bio char in wastewater treatment for nutrients recovery. *Physics and Chemistry of the Earth, Parts A/B/C*, 107, 92-95.
- Martinez, J. D., Veses, A., Mastral, A. M., Murillo, R., Navarro, M. V., Puy, N., Artigues, A., Bartrolí, J., & García, T. (2014). Co-pyrolysis of biomass with waste tyres: Upgrading of liquid bio-fuel. *Fuel Processing Technology*, 119, 263-271.
- Maschio, G., Koufopoulos, C., & Lucchesi, A. (1992). Pyrolysis, a promising route for biomass utilization. *Bioresource Technology*. 42(3), 219-231.
- Mateo-Sagasta, J., Raschid-Sally, L., & Thebo, A. (2015). Global wastewater and sludge production, treatment and use. In *Wastewater*, Springer, Dordrecht, 15-38.
- Meier, D., Van De Beld, B., Bridgwater, A. V., Elliott, D. C., Oasmaa, A., & Preto, F. (2013). State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renewable and Sustainable Energy Reviews*, 20, 619-641.
- Mininni, G., Sbrilli, A., Guerriero, E., & Rotatori, M. (2004). Dioxins and furans formation in pilot incineration tests of sewage sludge spiked with organic chlorine. *Chemosphere*, 54(9), 1337-1350.
- MoEFCC (Ministry of environment, forests and climate change) (2019) National status of waste water generation & treatment. *ENVIS newsletter, Government of India*.
- Mohan, D., Pittman Jr, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & fuels*, 20(3), 848-889.
- Molina-Sabio, M., Rodriguez-Reinoso, F., Caturla, F., & Sellés, M. J. (1995). Porosity in granular carbons activated with phosphoric acid. *Carbon*, 33(8), 1105-1113.
- Mondala, A., Liang, K., Toghiani, H., Hernandez, R., & French, T. (2009). Biodiesel production by in situ transesterifications of municipal primary and secondary sludges. *Bioresource Technology*. 100,1203-1210.
- Montes-Morán, M. A., Suárez, D., Menéndez, J. A., & Fuente, E. (2004). On the nature of basic sites on carbon surfaces: an overview. *Carbon*, 42(7), 1219-1225.

- Montoya, J., Pecha, B., Roman, D., Janna, F. C., & Garcia-Perez, M. (2017). Effect of temperature and heating rate on product distribution from the pyrolysis of sugarcane bagasse in a hot plate reactor. *Journal of analytical and applied pyrolysis*, 123, 347-363.
- Mosko, J., Pohorely, M., Skoblia, S., Beno, Z., and Jeremias, M. (2020). Detailed Analysis of Sewage Sludge Pyrolysis Gas: Effect of Pyrolysis Temperature. *Energies* 13(16), 4087.
- Moyo, M., Lindiwe, S. T., Sebata, E., Nyamunda, B. C., & Guyo, U. (2016). Equilibrium, kinetic, and thermodynamic studies on biosorption of Cd (II) from aqueous solution by biochar. *Research on chemical intermediates*, 42(2), 1349-1362.
- Mueller, A., Hausteine, H. D., Stoesser, P., Kreitzberg, T., Kneer, R., & Kolb, T. (2015). Gasification kinetics of biomass-and fossil-based fuels: comparison study using fluidized bed and thermogravimetric analysis. *Energy & Fuels*, 29(10), 6717-6723.
- Mukome, F.N.D., Parikh, S.J. (2013). UC Davis Biochar Database. University of California Davis, Davis, CA. <http://ucdavis.biochar.edu>
- Murwanashyaka, J. N., Pakdel, H., & Roy, C. (2001). Step-wise and one-step vacuum pyrolysis of birch-derived biomass to monitor the evolution of phenols. *Journal of Analytical and Applied Pyrolysis*, 60(2), 219-231.
- Mutanda, T., Ramesh, D., Karthikeyan, S., Kumari, S., Anandraj, A., & Bux, F. (2011). Bioprospecting for hyper-lipid producing microalgal strains for sustainable biofuel production. *Bioresource technology*, 102(1), 57-70.
- Naqvi, S. R., Tariq, R., Hameed, Z., Ali, I., Naqvi, M., Chen, W. H., Ceylan, S., Rashid, H., Ahmad, J., Taqvi, S.A., & Shahbaz, M. (2019). Pyrolysis of high ash sewage sludge: Kinetics and thermodynamic analysis using Coats-Redfern method. *Renewable energy*, 131, 854-860.
- National Federation of Co-operative Sugar Factories Limited, Cooperative Sugar, National Federation of Cooperative Sugar Factories Ltd., New Delhi, 2019.
- Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das, K. C., Ahmedna, M., Rehrh, D., Watts, D.W., Busscher, W.J., & Schomberg, H. (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Annals of Environmental Science*, 3(1), 195-206.
- Oasmaa, A., & Meier, D. (2005). Norms and standards for fast pyrolysis liquids: 1. Round robin test. *Journal of Analytical and Applied Pyrolysis*, 73(2), 323-334.
- Onal, Y., Akmil-Basar, C., Sarici-Ozdemir, C., & Erdogan, S. (2007). Textural development of sugar beet bagasse activated with ZnCl₂. *Journal of hazardous materials*, 142, 138-143.
- Opfermann, J. R., Kaisersberger, E., & Flammersheim, H. J. (2002). Model-free analysis of thermoanalytical data-advantages and limitations. *Thermochemica acta*, 391(1-2), 119-127.
- Orhon D, Artan N. (1994). Modelling of activated sludge systems. *Technomic Publishing Co., Inc.*, Lancaster, PA. 39-110.
- Othman, M. R., Park, Y. H., Ngo, T. A., Kim, S. S., Kim, J., & Lee, K. S. (2010). Thermogravimetric characteristics and pyrolysis kinetics of GiheungRespia sewage sludge. *Korean journal of chemical engineering*, 27(1), 163-167.
- Parekh, D. B., Rotliwala, Y. C., & Parikh, P. A. (2009). Synergetic pyrolysis of high density polyethylene and Jatropha and Karanj cakes: A thermogravimetric study. *Journal of Renewable and Sustainable Energy*, 1(3), 033107.
- Parihar, M. F., Kamil, M., Goyal, H. B., Gupta, A. K., & Bhatnagar, A. K. (2007). An experimental study on pyrolysis of biomass. *Process Safety and Environmental Protection*, 85(5), 458-465.
- Parikh, S. J., Goyne, K. W., Margenot, A. J., Mukome, F. N., & Calderón, F. J. (2014). Soil chemical insights provided through vibrational spectroscopy. *Advances in agronomy*, 126, 1-148.
- Park, E. S., Kang, B. S., & Kim, J. S. (2008). Recovery of oils with high caloric value and low contaminant content by pyrolysis of digested and dried sewage sludge containing polymer flocculants. *Energy & Fuels*, 22(2), 1335-1340.
- Park, H. J., Heo, H. S., Park, Y. K., Yim, J. H., Jeon, J. K., Park, J., Ryu, K., & Kim, S. S. (2010). Clean bio-oil production from fast pyrolysis of sewage sludge: effects of reaction conditions and metal oxide catalysts. *Bioresource technology*, 101(1), S83-S85.
- Patnukao, P., & Pavasant, P. (2008). Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation. *Bioresource technology*, 99(17), 8540-8543.
- Peerbhoy, Z.M., Mehrotra, I., & Shrivastava, A.K. (2003). Treatability studies of black liquor by up-flow anaerobic sludge blanket reactor. *Journal of environmental engineering and science*, 2, 307-313.

- Peng, X. Y. L. L., Ye, L. L., Wang, C. H., Zhou, H., & Sun, B. (2011). Temperature-and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil and Tillage Research*, *112*(2), 159-166.
- Piskorz, J., Scott, D. S., & Westerberg, I. B. (1986). Flash pyrolysis of sewage sludge. *Industrial & Engineering Chemistry Process Design and Development*, *25*(1), 265-270.
- Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater - A review. *Science to the total environment*, *333*, 37-58.
- Pokorna, E., Postelmans, N., Jenicek, P., Schreurs, S., Carleer, R., & Yperman, J. (2009). Study of bio-oils and solids from flash pyrolysis of sewage sludges. *Fuel*, *88*(8), 1344-1350.
- Poonam, Bharti, S.K., & Kumar, N. (2018). Kinetic study of lead (Pb²⁺) removal from battery manufacturing wastewater using bagasse biochar as biosorbent. *Applied Water Science* *8*, 119.
- Quereshi, S., Naiya, T.K., Mandal, A., Dutta, S. (2020). Residual sugarcane bagasse conversion in India: status, technologies, and policies. *Biomass Conversion and Biorefinery*.
- Rashidi, N.A., & Yusup, S.A. (2017). Review on recent technological advancement in the activated carbon production from oil palm wastes. *Chemical Engineering Journal*, *314*, 277-290.
- Ren, Q. & Zhao, C. (2012). NOx and N₂O Precursors from Biomass Pyrolysis: Nitrogen Transformation from Amino Acid. *Environmental Science & Technology* *2012* *46* (7), 4236-4240.
- Ren, Q. (2013). NOx and N₂O precursors from co-pyrolysis of biomass and sludge. *Journal of thermal analysis and calorimetry*, *112*(2), 997-1002.
- Ren, Q.Q., Zhao, C.S., Chen, X.P., Duan, L.B., Li, Y.J., & Ma, C.Y. (2011). NOx and N₂O precursors (NH₃ and HCN) from biomass pyrolysis: co-pyrolysis of amino acids and cellulose, hemicellulose and lignin. *Proceedings of the Combustion Institute*, *33*(2), 1715-1722
- Rosas, J.M., Berenguer, R., Valero-Romero, M.J, Rodríguez-Mirasol, J., Cordero, T.. (2014). Preparation of different carbon materials by thermochemical conversion of lignin. *Frontiers in Materials*, *1*, 1-17.
- Rotliwala, Y. C., & Parikh, P. A. (2011). Thermal degradation of rice-bran with high density polyethylene: A kinetic study. *Korean journal of chemical engineering*, *28*(3), 788-792.
- Rozada, F., Calvo, L. F., Garcia, A. I., Martín-Villacorta, J., & Otero, M. (2003). Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems. *Bioresource technology*, *87*(3), 221-230.
- Ruiz-Gómez, N., Quispe, V., Ábrego, J., Atienza-Martínez, M., Murillo, M. B., & Gea, G. (2017). Co-pyrolysis of sewage sludge and manure. *Waste management*, *59*, 211-221.
- Samanya, J., Hornung, A., Apfelbacher, A., & Vale, P. (2012). Characteristics of the upper phase of bio-oil obtained from co-pyrolysis of sewage sludge with wood, rapeseed and straw. *Journal of analytical and applied pyrolysis*, *94*, 120-125.
- Samolada, M. C., & Zabaniotou, A. A. (2014). Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. *Waste management*, *34*(2), 411-420.
- Sanchez, M. E., Menéndez, J. A., Domínguez, A., Pis, J. J., Martínez, O., Calvo, L. F., & Bernad, P. L. (2009). Effect of pyrolysis temperature on the composition of the oils obtained from sewage sludge. *biomass and bioenergy*, *33*(6-7), 933-940.
- Savant, D., Abdul-rahman, R., & Ranade, D.R. (2006). Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. *Bioresource technology*, *97*, 1092-1104.
- Shahbeig, H., & Nosrati, M. (2020). Pyrolysis of municipal sewage sludge for bioenergy production: thermo-kinetic studies, evolved gas analysis, and techno-socio-economic assessment. *Renewable and Sustainable Energy Reviews*, *119*, 109567.
- Shao, J., Yan, R., Chen, H., Wang, B., Lee, D. H., & Liang, D. T. (2008). Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry Fourier transform infrared analysis. *Energy & Fuels*, *22*(1), 38-45.
- Shen, F., Liu, J., Dong, Y., & Gu, C. (2018). Insights into the effect of chlorine on arsenic release during MSW incineration: An on-line analysis and kinetic study. *Waste Management*, *75*, 327-332.
- Shen, L., & Zhang, D. K. (2003). An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed. *Fuel*, *82*(4), 465-472.
- Shen, L., & Zhang, D. K. (2005). Low-temperature pyrolysis of sewage sludge and putrescible garbage for fuel oil production. *Fuel*, *84*(7-8), 809-815.
- Shi, L., Zhang, G., Wei, D., Yan, T., Xue, X., Shi, S., & Wei, Q. (2014). Preparation and utilization of anaerobic granular sludge-based biochar for the adsorption of methylene blue from aqueous solutions. *Journal of molecular liquids*, *198*, 334-340.

- Shuang-quan, Z., Xiao-ming, Y., Zhi-yuan, Y., Ting-ting, P., Ming-jian, D., & Tian-yu, S. (2009). Study of the co-pyrolysis behavior of sewage-sludge/rice-straw and the kinetics. *Procedia Earth and Planetary Science*, 1(1), 661-666.
- Singh, K.P., Malik, A., Sinha, S., & Ojha, P. (2008). Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material. *Journal of hazardous materials*, 150, 626-641.
- Singh, V., Phuleria, H. C., & Chandel, M. K. (2020). Estimation of energy recovery potential of sewage sludge in India: Waste to watt approach. *Journal of Cleaner Production*, 276, 122538.
- Slopiecka, K., Bartocci, P., & Fantozzi, F. (2012). Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. *Applied Energy*, 97, 491-497.
- Smith, K. M., Fowler, G. D., Pullket, S., & Graham, N. D. (2009). Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications. *Water research*, 43(10), 2569-2594.
- Sohi, S. P., Krull, E., Lopez-Capel, E., & Bol, R. (2010). A review of biochar and its use and function in soil. *Advances in agronomy*, 105, 47-82.
- Solomon, S. (2011). The Indian sugar industry: an overview. *Sugar Tech*, 13(4), 255-265.
- Sonobe, T., Worasuwannarak, N., & Pipatmanomai, S. (2008). Synergies in co-pyrolysis of Thai lignite and corncob. *Fuel Processing Technology* 89, 1371-1378.
- Spokas, K. A. (2010). Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Management*, 1(2), 289-303.
- Srivastava, V. C., Mall, I. D., & Mishra, I. M. (2005). Treatment of pulp and paper mill wastewaters with poly aluminium chloride and bagasse fly ash. *Colloids and surfaces A: Physicochemical and engineering aspects*, 260(1-3), 17-28.
- Stammbach, M. R., Kraaz, B., Hagenbucher, R., & Richarz, W. (1989). Pyrolysis of sewage sludge in a fluidized bed. *Energy & fuels*, 3(2), 255-259.
- Suarez-Garcia, F., Martinez-Alonso, A., & Tascon, J.M.D. (2002). Pyrolysis of apple pulp: chemical activation with phosphoric acid. *Journal of Analytical and Applied Pyrolysis*, 63, 283-301.
- Sudaryanto, Y., Hartono, S.B., Irawaty, W., Hindarso, H., & Ismadji, S. (2006). High surface area activated carbon prepared from cassava peel by chemical activation. *Bioresource Technology*, 97, 734-739.
- Sugarcane statistics, (2020) National Federation of Cooperative Sugar Factories limited of India 51(5).
- Sun, Y., Jin, B., Wu, W., Zuo, W., Zhang, Y., Zhang, Y., & Huang, Y. (2015). Effects of temperature and composite alumina on pyrolysis of sewage sludge. *Journal of Environmental Sciences*, 30, 1-8.
- Sun, Y., Yue, Q., Gao, B., Huang, L., Xu, X., & Li, Q. (2012). Comparative study on characterization and adsorption properties of activated carbons with H₃PO₄ and H₄P₂O₇ activation employing *Cyperus alternifolius* as precursor. *Chemical Engineering Journal*, 181, 790-797.
- Swierczek, L., Cieslik, B. M., & Konieczka, P. (2018). The potential of raw sewage sludge in construction industry—a review. *Journal of cleaner production*, 200, 342-356.
- Syed-Hassan, S. S. A., Wang, Y., Hu, S., Su, S., & Xiang, J. (2017). Thermochemical processing of sewage sludge to energy and fuel: Fundamentals, challenges and considerations. *Renewable and Sustainable Energy Reviews*, 80, 888-913.
- Tan, I.A.W., Hameed, B.H., & Ahmad, A.L. (2007). Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical engineering journal*, 127, 111-119.
- Tang, Y., Alam, M. S., Konhauser, K. O., Alessi, D. S., Xu, S., Tian, W., & Liu, Y. (2019). Influence of pyrolysis temperature on production of digested sludge biochar and its application for ammonium removal from municipal wastewater. *Journal of Cleaner Production*, 209, 927-936.
- Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2003). Wastewater engineering treatment and reuse. Boston, US: McGraw-Hill Higher Education.
- Tezel, U., Tandukar, M., Pavlostathis, S.G. (2011). 6.35 Anaerobic biotreatment of municipal sewage sludge. In: Moo-Young, M. Comprehensive biotechnology, 2nd edition. *Academic Press*, 447-461.
- Thamburaj, R. (2000). Fast pyrolysis of biomass for green power generation. In *First World Conference on Biomass for Energy and Industry, Energia TA, Seville, Spain*.
- Thompson, G., Swain, J., Kay, M., & Forster, C.F. (2001). The treatment of pulp and paper mill effluent: a review. *Bioresource technology*, 177, 275-286.
- Tian, Y., Zhang, J., Zuo, W., Chen, L., Cui, Y., Tan T. (2013). Nitrogen conversion in relation to NH₃ and HCN during microwave pyrolysis of sewage sludge, *Environmental Science & Technology*, 47, 3498-3505.
- Tian, Y., Zuo, W., Ren, Z., & Chen, D. (2011). Estimation of a novel method to produce bio-oil from sewage sludge by microwave pyrolysis with the consideration of efficiency and safety. *Bioresource technology*, 102(2), 2053-2061.

- Toba, M., Abe, Y., Kuramochi, H., Osako, M., Mochizuki, T., & Yoshimura, Y. (2011). Hydrodeoxygenation of waste vegetable oil over sulfide catalysts. *Catalysis Today*, 164(1), 533-537.
- Tsai, W. T., Lee, M. K., & Chang, D. Y. (2006). Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of analytical and applied pyrolysis*, 76(1-2), 230-237.
- Tsai, W.T., Lee, M.K., Chang, Y.M. (2007). Fast pyrolysis of rice husk: Product yields and compositions. *Bioresource Technology*. 98(1),22-28
- Uchimiya, M., Chang, S., & Klasson, K. T. (2011). Screening biochars for heavy metal retention in soil: role of oxygen functional groups. *Journal of Hazardous Materials*, 190(1-3), 432-441.
- Umamaheswaran, K., & Batra, V.S. (2008). Physico-chemical characterization of Indian biomass ashes, *Fuel* 87, 628–638.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., & Cowie, A. (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant & Soil*. 327. 235-246.
- Varma, A. K., & Mondal, P. (2017). Pyrolysis of sugarcane bagasse in semi batch reactor: effects of process parameters on product yields and characterization of products. *Industrial Crops and Products*, 95, 704-717.
- Vasseur, L., Shipley, W., & Anseau, C. (1999). Potential for municipal sewage sludge application on agricultural lands in southern Quebec. *Water Quality Research Journal*. 34, 469-480.
- Vernersson, T., Bonelli, P. R., Cerrella, E. G., & Cukierman, A. L. (2002). Arundo donax cane as a precursor for activated carbons preparation by phosphoric acid activation. *Bioresource Technology*, 83(2), 95-104.
- Wang, B., Gao, B., & Fang, J. (2017). Recent advances in engineered biochar productions and applications. *Critical reviews in environmental science and technology*, 47(22), 2158-2207.
- Wang, B., Xu, F., Zong, P., Zhang, J., Tian, Y., & Qiao, Y. (2019). Effects of heating rate on fast pyrolysis behavior and product distribution of Jerusalem artichoke stalk by using TG-FTIR and Py-GC/MS. *Renewable energy*, 132, 486-496.
- Wang, H., Gao, B., Wang, S., Fang, J., Xue, Y., & Yang, K. (2015). Removal of Pb (II), Cu (II), and Cd (II) from aqueous solutions by biochar derived from KMnO₄ treated hickory wood. *Bioresource Technology*, 197, 356-362.
- Wang, S. R., Luo, Z. Y., Tan, H., Hong, J., Dong, L. J., Fang, M. X., & Cen, K. F. (2004). The analyses of characteristics of bio-oil produced from biomass by flash pyrolysis. *Journal of Engineering Thermophysics*, 25(6), 1049-1052.
- Wang, X., Deng, S., Tan, H., Adeosun, A., Vujanovic, M., Yang, F., & Duic, N. (2016). Synergetic effect of sewage sludge and biomass co-pyrolysis: a combined study in thermogravimetric analyzer and a fixed bed reactor. *Energy conversion and management*, 118, 399-405.
- Werther, J., & Ogada, T. (1999). Sewage sludge combustion. *Progress in energy and combustion science*, 25(1), 55-116.
- Westerhof, R. J., Brilman, D. W., Van Swaaij, W. P., & Kersten, S. R. (2010). Effect of temperature in fluidized bed fast pyrolysis of biomass: oil quality assessment in test units. *Industrial & engineering chemistry research*, 49(3), 1160-1168.
- Williams, P. T. (2005). *Waste treatment and disposal*. John Wiley & Sons.
- Wong, S.S., Teng, T.T., Ahmad, A.L., Zuhairi, A., & Najafpour, G. (2006). Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation. *Journal of hazardous materials*, 135, 378-388.
- Xu, G., Lv, Y., Sun, J., Shao, H., & Wei, L. (2012). Recent advances in biochar applications in agricultural soils: benefits and environmental implications. *CLEAN–Soil, Air, Water*, 40(10), 1093-1098.
- Xu, J., Chen, L., Qu, H., Jiao, Y., Xie, J., & Xing, G. (2014). Preparation and characterization of activated carbon from reedy grass leaves by chemical activation with H₃PO₄. *Applied Surface Science*, 320, 674-680.
- Xu, X., Zhao, B., Sun, M., Chen, X., Zhang, M., Li, H., & Xu, S. (2017). Co-pyrolysis characteristics of municipal sewage sludge and hazelnut shell by TG-DTG-MS and residue analysis. *Waste Management*, 62, 91-100.
- Yadav, J.P., & Singh, B.R. (2011). Study on Future Prospects of Power Generation by Bagasse, Rice Husk and Municipal Waste in Uttar Pradesh. *SAMRIDDHI-A Journal of Physical Sciences, Engineering and Technology (S-JPSET)* 2(2),2-4.
- Yahya, M.A., Al-Qodah, Z., & Ngah, C.Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable & Sustainable Energy Reviews*, 46, 218-235.

- Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J., Wang, H., Sik, Y., Jiang, Y., & Gao, B. (2019). Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review. *Chemical Engineering Journal*, 366, 608-621.
- Yi, Y., Lv, J., Liu, Y., & Wu, G. (2017). Synthesis and application of modified Litchi peel for removal of hexavalent chromium from aqueous solutions. *Journal of Molecular Liquids*, 225, 28-33.
- Zhai, Y., Peng, W., Zeng, G., Fu, Z., Lan, Y., Chen, H., Wang, C., & Fan, X. (2012). Pyrolysis characteristics and kinetics of sewage sludge for different sizes and heating rates. *Journal of Thermal Analysis and Calorimetry*, 107, 1015-1022.
- Zhang, D., Liu, S., Fu, X., Jia, S., Min, C., & Pan, Z. (2019). Adsorption and desorption behaviors of nitrous oxide on various rank coals: implications for oxy-coal combustion flue gas sequestration in deep coal seams. *Energy & fuels*, 33(11), 11494-11506.
- Zhang, H., Lin, K., Wang, H., & Gan, J. (2010). Effect of *Pinus radiata* derived biochars on soil sorption and desorption of phenanthrene. *Environmental Pollution*, 158(9), 2821-2825.
- Zhang, L., Xu, S., Zhao, W., & Liu, S. (2007B). Co-pyrolysis of biomass and coal in a free fall reactor. *Fuel*, 86(3), 353-359.
- Zhang, Q. R., Zhang, S. Q., & Pan, T. T. (2011). Fraction distribution changes of heavy metals in co-pyrolysis of sewage sludge and corn straw. In *Advanced Materials Research*, 236, 187-191.
- Zhang, Q., Chang, J., Wang, T., & Xu, Y. (2007A). Review of biomass pyrolysis oil properties and upgrading research. *Energy conversion and management*, 48(1), 87-92.
- Zhang, S., Yue X., Yin, Z., Pan, T., Dong M. & Sun T. (2009). Study of the co-pyrolysis behavior of sewage-sludge/rice-straw and the kinetics, *Procedia Earth and Planetary Science*, 1(1), 661-666.
- Zhang, W., Yuan, C., Xu, J., & Yang, X. (2015). Beneficial synergetic effect on gas production during co-pyrolysis of sewage sludge and biomass in a vacuum reactor. *Bioresource technology*, 183, 255-258.
- Zhang, X., Lei, H., Zhu, L., Zhu, X., Qian, M., Yadavalli, G., Wu, J., & Chen, S. (2016). Thermal behavior and kinetic study for catalytic co-pyrolysis of biomass with plastics. *Bioresource technology*, 220, 233-238.
- Zhao, B., Xu, X., Li, H., Chen, X., & Zeng, F. (2018). Kinetics evaluation and thermal decomposition characteristics of co-pyrolysis of municipal sewage sludge and hazelnut shell. *Bioresource technology*, 247, 21-29.
- Zhou, N., Chen, H., Xi, J., Yao, D., Zhou, Z., Tian, Y., & Lu, X. (2017). Biochars with excellent Pb (II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization. *Bioresource technology*, 232, 204-210.
- Zhu, X., Chen, Z., Xiao, B., Hu, Z., Hu, M., Liu, C., & Zhang, Q. (2015). Co-pyrolysis behaviors and kinetics of sewage sludge and pine sawdust blends under non-isothermal conditions. *Journal of Thermal Analysis and Calorimetry*, 119(3), 2269-2279.
- Zuo, S., Yang, J., Liu, J., & Cai, X. (2009). Significance of the carbonization of volatile pyrolytic products on the properties of activated carbons from phosphoric acid activation of lignocellulosic material. *Fuel Processing Technology*, 90, 994-1001.
- Zuo, W., Jin, B., Huang, Y., & Sun, Y. (2014). Characterization of top phase oil obtained from co-pyrolysis of sewage sludge and poplar sawdust. *Environmental Science and Pollution Research*, 21(16), 9717-9726.

List of publications

Journal (UGC Care)

1. Kapatel, D. V., & Rotliwala Y. C. (2021) Municipal sewage sludge/Biomass co-pyrolysis in a batch reactor: Physico-Chemical analysis of the products. *The ADBU Journal of Engineering Technology*. 10(2), 0100200372. ISSN:2348-7305. <http://journals.dbuniversity.ac.in/ojs/index.php/AJET/article/view/2429>

Journal (SCI/SCOPUS Indexed)

1. Kapatel, D. V., Rotliwala, Y. C., & Patel, H. J., (2022) Co-pyrolysis based activated Bio-char: Characterization and its utilization for secondary treated pulp and paper industry wastewater. *Materials Today: Proceedings*. 57(4), 1724-1729. ISSN 2214-7853, <https://doi.org/10.1016/j.matpr.2021.12.361>.
2. Kapatel, D. V., & Rotliwala, Y. C., (2022) Influence of sugarcane bagasse addition in co-pyrolysis with sewage sludge on the thermogravimetric characteristics and study of kinetic. *Materials Today: Proceedings*. 57(4), 1776-1780. ISSN 2214-7853, <https://doi.org/10.1016/j.matpr.2021.12.455>.
3. Kapatel, D. V., Chavda, M., Kothari, Y., Modi, H., & Movalia, A., (2019) Characterization and Utilization of Biochar derived from pyrolysis and co-pyrolysis of MSS and waste biomass as an adsorbent. *International Journal of Innovative Technology and Exploring Engineering*, 8, 6S2. ISSN: 2278-3075. <https://www.ijitee.org/wp-content/uploads/papers/v8i6s2/F22210486S219.pdf>

Conference Proceedings:

1. Kapatel, D. V., & Rotliwala, Y. C. (2015) Bio oil from Municipal Sewage Sludge by Pyrolysis – A Review. *Proceedings of International Conference on Engineering - Issues, Opportunities, and challenges for development* organized by S. N. Patel

Institute of Technology and Research Centre, Umarakh, on 11th April 2015.
[https://www.snpitrc.ac.in /EIOCD-2015.aspx](https://www.snpitrc.ac.in/EIOCD-2015.aspx) (Accessed on April 15). ISBN: 978-81-929339-1-7

2. Kapatel, D. V., & Rotliwala, Y. C. (2021) Co-pyrolysis based activated bio-char assisted pulp and paper industry biologically treated wastewater for removal of COD and colour. *E-Proceedings on International conference on Green Technologies for sustainable development* organized by Dharmsinh Desai University, Nadiad on 9-11 March 2021. p 73-83. <https://www.scribd.com/document/523042792/e-Proceedings-gtsd-2021-spp-Paper>. ISBN: 978-93-5457-142-8.