BIOFUELS AND PLATFORM CHEMICALS FROM BIO-WASTES BY COUPLING THERMOCHEMICAL AND BIOCHEMICAL PROCESSES– EXPERIMENTAL STUDIES AND PROCESS MODELLING

Thesis

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Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of her **Master of Chemical Engineering** studies during academic session 2022-2024. All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

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CERTIFICATE

This is to certify that the thesis entitled "**Biofuels and Platform Chemicals from Bio-wastes By Coupling Thermochemical and Biochemical Processes- Experimental Studies and Process Modelling**" has been carried out by Suroj Ikbal in partial fulfilment of the requirements for thedegree of Master of Chemical Engineering from Jadavpur University, Kolkata is recorded as bona fide work that has been conducted under the supervision of Prof. (Dr.) Ranjana Chowdhury. The contents embodied in the thesis have not been submitted to any otheruniversity for the award of any degree or diploma.

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ABSTRACT

Increasing energy demand due to population growth and technological advancement, coupled with the overexploitation of fossil fuels, has pushed humanity to an irreversible point where it is essential to find more and alternative sources of energy. Biowastes can play a significant role in this regard. Two major types of technologies are available to convert waste into energy: thermochemical processes (such as pyrolysis, gasification, hydrothermal liquefaction, and hydrothermal carbonization) and biochemical processes (such as anaerobic digestion and fermentation). Among these, anaerobic digestion (AD) is already commercially established due to its low cost, low energy input, easy installation, and ability to treat a wide variety of organic matter. Another advantage of AD is its potential to be integrated with thermochemical processes both upstream and downstream, thereby enhancing energy and material recovery.

In this study, Kitchen waste and grass were used as feedstock, with cow dung serving as the inoculum. Cumulative biogas production was found to be 172.5, 301.875, 248.58, 275.625 ml/g VS for cow dung, grass, kitchen waste1, kitchen waste2 respectively. Methane content of the biogas was between 69 to 80 %. The undegraded anaerobic digestate was subjected to pyrolysis and hydrothermal liquefaction (HTL). Pyrolysis was performed at three different temperatures, while HTL was conducted at 200°C with a residence time of 1 hour. A comparative study of the characteristics of the products from pyrolysis and HTL was conducted, revealing that both pyrochar and hydrochar could have better soil amending properties compared to digestate. Hydrochar was found be more effective than pyrochar in case of dye removal when Congo red was used. A comprehensive kinetic model for both AD and pyrolysis was investigated, and a process model based on this was developed using ASPEN Plus V10.

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Chapter1

INTRODUCTION

1.1. Energy Crisis

The contemporary global energy landscape is marred by an escalating crisis, characterized by a confluence of depleting fossil fuel reserves, burgeoning energy demands, and exacerbating environmental degradation. Crude oil is currently the primary source of energy, which is deemed unsustainable and global energy consumption [1] is expected to increase by 57% by 2030.This scenario necessitates an urgent paradigm shift towards sustainable and renewable energy sources. Bioenergy emerges as a pivotal component in this transition, offering a viable alternative that aligns with environmental sustainability and energy security imperatives.

Bioenergy [2], derived from organic materials such as plant and animal biomass, presents several advantages over conventional fossil fuels [3]. Firstly, it is inherently renewable, with the potential for continuous replenishment through sustainable agricultural and forestry practices. Secondly, bioenergy production and utilization typically result in lower net greenhouse gas emissions, thus mitigating the adverse impacts of climate change. For instance, the carbon dioxide emitted during the combustion of biofuels is offset by the carbon sequestration that occurs during the growth phase of the biomass, establishing a more balanced carbon cycle.

Bioenergy encompasses a diverse array of energy forms derived from biological sources. The primary types of bioenergy include biofuels, biogas, biomass, and bioelectricity. Each type offers unique applications and advantages, contributing to a comprehensive approach to sustainable energy production. The diversification of energy portfolios through the incorporation of bioenergy can also enhance energy security by reducing dependency on finite fossil fuel resources and insulating economies from volatile oil markets. Moreover, the bioenergy sector can stimulate rural development and generate employment opportunities, thereby contributing to socioeconomic stability.

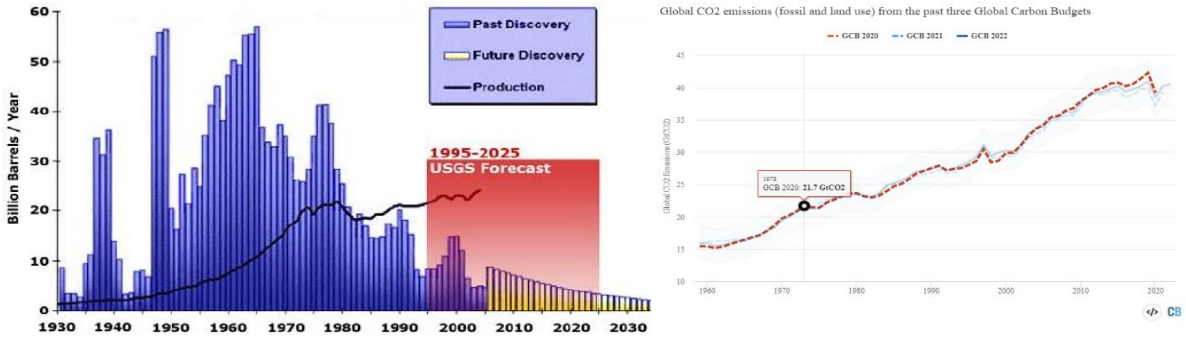


Figure 1.1. (a) World Oil Discovery Trend, (b) Analysis Global CO2 emissions from fossil fuels hits record high in 2022

1.2. Role of Biowaste

Biowaste [4], comprising organic waste materials derived from agricultural (Crop residues e.g., straw, husks, and stalks; Animal manure and slurry; Food processing by-products), industrial (Organic waste from food and beverage industries, Waste from the paper and pulp industry, Residues from bio-refineries), and household activities (Household organic waste, food scraps, yard waste, Sewage sludge from wastewater treatment plants), holds a significant place within the bioenergy sector. Its utilization not only contributes to sustainable energy production but also addresses waste management and environmental challenges. Biowaste can pose environmental and health risks if not managed properly. Improper disposal can lead to pollution of soil, water, and air, as well as the spread of diseases. Therefore, proper treatment and disposal methods are crucial to minimize these risks. The integration of biowaste into bioenergy systems exemplifies a circular economy approach, where waste materials are transformed into valuable energy resources. It can either be used as a solid fuel, or converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or fuels.



Figure 1.2. Different types of Bio-wastes

Among all kinds of Bio-waste, agro-food waste is the most abundant renewable biomass. Agro-food waste is generated after processing of crops which is produced in different amount depending upon the type of crops. Agricultural waste such as straws (Rice, Wheat), stalks (Corn), and leaves consist of cellulose and hemicellulose and is termed as on-farm agricultural waste (Fig 1.2). The estimated global production of Lignocellulosic biomass is about 181.5 billion tons per year [5]. Most of this material is involved in the natural carbon cycle of terrestrial ecosystems, undergoing microbial decomposition and transformations which ultimately afford CO_2 and water. However, a significant portion of lignocellulose generates biowaste, mostly coming from forestry and agricultural industries, which are promising sources for energy, bio fuels, platform chemicals [6] (Fig1.3 and Table 1.1).

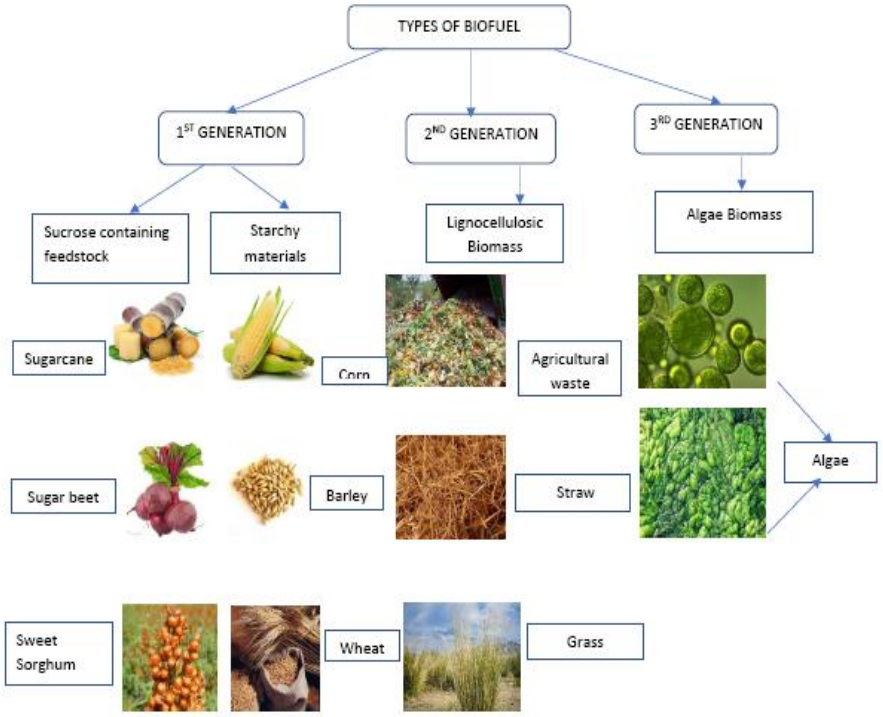


Figure 1.3. Types of Bio-fuels

Table 1.1. Biomass components and their major products upon pyrolysis [7]

Components	Products	Applications
	Levoglucosan	Often used as a chemical tracer for investigating biomass combustion in atmospheric chemistry studies.

Cellulose	5-HMF	Used as a biomarker and flavoring agent in the food industry.
	Furfural	Used in the synthesis of solvents (tetrahydrofurfuryl alcohol (THFA), polymers (Furan resins), fuels and other useful chemicals (furfuryl alcohol).
	Methyl glyoxal	Used as a medicine in the treatment of cancer.
	Hydroxy acetaldehyde	Used in the synthesis of Glyceraldehyde.
Hemicellulose	Phenols	Used as a precursor to synthesize plastics.
	Cyclic ketone	Used in the production of Nylon (Cyclohexanone)
	Hydroxy acetone	Used as a flavoring agent in the food industry.
	Propionic acid	Used in the synthesis polymers.
	Acetic acid	Used primarily in the production of cellulose acetate, polyvinyl acetate, synthetic fibers and fabrics.
Lignin	Benzenediols	Used in the synthesis of pesticides, pharmaceuticals, and perfumes.
	Catechol (phenol)	Used as a precursor to synthesize pesticides, flavors and fragrances.
	Methoxyphenol	Used as an intermediate in the synthesis of antioxidants, pharmaceuticals, plasticizers and dyestuffs.

1.3. WTE (Waste to Energy) Conversion

There are mainly two types of technologies [8] used for the conversion of biomass to energy are:

1) Bio-chemical/Biological conversion:
    a) Fermentation
    b) Anaerobic digestion (AD)
2) Thermo-chemical conversion:
    a) Gasification
    b) Hydro Thermal Combustion (HTC)
    c) Hydro Thermal Liquefaction (HTL)
    d) Pyrolysis

Biochemical conversion of biomass involves the use of bacteria, microorganism or enzymes to breakdown biomass into gaseous and liquid fuels. Whereas thermochemical conversion uses heat and chemical processes to produce energy products from biomass, including combustion, pyrolysis, gasification and liquefaction. Generally, these technologies are employed individually. But if integrated it can solve the drawbacks regarding individual processes.

Among these conversion technologies Anaerobic digestion (AD) [9] is one the most promising technology, and it is already commercially established process. Installation and maintenance cost, energy requirement is also very low in case of AD. Another advantage of anaerobic digestion is that it can treat a wide range of waste materials. Product Biogas can be processed to produce biomethane, which can possibly replace CNG. AD can be integrated with several thermochemical processes, especially with pyrolysis and hydrothermal processes (HTC and HTL), both upstream and downstream. AD by-product can be fed to thermochemical processes; vis a vis products derived from pyrolysis can be fed to AD. Before diving into this work, these processes are described briefly in the next section.

1.4. Anaerobic digestion

Anaerobic digestion is a series of processes by which microorganisms degrade the bio-waste in the absence of oxygen. The process has found its application in both industrial and domestic uses

for waste reduction and production of fuels. The products of this process are biogas, liquid digestate, and solid digestate. Anaerobic digestion (AD) systems are designed to capture the biogas produced from this breakdown and produce energy. Anaerobic digestion is a Biological Process, and there are four stages (Fig 1.4): a) Hydrolysis, b) Acidogenesis, c) Acetogenesis, d) Methanogenesis. **(a). Hydrolysis**- This is the first step in the conversion of organic material to biogas. In this stage, certain bacteria break down carbohydrate polymers like cellulose, hemicellulose etc. into simple sugars like glucose, xylose etc. so that the next group of bacteria can further act on the sugars. The protein compounds, if present in the waste, is converted to monomers i.e., amino acids **(b). Acidogenesis**- This is the second step in the conversion of organic material to biogas. In this stage, certain bacteria called acidogenic bacteria convert the simple sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. **(c). Acetogenesis**- This is the third step in the conversion of organic materials to biogas. In this stage, certain bacteria called acetogenic bacteria convert the organic acids into acetic acid, carbon dioxide, and hydrogen. **(d). Methanogenesis**- This is the final step in the conversion of organic materials to biogas. In this stage, certain single-celled organisms called methanogens convert the intermediate products produced in the preceding stages into biogas (primarily methane and carbon dioxide). The solid and liquid leftover from this process, digestate, consists of material that the microbes cannot use as well as dead bacteria.

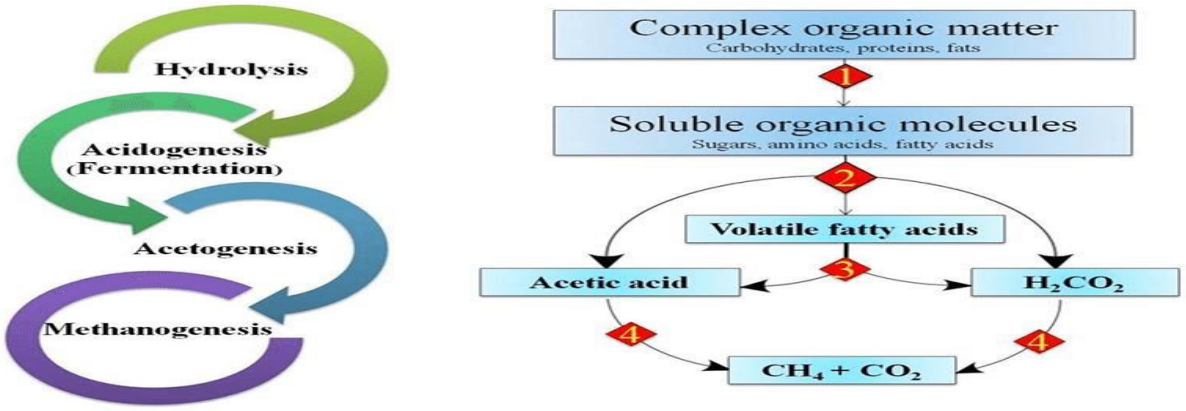


Figure 1.4. Flow diagram of the anaerobic digestion process [10]

1.5. Pyrolysis

Pyrolysis [11] has been derived from the Greek words: pyro meaning "fire" and lysis meaning "separating". It is used for converting lignocellulosic materials resistant to biotreatment (generally which are having high lignin content) into materials that are highly amenable to biotreatment processes for forming energetic fuels in gaseous and/or liquid states. Pyrolysis is a thermochemical

decomposition process that involves heating biomass or organic material in the absence of oxygen or with limited oxygen supply. In conventional pyrolysis, oxygen is substantially excluded and the operating temperatures to achieve destructive distillation are typically about 300 C to 700°C. On the different operating conditions there has three types slow pyrolysis, fast pyrolysis and flash pyrolysis (Table 1.2). The destructive distillation results in a gas, a liquid and solid matter, i.e., char. The main products after the pyrolysis are Pyro-Char, Pyro-Liquid, Pyro-Gas (Table 1.5).

Pyro-Char- Solid carbon-rich material, known as pyro-char, is formed as a result of pyrolysis. Pyro-char can be used as a soil amendment to improve soil fertility, water retention, and carbon sequestration.

Pyro-Liquid- Liquid mixture consisting of various organic compounds, such as phenols, aldehydes, and ketones, is produced during pyrolysis. Pyro-liquid can be further processed into biofuels or used in chemical applications.

Pyro-Gas- Gaseous mixture containing carbon monoxide, hydrogen, methane, and other gases is generated alongside pyro-char and pyro-liquid. Pyro-gas can be utilized as a fuel for heat and power generation or further processed into synthetic fuels and chemicals.

The pyro-liquid and pyro-gas produced during pyrolysis are typically cooled and condensed to separate them into their respective liquid and gaseous components. Various separation techniques such as fractional condensation or scrubbing may be employed to obtain purified pyro-liquid and pyro-gas.

Overall, pyrolysis offers a versatile and efficient means of converting biomass into valuable products, including biochar, bio-oil, and Bio-gas, thereby contributing to renewable energy production, waste management, and sustainable agriculture.

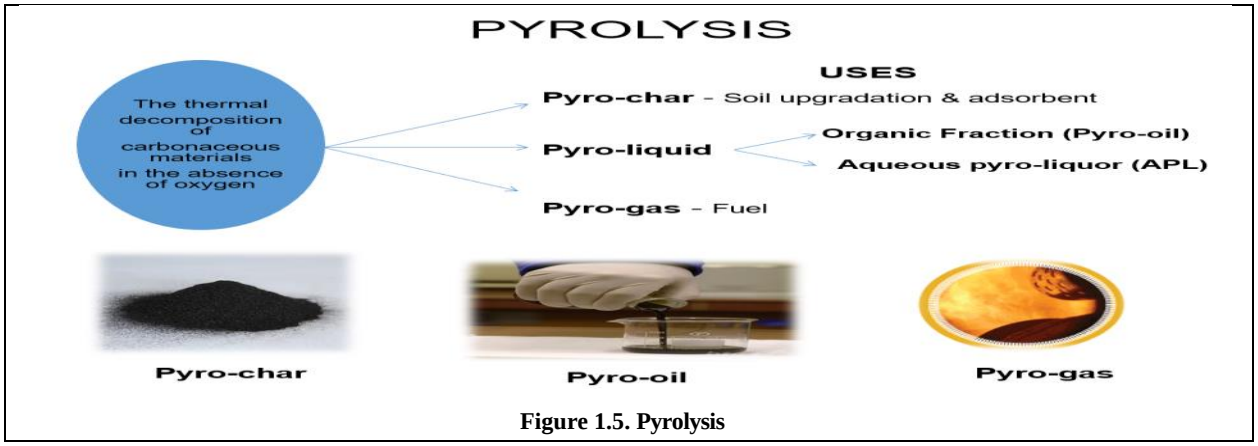


Figure 1.5. Pyrolysis

Table 1.2. Pyrolysis Products under Different Operating Conditions [12]

pyrolysis	operating conditions	Results
slow pyrolysis	feedstock size: 5-50 mm	gases: 35 wt. %
	temperature: 300-700 C	biochar: 35 wt. %
	heating rate: 0.1-1 C/s	bio-oil: 30 wt. %
	vapor residence time: 10-100 min	
fast pyrolysis	feedstock size: 3 mm	gases: 30 wt. %
	temperature: 400-800 C	biochar: 20 wt. %
	heating rate: 10-200 C/s	bio-oil: 50 wt. %
	vapor residence time: 0.5-5 min	
flash pyrolysis	feedstock size: 0.2 mm	gases: 13 wt. %
	temperature: 800-1000 C	biochar: 12 wt. %
	heating rate: 1000 C/s	bio-oil: 75 wt. %
	vapor residence time: 0.5 s	

1.6. Hydrothermal Carbonization (HTC)

Hydrothermal carbonization (HTC) [13] is a thermochemical process that converts wet biomass into carbon-rich solids called hydrochar by heating it to 180-250°C under pressures of 2-10 MPa in a water medium. This method breaks down complex organic structures through hydrolysis, dehydration, and decarboxylation, producing hydrochar, a liquid phase with dissolved organics, and a gaseous phase mainly of CO_2. HTC's advantages include the ability to process wet biomass without drying, lower energy requirements, and the production of valuable by-products. The resulting hydrochar, with its high carbon content and energy density, can be used as fuel, soil amendment, or precursor for activated carbon, promoting sustainable waste management and resource recovery.

1.7. Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction (HTL) [14] is a process that transforms wet biomass into liquid bio-crude oil by applying high temperatures (250°C to 374°C) and pressures (4 to 22 MPa) in a water-based environment. This method involves chemical reactions such as depolymerization, hydrolysis, and thermochemical conversion, which break down the biomass into bio-crude oil, an aqueous phase with dissolved organics, a gaseous phase primarily composed of CO2, and a solid residue called biochar. The resulting bio-crude oil can be further refined into renewable fuels and chemicals. HTL is effective for processing wet biomass without the need for drying and is highly energy-efficient, making it a valuable technology for producing biofuels and supporting renewable energy development and a circular economy.

1.8. Compatibility of AD with thermochemical processes

a) The integration of AD-PY allows for the valorization [15] of diverse organic wastes such as agricultural biomass, food scraps, and sewage sludge. Both methods efficiently convert these materials into valuable products like biogas, biochar, bio-oil, and syngas, thus aiding in waste management and resource recovery.

b) Combining AD and PY broadens the range of products compared to using either method alone. This includes generating biogas from anaerobic digestion and producing biochar, bio-oil, and syngas from pyrolysis, offering multiple revenue streams and versatile applications.[16]

c) Although AD can treat a variety of materials, it is not very effective in the case of feedstocks with high lignin content. In such cases, a large amount of organic material remains undigested. This problem can be solved by integrating AD with thermochemical processes. Pyrolysis can convert the lignin part of anaerobic digestate residue into various useful products. Hydrothermal processes can also be deployed in such scenarios.

d) Thermochemical processes such as pyrolysis and HTL can also be used as pre-treatment methods to break down the lignin part and make it more viable to feed to AD. This can make the whole process more effective in terms of material and energy recovery.

e) On the other hand, thermochemical processes are less effective in treating materials with high moisture content. In these cases, AD can be used primarily, after which pyrolysis and HTL could be used to recover organic remains in anaerobic digestion residue.

f) Integrating AD and PY can improve energy generation and utilization. Biogas generated from anaerobic digestion can be used to supply heat for the pyrolysis process, reducing external energy demands and enhancing overall energy self-sufficiency.

g) Biochar and hydrochar derived from pyrolysis and HTL of the digestate can enhance soil amending properties compared to the direct use of digestate in soil.
h) Biochar and hydrochar can also be fed back to AD to improve biomethanation efficiency [17], as they can improve biofilm formation and reduce inhibition effects by absorbing NH_3 and H_2S.
i) The aqueous part of the liquid product produced from pyrolysis, HTL, and HTC apparently have to no use. This can also be fed to AD to generate biogas.
j) The gaseous product of thermochemical processes can be upgraded to biogas through AD.

1.9. Ways of Integration of Pyrolysis (PY) and Anaerobic Digestion (AD)

According to the sequencing of anaerobic digestion and pyrolysis operations, integrated processes can be categorized into three primary forms: anaerobic digestion-pyrolysis (AD-PY), pyrolysis-anaerobic digestion (PY-AD), and anaerobic digestion-pyrolysis-anaerobic digestion (AD-PY-AD). Each of these variants possesses distinct technical advantages and has been the subject of ongoing investigation in recent years.

a). AD-PY:

The integration of anaerobic digestate utilization in pyrolysis [18] represents a promising avenue for enhancing energy efficiency and producing biochar for soil enhancement. While the management costs associated with anaerobic digestate are substantial, particularly due to environmental concerns like greenhouse gas emissions, coupling anaerobic digestion with pyrolysis offers notable benefits.

Experimental findings demonstrate that the heat generated during anaerobic digestion can efficiently fulfill the energy requirements for digestate drying before pyrolysis, thereby reducing costs. Moreover, integrating anaerobic digestion with pyrolysis significantly boosts electricity generation compared to standalone anaerobic digestion plants, resulting in surplus energy that can be sold to the grid, yielding additional income.

Comparative analyses between pyrolysis and post-digestion reveal the superior energy recovery efficiency of pyrolysis, making it a favorable method for managing anaerobic digestate and maximizing bioenergy yields. This integrated approach also alters the physicochemical properties of the resulting products, with biochar exhibiting enhanced characteristics conducive to soil carbon sequestration.

Furthermore, recent advancements demonstrate the potential of bio-oil derived from the pyrolysis

of anaerobic digestate as a viable renewable fuel source. Comparative assessments with traditional biofuels show comparable properties, with bio-oil exhibiting favorable heating values, stability, and combustion characteristics. Consequently, bio-oil from anaerobic digestate pyrolysis holds promise for various applications, including combustion and stationary power generation units (Fig 1.6).

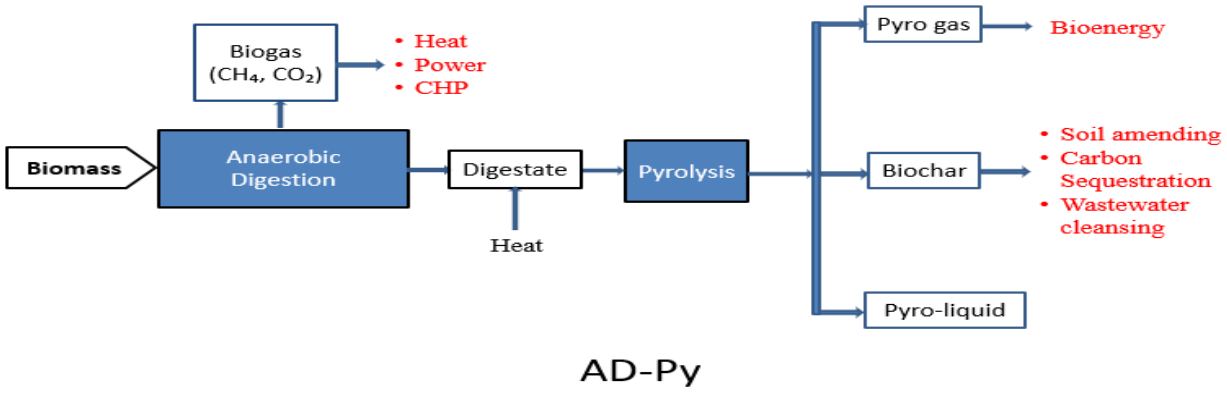


Figure 1.6. Block diagram of AD-PY

b). PY-AD:

The PY-AD process [19], combines pyrolysis with anaerobic digestion by utilizing pyrolysis products in the AD process effectively. A significant portion of the aqueous pyrolysis liquid (APL) can be converted into methane, offering a cost-effective and environmentally less threatening bioconversion feedstock. Biochar from pyrolysis aids in detoxification and enhances anaerobic digestion by facilitating bio-methanation. Despite benefits, attention to potential toxic compounds like furans and phenols is crucial. Strategies include pretreatments to increase pyrolysis selectivity and enhance residue digestibility. Detoxified byproducts, like APL, can be converted into valuable products such as bioethanol. The use of mixed consortia can improve resistance to inhibitory compounds, enhancing degradation efficiency. Further research is needed to optimize PY-AD processes for effective recycling and utilization of pyrolysis residues (Fig 1.7).

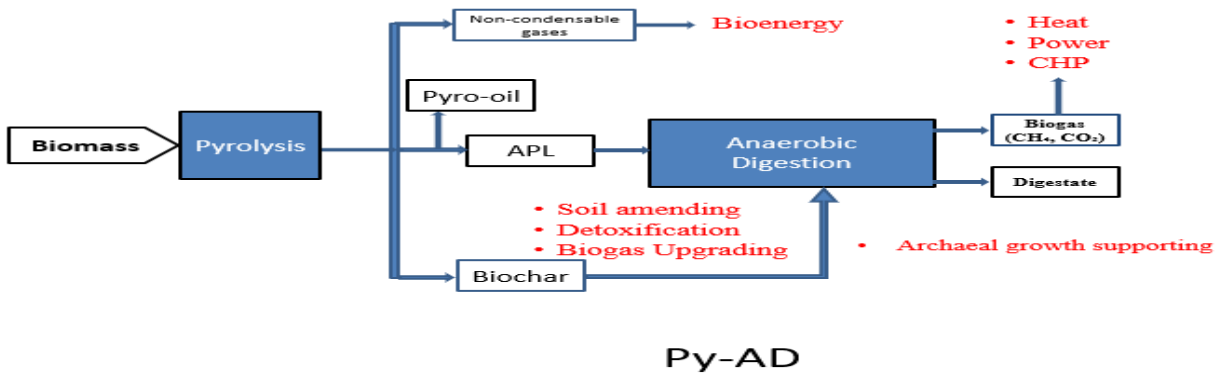


Figure 1.7. Block diagram of PY-AD

c). AD-PY-AD:

The AD-PY-AD process [20], a triple combination approach, aims to maximize the recycling of digestate and residue. Recent studies have demonstrated the feasibility and growing popularity of pyrolyzing anaerobic digestate and digesting resulting aqueous pyrolysis liquor. This method shows promise for biomass degradation and residue utilization. Researchers have explored using pyrolysis liquors as feedstock for biogas production in anaerobic digestion, noting inhibitory effects on methane production, especially in residues with high chemical oxygen demand (COD) and elevated pyrolysis temperatures. However, through the AD-PY-AD process, significant COD removal and methane yields can be achieved, along with the elimination of most volatile organic compounds (VOCs) in pyrolysis liquors. This process involves detoxifying pyrolysis liquors through anaerobic digestion after pyrolyzing the digestate, promising further recycling of pyrolysis liquors and residue (Fig 1.8).

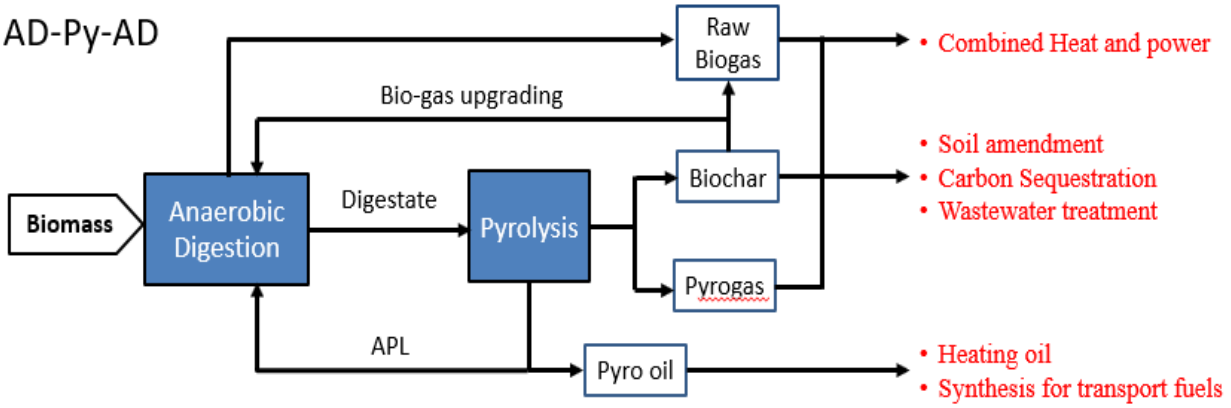


Figure 1.8. Block diagram of AD-PY-AD

1.10. Ways of Integration of Hydrothermal liquefaction (HTL) and Anaerobic Digestion (AD)

Similarly, to pyrolysis, hydrothermal liquefaction (HTL) can be integrated with anaerobic digestion (AD) [21] both upstream and downstream. An advantage of HTL compared to conventional thermochemical processes such as pyrolysis or gasification lies in the fact that anaerobic digestate can directly serve as a feedstock for the HTL process without the necessity for drying or liquid phase separation prior to entering the thermochemical unit. This methodology has demonstrated efficacy in managing feedstocks characterized by high moisture content. Conversely, the aqueous phase produced from HTL can also be introduced into the anaerobic digestion unit to facilitate the generation of biogas. Furthermore, the hydrochar obtained can be utilized as an additive to the digester, thereby augmenting the overall process and rendering this approach to be sustainable.

1.11. Process Modelling using ASPEN Plus

Process modeling using ASPEN Plus [22] is essential for several reasons:

1. ASPEN Plus allows engineers and researchers to design, simulate, and optimize chemical processes. By creating a virtual model of a process, users can explore various operating conditions, equipment configurations, and feedstock compositions to optimize performance, minimize costs, and maximize efficiency before implementing changes in the real world.

2. With ASPEN Plus, users can predict the behavior of complex chemical processes under different scenarios. This predictive capability is crucial for troubleshooting existing processes, identifying potential bottlenecks, and assessing the impact of changes in operating conditions or feedstock properties.

3. Process modeling enables engineers to identify opportunities for improving resource efficiency, such as reducing energy consumption, minimizing waste generation, and maximizing the utilization of raw materials. By optimizing process parameters and equipment design, ASPEN Plus helps minimize environmental impact and enhance sustainability.

4. ASPEN Plus allows users to simulate the production of chemicals, materials, and products with a high degree of accuracy. By controlling process variables and analyzing the effects of different operating conditions, engineers can ensure product quality, consistency, and compliance with regulatory standards.

5. Process modeling using ASPEN Plus facilitates safety and risk assessment by simulating the behavior of hazardous substances, identifying potential hazards, and evaluating the effectiveness of mitigation measures. By conducting virtual "what-if" analyses, engineers can proactively identify and address safety concerns before they arise in the real world.

6. ASPEN Plus supports scale-up and commercialization by enabling engineers to simulate processes at different scales, from laboratory experiments to pilot plants to full-scale production facilities. By validating process models against experimental data and real-world operating conditions, engineers can confidently scale up processes for commercialization while minimizing risks and uncertainties.

Overall, process modeling using ASPEN Plus is a valuable tool for engineers and researchers across various industries, enabling them to design, optimize, analyze, and scale up chemical processes efficiently and effectively.

1.12 Overview of Thesis

The present research focuses on the experimental studies of anaerobic digestion of a lignocellulosic waste along with the development of mathematical models. The integration of anaerobic digestion process with pyrolysis and hydrothermal liquefaction has also been attempted separately for better utilization of digestate of AD. The utilization of char obtained through pyrolysis and HTL has also been explored. The thesis has been presented in six following chapters with the following lay-out: Chapter 2: Literature Review; Chapter 3: Aims and Objectives; Chapter 4: Materials and Methods; Chapter 5: Theoretical Analysis; Chapter 6: Results and Discussions; Chapter 7: Conclusions and Future Scope of Research.

Chapter 2

LITERATURE REVIEW

As stated in Chapter1, this research will focus on the experimental studies of anaerobic digestion of a lignocellulosic waste along with the development of mathematical models and on the integration of anaerobic digestion process with pyrolysis and hydrothermal liquefaction separately for better utilization of digestate of AD. Therefore, extensive literature review of experimental studies and mathematical modeling of AD, AD-PY and AD-HTL integration has been done to identify the research gaps.

Table 2.1. Literature Review of AD-PY

Methods of integration	Feed in AD&Feed in PY	Process Conditions	Key Findings	Ref.
AD-PY	AD-Corn Stalk PY-Solid Digestate	AD: 1Lt anaerobic digester, temperature: 35±0.5 °C Retention time: 50 days PY:5g of sample Temperature: 800°C.	Energy recovery improved, CMP played a crucial role for coupling AD-PY	[23]
AD-PY	AD-Sargassum PY-Dried solid digestate	AD: temperature: 35±2 °C PY: temperature:800° C Heating rate: 10 °C/min.	For the energy flow, the AD integrated PY process showed a superior performance compared with direct PY, as the total energy recovery increased from 5.88 to 6.42 MJ/kg TS	[24]
AD-PY	AD-Cattle Manuare, Duck Slurry, Agro	AD: Temperature : 40 to 45 °C Hydraulic Residence Time: 26 Days	The coupling of AD and PY has been demonstrated to serve as a promising strategy for solid digestate valorization into	[25]

	industrialwaste PY-Dried solid digestate sample	PY: Temperature: 500 ºC Heating rate:10 ºC/min, for 1 hr. at high temperature	syngas, bio-oil and biochar. Biochar application improved the GWR of soil by 10% at application of 50 t/ha	
AD-PY	AD-Rice Straw, Pigmanure PY-Digestate, Eggshell	AD: Temperature : 37±1ºC, For 30 Days PY: Temperature : 500 ºC, Residence time : 20 minutes	The suggested route showed 7602 MJ/ton energy output from bio-oil and biomethane.	[26]
AD-PY	AD-Kitchen Waste PY-Digestate from AD	AD: Mesophilic condition (35 to 37 ºC) PY: Temperature: 500ºC,600ºC and 700ºC.Heating Rate: 20ºC/min.	The pyrolysis characteristics of kitchen waste digestate were analyzed at different pyrolysis temperatures (500 ◦C, 600 ◦C, and 700 ◦C). The pyro gas yield increased (from 11.10 % to 13.41 %) with increasing temperature, and the oxygenated compounds, PAHs, and NHCs in the pyro-oil increased.	[27]
AD-PY	AD-wastewater sludge and quinoa residues PY- Dried solid digestate	AD: Mesophilic conditions (35 ± 2 °C, pH = 7) PY: 500 °C with a heating rate of 10 °C/min	An original cascading biorefinery approach that coupled AD and pyrolysis was investigated for the valorization of organic wastes. AD led to a methane production of 219 NL CH4/kg VS, and the organic phase (OP) of bio-oil and syngas from subsequent pyrolysis of the solid digestate exhibited higher and lower heating values of 34 MJ/kg and	[28]

			11.8 MJ/Nm^3.	
AD-PY	AD-cattle manure, duck slurry, agro-industrial wastes, agricultural by agricultural by-products. PY-Dried solid digestate sample	AD: Temperature Range between 40 and 45ºC HRT : 26 days	The coupling of AD and PY has been demonstrated to serve as a promising strategy for solid digestate valorization into syngas, bio-oil and biochar. A specific focus was made on combining biochar and anaerobic liquid digestate for agronomic issues. Bio- char application improved the GWR of soil by 10% at application of 50 t/ha.	[29]

Research Gap of Integration of AD & PY:

The integration of anaerobic digestion (AD) and pyrolysis presents a promising avenue for advancing waste-to-energy conversion technologies. The combination of AD and pyrolysis offers complementary advantages. AD primarily converts organic matter into biogas and digestate, while pyrolysis thermally decomposes organic materials into biochar, syngas, and bio-oil. The integration of these processes could enhance overall energy recovery and resource utilization from organic wastes. Despite growing interest and research in both AD and pyrolysis individually, the synergistic potential of their integration remains largely unexplored. Therefore, a significant research gaps remain. These are as follows:

1. There is a lack of comprehensive studies focusing on the optimal integration configurations, including process parameters, operating conditions, and feedstock characteristics. Research is needed to identify the most efficient coupling strategies to maximize energy output and product quality while minimizing environmental impacts and operational costs.

2. Different types of organic wastes exhibit varying biochemical compositions and degradation behaviors, affecting the performance of AD and pyrolysis processes. Investigating the compatibility of diverse feedstocks within integrated systems is essential to assess the scalability and versatility of the technology across different waste streams.

3. The integration of AD and pyrolysis introduces complex interactions between biochemical and thermochemical processes, potentially influencing system stability, microbial activity, and product

yields. Understanding the dynamic behavior of integrated systems under fluctuating operating conditions is crucial for ensuring process robustness and reliability.

4. While laboratory-scale studies have demonstrated the feasibility of integrating AD and pyrolysis, scaling up these integrated systems for commercial applications presents numerous challenges. Research efforts should address scale-up considerations, process intensification, and technology transfer barriers to facilitate the transition from lab-scale prototypes to real-world implementation.

Table 2.2. Literature Review of AD-HTL

Methods of integration	**Feed in AD&Feed in HTL**	**Process Conditions**	**Key Findings**	**Ref**
AD-HTL	AD: Dairy manure HTL: Digestate	Temperature: AD: 35°C, HRT: 20 days HTL: 300°C and 60 min	Improve energy production from organic waste, main product is biomethane.	[30]
AD-HTL	AD: Sewage sludge HTL: Digestate from AD	Temperature: AD: 37°C HTL: 160°C and 250°C Reaction time: 120 min.	The addition of hydrothermal carbonization improved the treatment cost by 42%. It might enhance the quality of AD products. An overall total solid and COD reduction up to 68 and 66% respectively.	[31]
AD-HTL	AD: Maize silage HTL: Maize silage digestate	Temperature: AD: 60°C, pH= 5.75, OLR= 8 kg/m^3 day HTL: 180,200 and 220 °C, 30 min	180°C and 30 minutes is the most favorable HTL condition for this case. Hydro char achieved best combustion rate, highest energy recovery.	[32]
AD-HTL	AD: Cow Manure	Temperature:	Biocrude derived from	[33]

	HTL: Cow manure digestate	AD: 29ºC, HRT: 10-60 days HTL: 350 ºC and 30 min	digestate via hydrothermal liquefaction (HTL) can be efficiently upgraded to produce drop-in transportation fuels. Integrating anaerobic digestion with HTL for the processing of animal wastes has the potential to generate substantial quantities of renewable energy while significantly mitigating environmental risks associated with digestate disposal.	

Research Gap of Integration of AD – HTL:

Despite the promising potential of integrating anaerobic digestion (AD) and hydrothermal liquefaction (HTL) for waste treatment and renewable energy production, several research gaps remain:

1. There is a need for detailed studies on the optimization of process parameters for both AD and HTL to maximize biogas and biocrude yields. Understanding the interplay between variables such as temperature, pressure, retention time, and feedstock composition is crucial.

2. The impact of different types of feedstocks on the efficiency and output of the integrated system requires further investigation. Variability in animal waste composition can affect the digestion process and the quality of the biocrude produced.

Table 2.3. Literature review of process simulation

Methods	**Process modelling**	**Key findings**	**Ref.**
Simulate ADM1	Aspen Plus ADM1-based flowsheet for this process. Selected parameters-conversion ratios, kinetic	Stoichiometric for the hydrolysis step. Kinetic for acidogenesis, acetogenesis, methanogenesis.	[34]

	pre-exponent and inhibitor factors.	Equilibrium for hydrogenotrophic methane production. Best fit model and experimental results	
ADM1 lab experiment and model application	ADM1 was implemented for process simulation of semi-continuous AD	First order hydrolysis constants and microbial growth rates were evaluated. practical application on agricultural biogas plants	[35]
ADM1 model development and stoichiometric analysis	ADM1 mass based	This is practical application on AD plants. Simplified model variations focus on nutrient degradation and biogas formation using first-order sum reactions, while more intricate models elaborate on individual degradation pathways and intermediates during acidogenesis and acetogenesis. By employing steady-state balancing, the effective biogas potentials and cumulative microbial biomass yields of ADM1 during continuous operation have been determined. These diverse process models and reference values offer a dependable basis for the standardized application of model-based monitoring and control strategies in industrial AD plant concepts.	[36]
Simulation of food waste	Aspen Plus	The optimal methane concentrations were obtained with OLRs of 2 l/day and 5 l/day at a fat concentration of	[37]

		40%, resulting in methane contents of 74.82% and 77.10%, respectively. HRT of 10-20 days with a fat concentration of 60% also yielded a high methane content of 77.10%. The lowest methane concentrations were observed with an OLR of 10 l/day at a 60% fat concentration (35.89%) and an HRT of 30 days at a 60% fat concentration (37.73%).	

Although research studies are coming up using different feedstocks, reported data on process modeling for Indian lignocellulosic feedstock are rarely available.

Chapter 3

AIMS AND OBJECTIVES

1. Experimental studies of anaerobic digestion of kitchen wastes of two seasons (summer and winter) and local grass
2. Development of mathematical models using reaction kinetics of different AD stages
3. Experimental studies on pyrolysis of AD digestate
4. Experimental studies on hydrothermal liquefaction of AD digestate
5. Development of Process models for AD and PY processes using ASPEN Plus
6. Experimental studies on adsorptive dye removal using hydro- and biochar generated through HTL and pyrolysis

Chapter 4

MATERIALS AND METHODS

4.1. Materials

The cow dung (CD) was collected from the dairy farm near the Jadavpur University campus, Kolkata, India and used for the study after manually removing solid/inert particles. Grass (GR) was collected from Jadavpur University campus. Two separate kitchen wastes (KW1 & KW2) (Fig 4.1) used in the study were collected from Jadavpur University Main Hostel canteens. In KW1 collected in summer main components were potato skin, papaya skin, Lauaki skin. In KW2 collected in winter the main components were potato skin, pumpkin skin, Carrot and beat skin. The KW1, KW2 and GR were grinded before using them for the study. The KW1 & KW2 substrates was composed of peels, and unused portions of different fruit and vegetable wastes.



(a) (b) (c) (d)

Figure 4.1. Feed Stocks (a) Inoculm Cow Dung (CD), (b) Kitchen Waste1 (KW1), (c) Grass, (d) Kitchen Waste2 (KW2)

4.2. Experimental methods

4.2.1. Anaerobic digestion

Anaerobic digestion was conducted in a 5L stainless steel reactor under batch mode. The reactor was run on different substrates, namely, CD, GR, KW1 and KW2 and accordingly operation modes are designated as R1, R2, R3 and R4 respectively. In R1 mode, 3L of water-CD slurry was fed to the bioreactor. The volatile suspended matter (VS) in the slurry was maintained at 6%. The reactor was run for forty days. The digestate from the R1 mode reactor was used as the inoculum for the bioreactor on R2, R3 and R4 modes of operation. In all three R2, R3 and R4 modes of operation working volume was as 50% of the total volume of the reactor, i.e., 2.5L slurry was used. While VS content was maintained at 2% in the water-GR slurry used in R2 mode, it was kept at 6% in the water-KW1 and water-KW2 slurries used in R3 and R4 modes respectively. In all R2, R3 and

R4 modes, 10% inoculum was used. In all R2, R3 and R4 modes, following the filling of the bioreactor with respective slurries 10% inoculum, it was tightly closed with the lid equipped with two vents connected to stop cocks. To initiate the AD process inside the reactor, anaerobic condition was maintained by purging with nitrogen for 5 min to flush out air. After confirming that the reactors were well sealed, the reactors environment maintained at a mesophilic condition. The volume of the produced biogas was determined using the water displacement method every 1 to 5 days. The photograph and the schematic diagram of the experimental set-up are shown in Figures 4.2.a and 4.2.b. pH was measured regularly for each reactor.

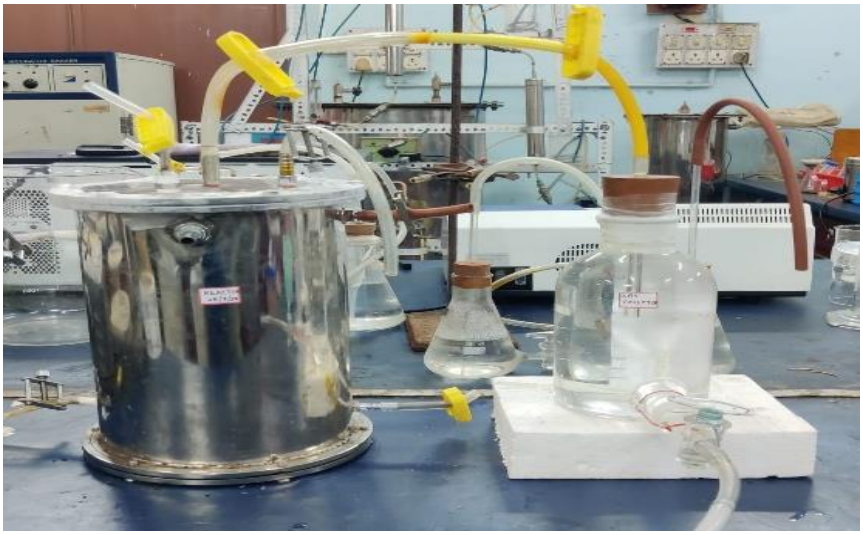


Figure 4.2.a

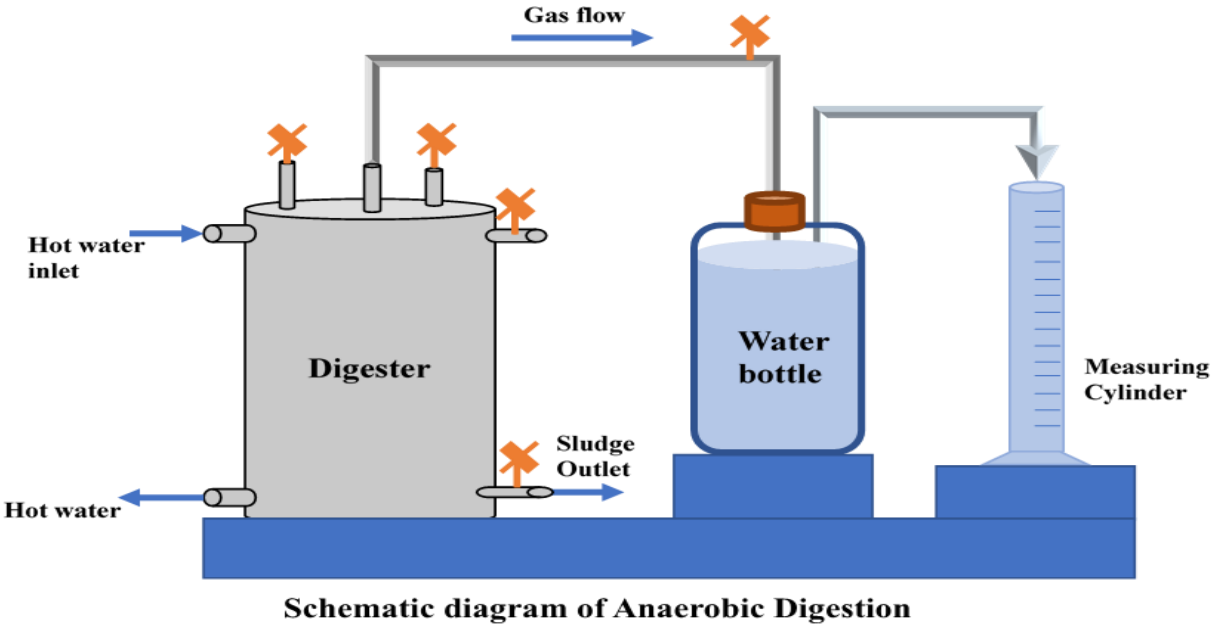


Figure 4.2.b

Figure 4.2. (a) Anaerobic digestion process, (b) Schematic diagram of anaerobic digestion

4.2.2. Pyrolysis

The pyrolysis of dried substates and digestates from AD reactors were carried out in a semi-batch reactor (35 mm diameter and 210 mm long) under isothermal condition at the temperature of 300, 450 and 600^{o}C in an inert atmosphere, maintained by nitrogen. The reactor equipped with furnace, temperature controller (PID controller) and digital weight box. The experiment was performed with 10 g biomass (on dry basis). The heating rate was maintained at 10^{o}C/min. The temperature of condenser was maintained 20^{o}C by using cold water circulating from water bath. After the experiments were completed, the reactor was allowed to cool at 25^{o}C. The solid product obtained from pyrolysis was collected from the reactor.



(a) **(b)** **(c)**

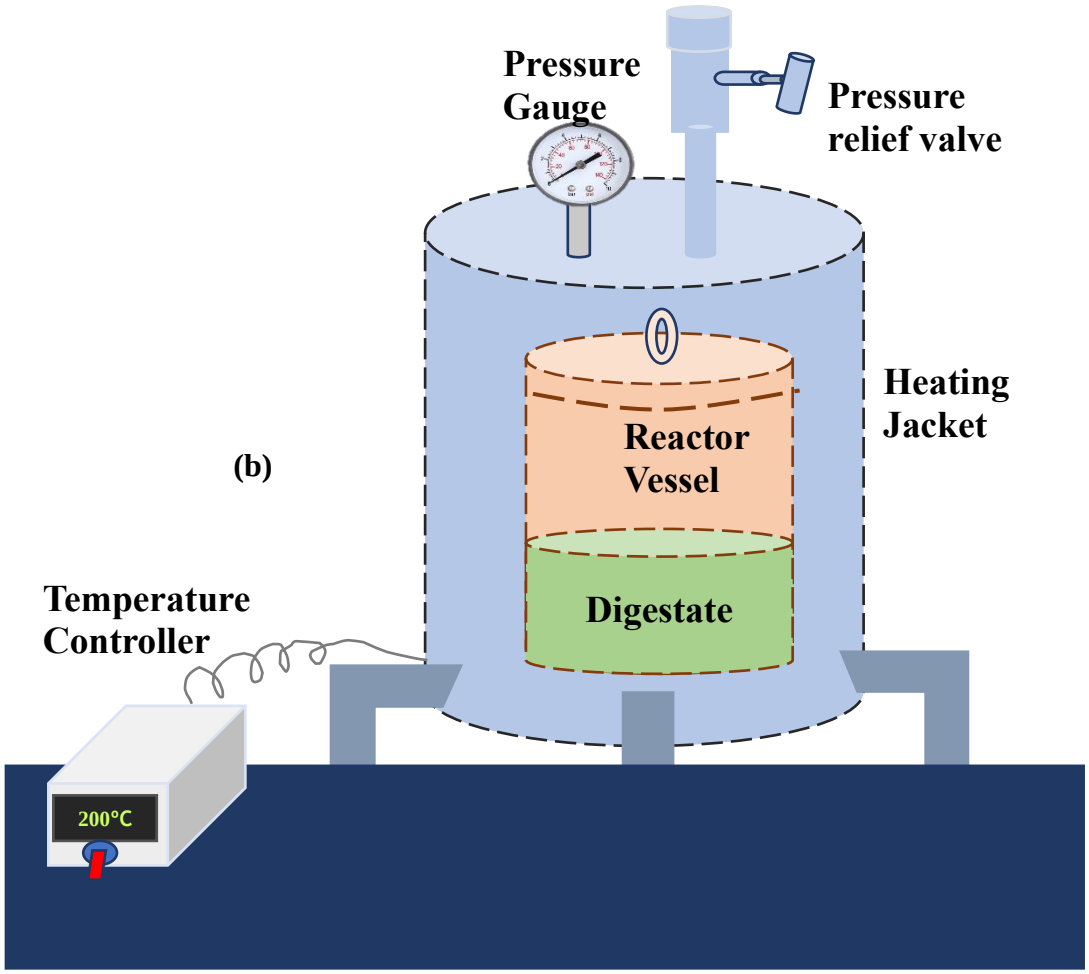
Fig4.3. (a) Pyrolysis Furnace with Weight box (b)PID Temperature Controller (c) Pyrolyzer

4.2.3. HTL

The hydrothermal liquefaction (HTL) of liquid digestate collected from R1 and R2 were carried out in a cylindrical stainless-steel reactor (45 mm inner diameter and 80 mm height, effective volume 250ml) in batch mode. 50% of the reactor was filled with reactants. The reactor was kept at 25^{o}C for 30 minutes for incubation. Thereafter, the reactor was placed in a programmable muffle furnace (NABER). The experiment was conducted at temperature of 200^{o}C with 30 minutes holding time. The heating rate was kept as 10^{o}C/min. After the experiments were completed, the reactor was allowed to cool to 25^{o}C. Vacuum filtration was applied for the separation of residual solids and aqueous phase, produced from HTL of digestate. Bio-oil was obtained from solvent (acetone) extraction of the solid residue. After acetone washing, the residual solid was dried at 70^{o}C for 1 hour and the dried mass was referred as the hydrochar.



(a)



(b)

Figure 4.3. (a) HTL Reactor Setup, (b) Schematic diagram of HTL Setup

4.2.4. Dye removal by pyrochar and hydrochar

Dye removal efficiencies of pyrochars and hydrochars were measured. Congo red (Hi-media, India) was used for the experiments. 40 mg of Pyrochar derived through pyrolysis (300, 450 and 600^{o}C) of digestate of R2 mode operation was used. Similarly, hydrochar of same digestate derived through HTL at 200 C was added to 10mg/L of dye solution and continuously stirred with magnetic stirrer for 1 hour. After that the chars were removed from the solution using micro filter. Absorbance of the solution was measured in spectrophotometer at 498 nm. All the experiments were conducted at room temperature and pH was maintained at 7 using buffer solution.

4.3. Analytical methods

4.3.1. Proximate analysis

The moisture, volatile matter, fixed carbon and ash content of feedstocks, digestates and chars (both pyrochar and hydrochar) were determined according to ASTM (D-3172-89) protocol.

4.3.2. Elemental analysis

Elemental analysis of feedstocks, digestates, chars (both pyrochar and hydrochar) and bio-oil were performed by using CHNS analysis to measure the amount of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) by vario MICRO Element Analyzer. Oxygen was calculated by difference. Higher heating value (HHV) and Lower heating value (LHV) of digestate, char and oil were measured by using Dulong Petit Law.

4.3.3. GC

Gas chromatography (GC) was conducted to identify constituent gases present in biogas and pyrogas. Biogas was collected using 1L tedlar bags for analysis. The GC (Thermo Scientific, Nashik, India TRACE1110) was equipped with Chromeleon 7 software and a thermal conductivity detector (TCD). Argon was used as the carrier gas.

The oven and TCD detector temperatures were 40 and 250 °C, respectively. A TR-FAME (60 m × 0.22 mm × 0.25 µm) column was used.

4.3.4. Spectroscopy

VIS Spectrophotometer (K-ROY®) was used for measuring the absorbance.

4.3.5. SEM

Scanning Electron Microscopy (SEM) used for the evaluation of surface morphology of the pyrochar and hydrochar.

4.3.6 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted for the identification of functional groups present in char and oil samples.

Chapter 5

THEORETICAL ANALYSIS

5.1. Theoretical Biomethane Potential & Biodegradability Index

The biodegradability index and Theoretical biomethane potential were calculated using the following Method. Biodegradability represents the performance of the AD process with respect to substrate degradation and biogas/biomethane production.

With knowledge of the chemical composition of a waste the quantity of methane can be predicted from the stoichiometric formula developed by Buswell and Hatfield [38] in 1936:

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}\right)CO_2 + dNH_3$$

------ (1)

or in simplistic form:

$$A + C_1B \rightarrow C_2C + C_3D + C_4E$$

A, B → reactants,

C, D & E→ products

And constants are C_1, C_2, C_3 & C_4

$$C_1 = a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}$$

$$C_2 = \frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}$$

$$C_3 = \frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}$$

$$C_4 = d$$

The biochemical reaction is automatically balanced and can be applied to any input with known relative ratios of carbon, hydrogen, oxygen, nitrogen. The model assumes that these elements are the only components of the feedstock. Moreover, the ultimate analysis is selected by the user of the model in order to determine the constants of the chemical reaction C1, C2, C3, C4 by estimating firstly the chemical formula of our feedstock. The constant of each element is equal to the ultimate analysis-based mass divided by the molar mass of the element and therefore ultimate analysis gives mass ratios C: H:O: N (in grams) which are then defined as variables. Then, for molar masses of carbon (m_C), hydrogen (m_H), oxygen (m_O), nitrogen (m_N) we have:

$$a = \frac{a_{ulti\ mass}}{m_C} = \frac{a_{ulti\ mass}}{12}$$

$$b = \frac{b_{ulti\ mass}}{m_H} = \frac{b_{ulti\ mass}}{1}$$

$$c = \frac{c_{ulti\ mass}}{m_O} = \frac{c_{ulti\ mass}}{16}$$

$$d = \frac{d_{ulti\ mass}}{m_N} = \frac{d_{ulti\ mass}}{14}$$

The molar mass of a compound with chemical formula A $C_aH_bO_cN_d$ is

$$M_A = a * m_C + b * m_H + c * m_O + d * m_N$$
$$= 12a + b + 16c + 14d \quad in\ \frac{g}{mol}$$

Respectively, the molar mass of each reactant and product can then also be calculated:

$$M_B = 2 * 1 + 16 = 18\ \frac{g}{mol}$$
$$M_C = 12 + 4 * 1 = 16\ \frac{g}{mol}$$
$$M_D = 12 + 2 * 16 = 44\ \frac{g}{mol}$$
$$M_E = 14 + 3 * 1 = 17\ \frac{g}{mol}$$

Hence,

$$TBMP = \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)}{12a + b + 16c + 14d} \qquad \text{------ (2)}$$

The biodegradability index was calculated as the ratio of experimental values (biogas/biomethane) obtained to the calculated theoretical values (biogas/biomethane) (Eq. (3)).

$$Biodegradability\ Index = \frac{Experimental\ biomethane\ potential}{Theoritical\ biomethane\ potential} - - - -(3)$$

5.2. Kinetics of AD

A kinetic model, adapted by Rajendran et al. [39] with a stoichiometric reactor for hydrolysis and a kinetic reactor for remaining steps like acidogenesis, acetogenesis and methanogenesis, was used. The model kinetics is according to Anaerobic Digestions Model No. 1 (ADM1) [40]. 1st order Monod type reaction kinetics were adopted for acidogenesis, acetogenesis and methanogenesis reactions.

General Monod kinetic expression:

$$\mu = \mu_{max} \frac{S}{K_S + S}$$

(a) Hydrolysis:

Cellulose: $Cellulose + H_2O \rightarrow C_6H_{12}O_6$

Hemicellulose: $Hemicellulose + H_2O \rightarrow 2.5\ CH_3COOH$

(b) Acidogenesis:

Dextrose: $C_6H_{12}O_6 \rightarrow 0.75\ C_3H_6O_2 + 0.5\ C_4H_8O_2 + 1.75\ CO_2 + 1.75\ H_2$

(c) Acetogenesis:

Propionic acid: $C_3H_6O_2 + H_2O \rightarrow 1.5\ CH_3COOH + H_2$

Iso-butyric acid: $C_4H_8O_2 + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ H_2$

(d) Methanogenesis:

(i) Acetic acid: $CH_3COOH \rightarrow CH_4 + CO_2$

(ii) Hydrogenophilic methane production: $CO_2 + 4\ H_2 \leftrightarrow CH_4 + 2\ H_2O$

Assumed that all reactions are obeying first order power law formula for kinetics.

The general expression of First Order Kinetics for reactant (i):

$$rate_{react,i} = \frac{dC_{react,i}}{dt} = -k_{react,i} * C_{react,i}(t)$$

The reactant concentration $C_{react,i}$ refers to the time dependent inside the batch reactor. The rate constant $k_{react,i}$ it is determined by Arrhenius law $k = k_{sub,0} * e^{-\frac{E_{a,sub,i}}{RT}}$.

Where, $k_{sub,0}$ is a pre-exponential factor which is specific for each operation,

$E_{a,sub,i}$ is the activation energy, R is the Universal gas constant and T is the given temperature

Inhibition effect of pH was taken into consideration. NH_3 and H_2S inhibition factor were ignored. The pH formula for the acidogenesis and acetogenesis steps indicates that inhibition occurred at low pH values and is non-existent for high pH but for methanogenesis at any pH (both low and

high pH) inhibition is occurred. Expression of pH inhibition factor:

$$I_{pH} = \begin{Bmatrix} 1, if\ acido - aceto\ genesis\ and\ pH > pH_{LL} \\ e^{-\left(\frac{pH-pH_{UL}}{pH_{UL}-pH_{LL}}\right)^2}, if\ acido - aceto\ genesis\ and\ pH < pH_{LL} \\ \frac{1+2*10^{\left(\frac{pH_{LL}-pH_{UL}}{2}\right)}}{1+10^{(pH-pH_{UL})}+10^{(pH_{LL}-pH)}}, methanogenesis \end{Bmatrix}$$

Kinetic parameters for all the steps and relevant constants were taken from the literature [40].

5.3. Kinetics of pyrolysis

5.2.1. Simple thermal deactivation model

The pyrolysis process of lignocellulosic material proceeds through a series of complex reactions. The reactions can be in series, parallel or combination of both. Various intermediates are formed in between the complex reactions. The main product of pyrolysis is the liquid pyro-oil and the by-products are the solid pyro-char and the pyro-gas. A simple model was proposed by Bandyopadhay et al. (1999) [41] where two parallel reactions occurred to produce two lumped products namely, condensable volatile and solid char. It was also assumed that the rate of active complex formation was instantaneous (Bradburyet al.1979) [42]

A scheme (Scheme1) was proposed by Bandyopadhay et al. (1999) [41] for the reaction pathway of the pyrolysis of biomass. This reaction scheme is described below:

$$\text{Lignocellulosic biomass} \rightarrow \text{Active complex} \rightarrow \begin{Bmatrix} \text{Volatiles}, k_v \\ \text{Char}, k_c \end{Bmatrix} \text{---- (4)}$$

$$-\frac{dW}{dt} = (k_v + k_c)W \text{---- (5)}$$

Let, $k_v + k_C = k$

Therefore,

$$-\frac{dW}{dt} = kW \text{---- (6)}$$

The profile of increase of weight of volatiles with time is given by the expression below:

$$\frac{dW_v}{dt} = k_v W$$

$$= k_v W_0 \,.\exp(-kt) \text{---- (7)}$$

The profile of increase of weight of char with time is given by the expression below:

$\frac{dW_c}{dt} = k_c W$

$= k_c W_0 \,.\exp(-kt)$ ––– (8)

Equation (6), (7), (8) have been solved analytically with the following initial conditions:

$(t \rightarrow 0) = W_0$, $W_v(t \rightarrow 0) = W_{v0} = 0, W_c(t \rightarrow 0) = W_{c0} = 0$ ––– (9)

The solution under isothermal conditions are as follows:

$W(t) = W_0 \exp(-kt)$ ––– (10)

$W_v(t) = \left(\frac{k_v}{k_c}\right) W_0[1 - \exp(-kt)]$ ––– (11)

$W_c(t) = \left(\frac{k_c}{k}\right) W_0[1 - \exp(-kt)]$ ––– (12)

Under isothermal condition:

$\frac{W_c(t) - W_{c0}}{W_v(t) - W_{vo}} = \frac{k_c W}{k_v W}$

$= \frac{k_c}{k_v}$

$= \frac{W_c(t \rightarrow 0) - W_{c0}}{W_v(t \rightarrow 0) - W_{v0}}$ ––– (13)

Assuming that at a pyrolysis temperature the residue obtained at infinite time is entirely comprised of char we can write,

$W_c(t \rightarrow \alpha) = W_R(t \rightarrow \alpha)$ [$t \rightarrow \alpha$ refers to the time when reaction stops inside the pyrolyzer]

And, $W_v(t \rightarrow \alpha) = W_0 - W_R(t \rightarrow \alpha)$ –––(14)

Therefore:

$\frac{W_c(t)}{W_v(t)} = \frac{W_R(t \rightarrow \alpha)}{W_0 - W_R(t \rightarrow \alpha)} = \frac{W_c(t \rightarrow \alpha)}{W_v(t \rightarrow \alpha)} = \frac{k_c}{k_v}$

Or, $W_c(t) = \frac{k_c}{k_v} * W_v(t)$ ––– (15)

Regression analysis of equations (10), (11), (12) gives the values of the rate constants k, k_v, k_c respectively, at different temperatures.

Kinetic parameters have been determined for the pyrolysis of all the feedstock.

5.2.2. Reaction kinetics

This mechanistic kinetic model of biomass pyrolysis was adapted from Ranzi et al. (2008) [43]. It includes different steps of solid fuel volatilization of cellulose (CELL), hemicellulose (HCE) and lignin (LIG). Lignin is further described as a combination LIGH, LIGO and LIGC, with different methoxylation degree, richer in hydrogen, oxygen and carbon, respectively. Complete kinetic mechanism and thermochemical data used in the model are given in the following Table 5.1.

Table 5.1. Kinetic mechanism and thermochemical data

Reaction	Kinetic Constants (1/s)	Activation Energies (kJ/mol)
CELL→ CELLA	8.00e+13	192.5
CELL→ 5 H_2O + 6 $Char$	8.00e+07	125.5
CELLA→ LVG	4T	41.8
CELLA → 0.95 HAA + 0.25 Glyoxal +0.2 Acetic acid + 0.25 HMFU + 0.2 Acetone + 0.16 CO_2 + 0.23 CO + 0.9 H_2O + 0.1 CH_4 + 0.61 Char	1.00e+09	133.9
HCE→ 0.4 $HCE1$ + 0.6 $HCE2$	1.00e+10	129.7
HCE1 →2.5 H_2 + 0.124 H_2O + CO +CO_2 + 0.25 Methanol + 0.5 Formaldehyde + 0.125 Ethanol + 2 Char	3.00e+09	113
HCE1→ $Xylan$	3T	46
HCE2→CO_2 + 0.5 CH_4 + 0.25 C_2H_4 + 0.8 CO + 0.8 H_2 + 0.7 Formaldehyde + 0.25 Methanol +0.125 Ethanol + 0.125 H_2O + Char	1.00e+10	138.1
LIG-C → 0.35 LIG_{CC} + 0.1 pCoumaryl + 0.08 Phenol + 0.41 C_2H_4 + H_2O + 0.495 CH_4 + 0.32	4.00e+15	202.9

$CO + 5.735\ Char + HCHO$		
LIG-H→ $LIG_{OH} + Acetone$	2.00e+13	156.9
LIG-O→ $LIG_{OH} + CO_2$	1.00e+09	106.7
LIG_{CC}→0.3 pCoumaryl + 0.2 Phenol + 0.35 Acrylic + 0.7 H_2O + 0.65 CH_4 + 0.6 C_2H_4 + 1.8 $CO + H_2$ + 6.4 Char	5.00e+06	131.8
LIG_{OH}→ $LIG + H_2O$ + Methanol + 0.45 CH_4 + 0.2 C_2H_4 + 2 CO + 0.7 H_2 + 4.15 Char	3.00e+08	125.5
LIG → Lumped-phenol	8T	50.2
LIG → H_2O + 2 CO + 0.2 Acetone + 0.4 Methanol + 0.2 Acetic acid + 0.2 Formaldehyde + 0.6 CH_4 + 0.65 C_2H_4 + 0.5 H_2 + 5.5 Char	1.20e+09	125.5

Primary biomass pyrolysis forms permanent gases (CH_4, CO_2, CO, H_2), light hydrocarbons, condensable hydrocarbons and oxygenated species (levoglucosan, hydroxyl methyl furfural, hydroxyacetone, hydroxyacetaldehyde, acetic acid etc.), and a solid residue. Here the solid residue char is assumed to contain 100% carbon. In secondary pyrolysis, conversion of all these volatile matters takes place.

5.3. Process modelling

For full-scale plant design, operation and optimization development of mathematical model for anaerobic digestion process is required. It would help to form a common basis for further model development and validation studies to make outcomes more compatible and comparable, assisting technology transfer from research to industry. AD and PY have modelled separately using ASPEN Plus V10.

5.4. ASPEN Modelling:

5.4.1. Anaerobic Digestion:

The process model is simulated in Aspen Plus V10. The NRTL (non-random two liquid) method

was employed with CH_4, CO_2 and H_2S as Henry components. A stoichiometric reactor (R-Stoic) was employed for the hydrolysis step. The employed reactions are in below. Cellulose is converted to dextrose, hemicellulose to acetic acid, xylose and furfural. The remaining three steps were modeled as a R-batch reactor. The occurring reactions of acidogenesis, acetogenesis and methanogenesis are provided below ((b) to (d-(i)) reactions). Reactants are converted to products as follows (b) dextrose to propionic and iso-butyric acids with carbon dioxide & hydrogen generation through acidogenesis. (c) propionic and iso-butyric acids to acetic acid and hydrogen generation through acetogenesis step. (d-(i)) acetic acid to carbon dioxide and methane through methanogenesis. And a continuous gas equilibrium reactor is used for hydrogenotrophic methanation (d-(ii)) where CO_2 and H_2 are converted to CH_4. This equilibrium reaction was modeled with the Aspen Plus steady state R-Equil reactor. Flowsheet of the model is given in the figure (Fig 5.1 and Table 5.2).

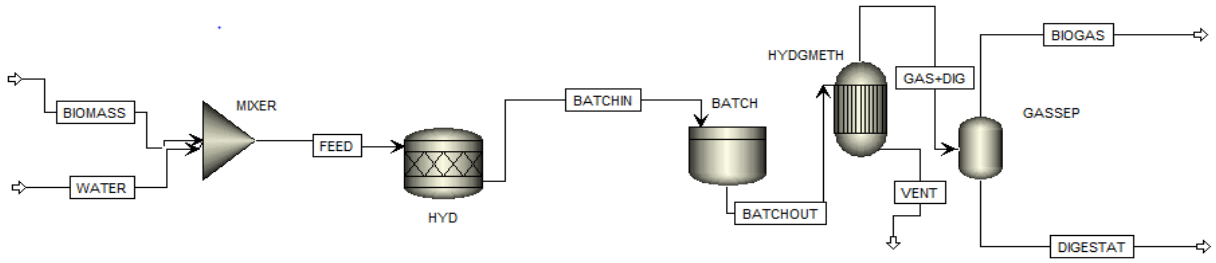


Figure 5.1. Flowsheet of the Anaerobic Digestion using Aspen Plus V10

Table 5.2

Block	ASPEN Block ID	Operation
MIXER	Mixer	Mixing biomass with water.
HYD	RStoic	Hydrolysis reaction takes place. Stoichiometry along with fractional conversion given.
BATCH	RBatch	Acidogenesis, acetogenesis, methanogenesis occurs. Stoichiometric equation along with kinetic information given.
HYDGMETH	REquil	Continuous gas-equilibrium reactor used for hydrogenotrophic methanation.
GASSEP	Flash2	Separates digestate and biogas.

5.4.2. Pyrolysis:

NRTL method was used. A batch reactor (RBatch) was employed for the pyrolysis reactions. Reaction stoichiometry and kinetics were given in Table 10. The product from batch reactor was then fed to a component separator (SEP), where char was being separated from the volatiles. In the next step, volatile entered to Flash2 for separating gas and liquid products. Flowsheet of the model is given in the figure (Fig 5.2 and Table 5.3).

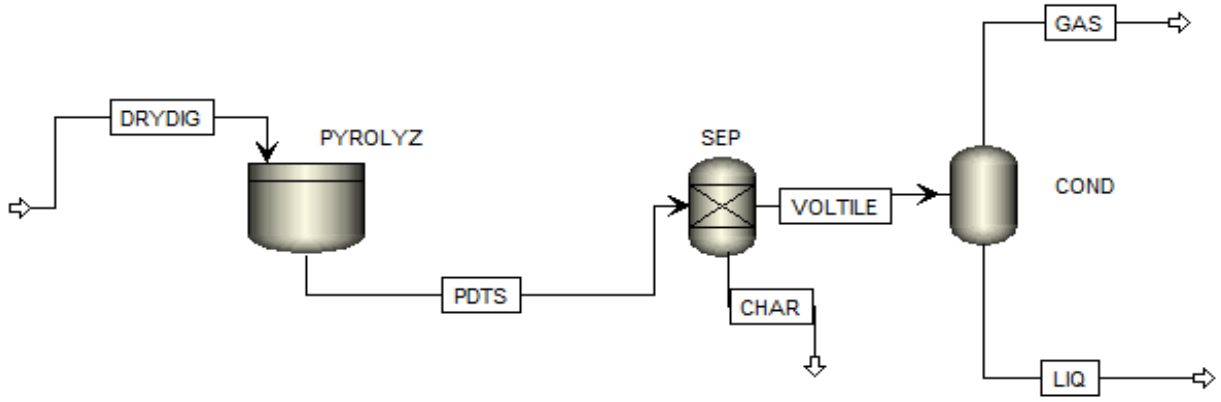


Figure 5.2. Flowsheet of the Pyrolysis using Aspen Plus V10

Table 5.3

Block	ASPEN Block ID	Operation
PYROLYZ	RBatch	Pyrolysis reaction takes place
SEP	Sep	Char being separated
COND	Flash2	Gaseous and liquid products get separated.

Chapter 6

RESULTS AND DISCUSSION

6.1. Characterizations of feedstocks

Results of proximate and ultimate analysis of the feedstocks Cow Dung (CD), Grass (GR), Kitchen Waste1 (KW1) and Kitchen Waste2 (KW2) are given below in the Table 6.1 & 6.2. In addition, H/C ratio, O/C ratio and HHV was calculated and shown in the Table. Carbon content maximum for KW1 and also maximum higher heating value (HHV) is 10.70179 MJ/kg, minimum carbon content and minimum HHV for CD is 6.258913 MJ/kg.

Table 6.1. Proximate analysis of feedstocks

Feed stocks	Moisture (%)	TS (%)	VS (%)	Fixed Carbon (%)	Ash (%)
CD	82.8	17.28	13.82	1.79	1.67
GR	83.41	16.59	11.78	2.65	2.16
KW1	86.4	13.6	9.66	2.79	1.15
KW2	85.8	13.3	9.49	2.83	0.98

(TS%, VS%, FC%, Ash% are given in wet basis)

Table 6.2. Ultimate analysis of feedstocks

Feedstocks	C (mass %)	H (mass %)	N (mass %)	S (mass %)	O (mass %)	H/C	O/C	HHV (MJ/kg)
CD	32.56	4.96	0.61	0.241	61.629	0.152334	1.892783	6.258913
GR	33.74	5.111	1.4	0.242	59.507	0.151482	1.763693	7.390894
KW1	37.64	5.403	3.25	0.378	53.329	0.143544	1.416817	10.70179
KW2	32.91	5.056	1.54	0.139	60.355	0.153631	1.833941	6.77753

6.2. Biogas production

CD and KW2 showed better biogas yield compared to GR and KW1. The lag phase for digestion for KW2 was found higher. Biogas generated from KW1 showed maximum methane percentage. Total biomethane production (TBMP) was calculated by equation (2). Biodegradability Index was calculated by using equations (3) and shown in the Table 6.3. Biodegradability is maximum for GR and the value of biodegradability index is 90.18672.

Table 6.3.

Feedstocks	CD	GR	KW1	KW2
Reactor Volume	6	1	2.5	2.5
Working Volume	2.6	0.6	1.3	1.3
Type	Mesophilic	Mesophilic	Mesophilic	Mesophilic
VS%	6	2	6	6
Retention time	58	40	40	42
Total Biogas Produced (L)	269.1	36.225	193.9	214.99
Methane content (%)	69	72	80	70
Cumulative biogas (mL/gVS)	172.5	301.875	248.58	275.625
BMP (Experimental) (ml/gVS)	119.025	217.35	198.864	192.9375
BMP (Theoretical) (ml/gVS)	224	241	297	228
Biodegradability Index (%)	53.13616	90.18672	66.95758	84.62171

Daily biogas production and cumulative biogas production were plotted against time (days) and shown in the Figure 6.1 & 6.2. Cumulative biogas production (in ml/gVS) of CD, GR, KW1 & KW2 are 172.5, 301.875,248.58 & 275.625 respectively. Flow pattern of the all feedstocks is same but lag phase is maximum for kitchen waste1 (KW1) and also daily biogas production is maximum for KW1. For CD, minimum daily biogas production occurred. Lag phase minimum for GR. For cumulative biogas production GR give maximum production of biogas and CD gives minimum cumulative biogas production. Peak gas formation was found at day 15-20 for different feedstocks.

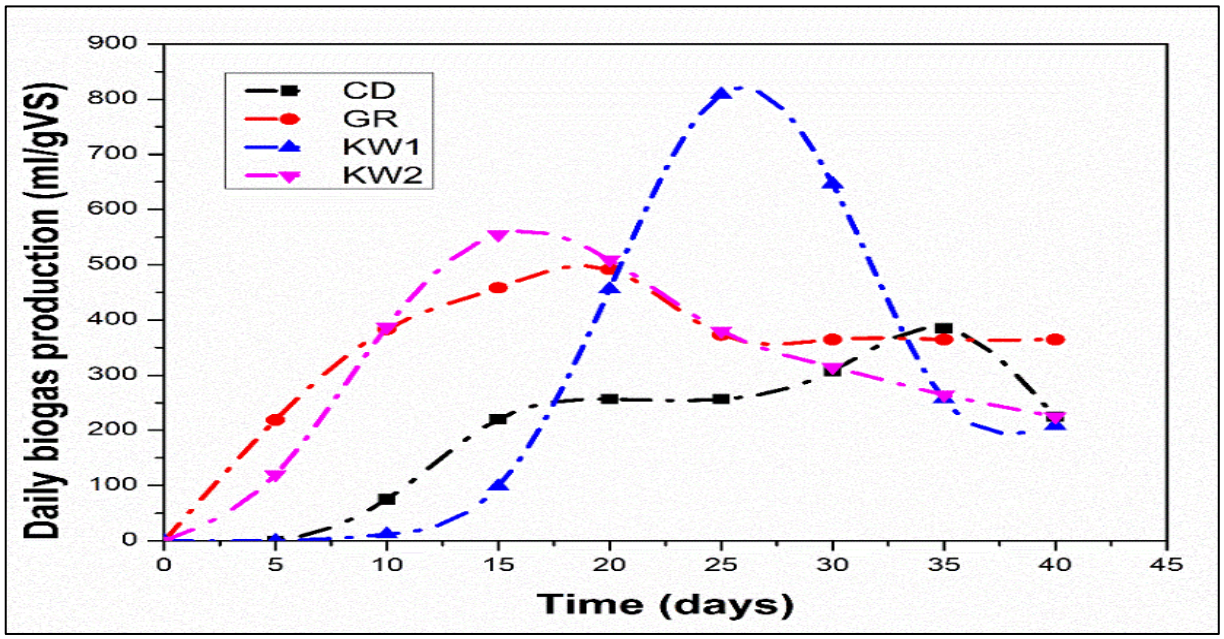
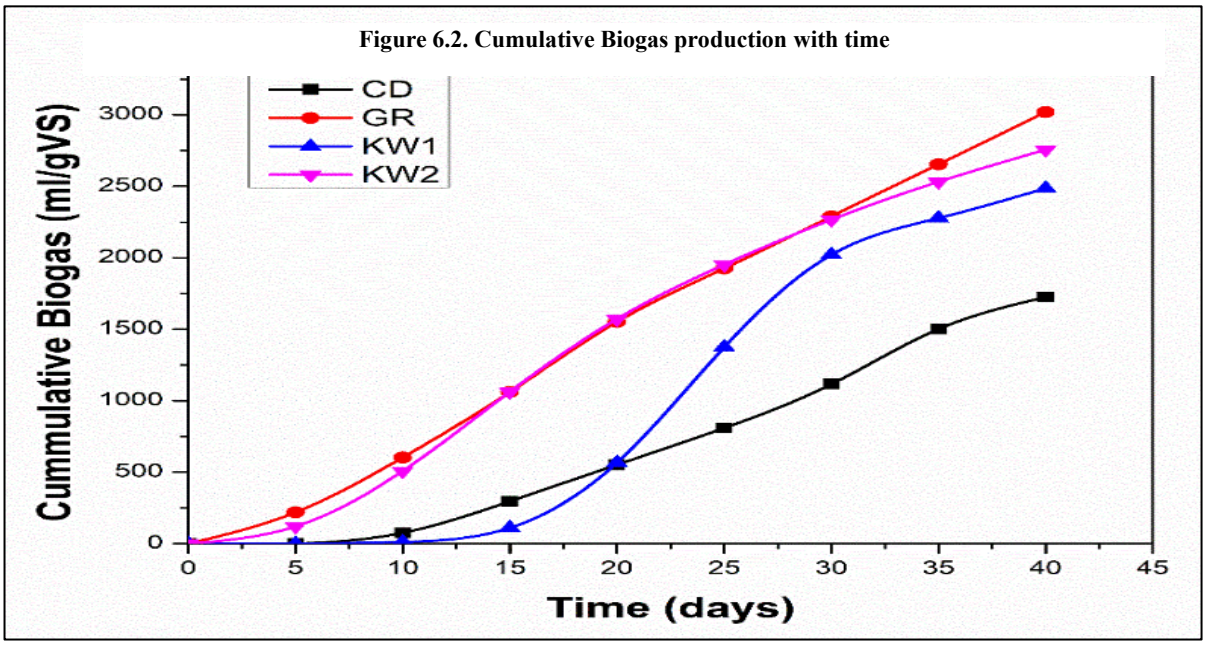


Figure 6.1. Daily biogas production with time

Figure 6.2. Cumulative Biogas production with time



6.3. Characterization of digestate

Results of ultimate analysis of the anaerobic digestates are given below in the Table 6.4. In addition, H/C ratio, O/C ratio and HHV was calculated and shown in the Table 6.4. Carbon content is maximum for GRD and minimum carbon content for KWD2. Higher H/C ratios tend to have higher energy content and are more suitable for applications such as diesel fuel, while lower H/C ratios are characteristic of lighter, more volatile fuels like gasoline. Higher H/C ratios typically indicate more saturated compounds (e.g., alkanes), while lower ratios suggest more unsaturated compounds (e.g., alkenes, alkynes, aromatics). Low C/O ratios typically have undergone more extensive oxidation, while higher C/O ratios indicate less oxidation. High C/O ratio may indicate the presence of hydrocarbons, while lower ratios suggest the presence of oxygen-containing functional groups. H/C ratios were found similar for all the samples, whereas O/C ratio for KWD2 was comparatively higher than the rest.

Table 6.4. Ultimate Analysis of different digestate

Feedstock	C (mass %)	H (mass %)	N (mass %)	S (mass %)	O (mass %)	H/C	O/C	HHV (MJ/kg)
CDD	35.625	5.419	2.16	0.597	56.199	0.152112	1.577	9.55776
GRD	40.85	6.008	2.63	0.686	49.826	0.147075	1.219	13.6072
KWD1	34.96	5.203	1.99	0.26	57.587	0.148827	1.647	8.40340
KWD2	32.54	4.698	1.79	0.24	60.732	0.144376	1.866	6.85405

6.4. Pyrolysis Yields

Mass yield (%) of pyro char, pyro liquid and pyro gas for different feedstocks Cow Dung (CD), Cow Dung Digestate (CDD), Kitchen Waste (KW1) and Kitchen Waste Digestate (KWD1) at different temperatures 300 ℃, 450 ℃ and 600 ℃ are shown in the following tables. For all the samples char yield decreased with temperature, while gas yield increased with temperature. Oil yield was maximum at 450 ℃. Maximum oil yields were found to be 9.52, 27, 19.7 and 25% for CD, CDD, KW1 and KWD1 respectively. For all the cases oil and char yield increased when digestates were used instead of raw stock, making AD a good pre-treatment process for pyrolysis process.

The value of pyro char decreased from temperature 300 to 600 ℃, maximum oil yield obtained 9.52% at 450 ℃. Pyro gas increased from 300-600 ℃ and maximum gas obtained 47.69% at 600℃.

Table 6.5. Yield (%) vs Temperature for Cow Dung (CD)

Temperature (℃)	Yield (%)		
	Pyro Char	Pyro Oil	Pyro Gas
300	67.04	2.377	30.583
450	49.36	9.52	41.12
600	47.31	5	47.69

CDD gave better results compared to CD. Maximum oil yield 27% at 450 ℃. Pyro gas increased with increase in temperature because of higher reactive conversion. Maximum pyrogas of 39.18% was obtained. Maximum char of 86.14% was obtained at 300℃. At low temperature incomplete conversion occurred.

Table 6.6. Yield (%) vs Temperature for Cow Dung Digestate (CDD)

Temperature (℃)	Yield (%)		
	Pyro Char	Pyro Oil	Pyro Gas
300	86.14	3.14	10.72
450	53.15	27	19.85
600	43.86	16.96	39.18

For KW1 maximum oil yield of 19.7% was obtained at 450℃, maximum pyro-char yield of 69.4% was obtained at 300℃, maximum pyro-gas yield of 46.58% was obtained at 600℃.

Table 6.7. Yield (%) vs Temperature for Kitchen Waste (KW1)

Temperature (℃)	Yield (%)		
	Pyro Char	Pyro Oil	Pyro Gas
300	69.4	7.2	23.4
450	43.2	19.7	37.1
600	36.12	17.3	46.58

Maximum oil yield 25% for KWD1 at 450℃. Maximum pyro char obtained 75% at 300℃.

Table 6.8. Yield (%) vs Temperature for Kitchen Waste Digestate (KWD1)

Temperature (°C)	Yield (%)		
	Pyro Char	Pyro Oil	Pyro Gas
300	75	7.65	17.35
450	57	25	18
600	51.14	19.57	29.29

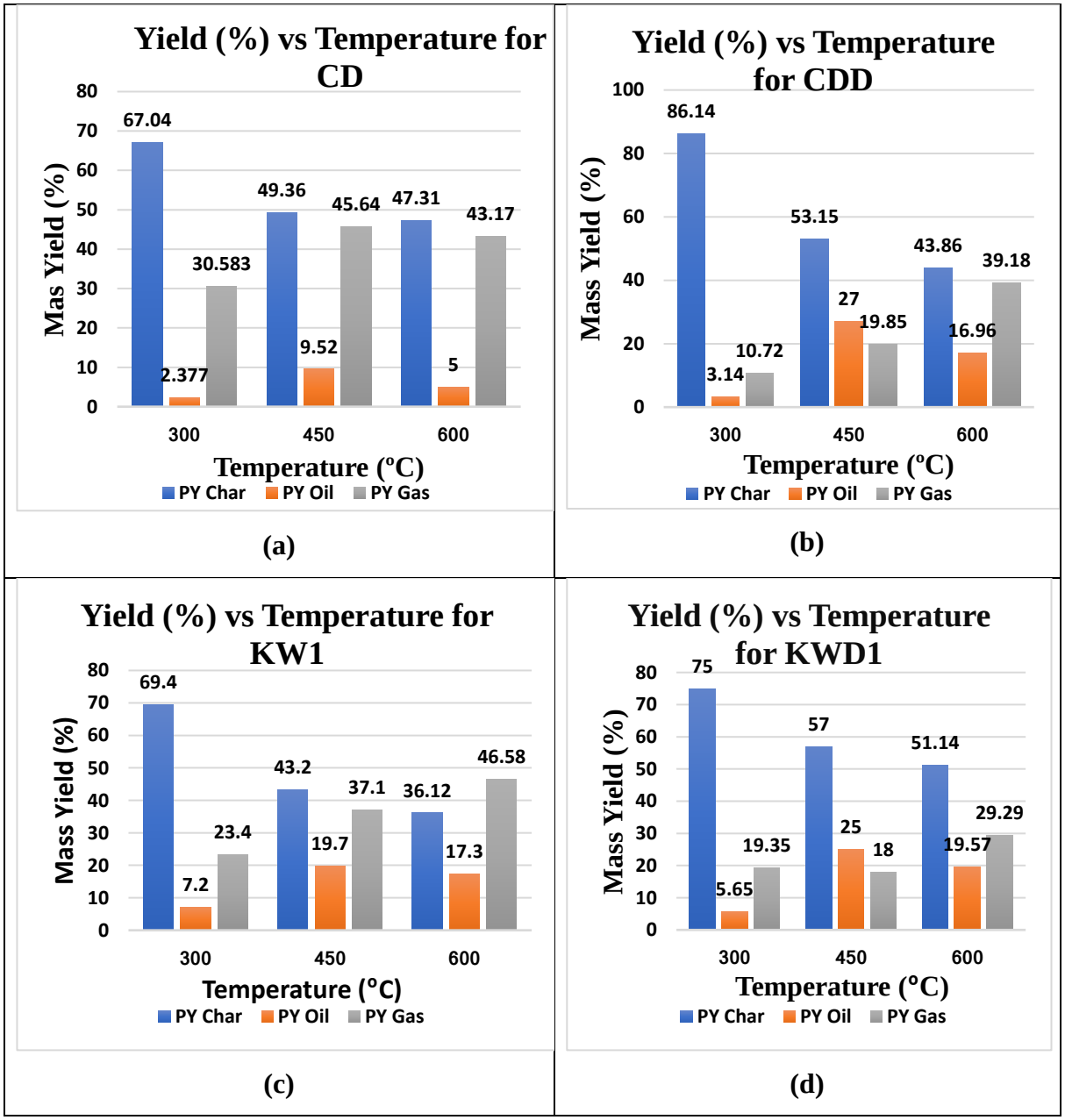
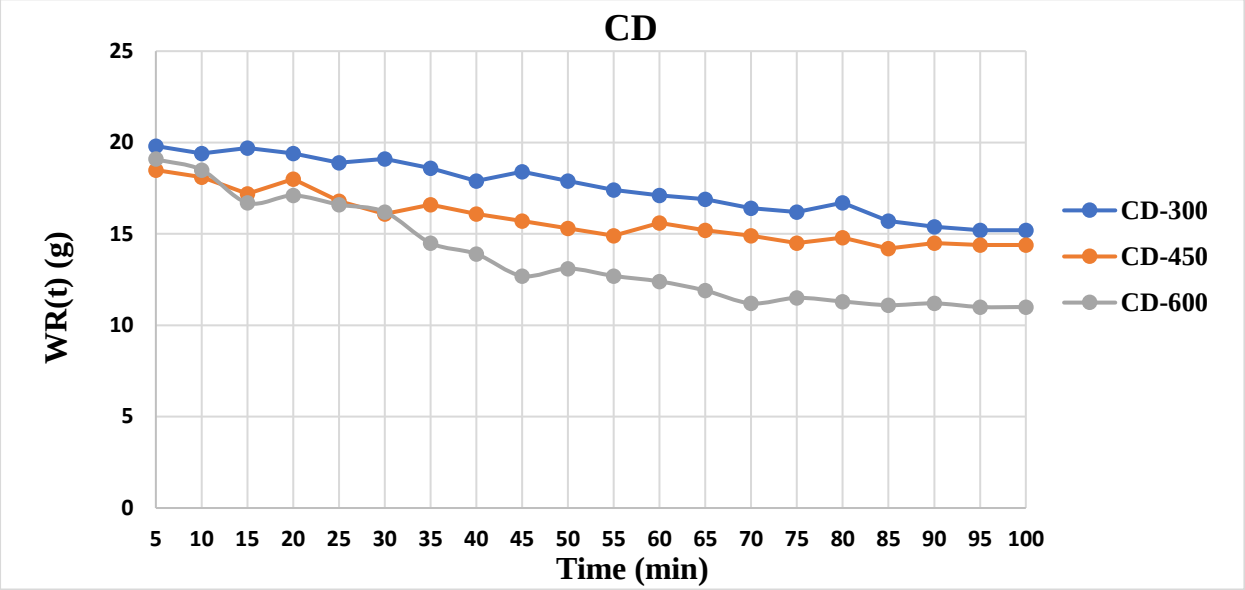


Figure 6.3. Yield of pyro char, pyro oil, pyro gas for (a) CD, (b) CDD, (c) KW1, (d) KWD1

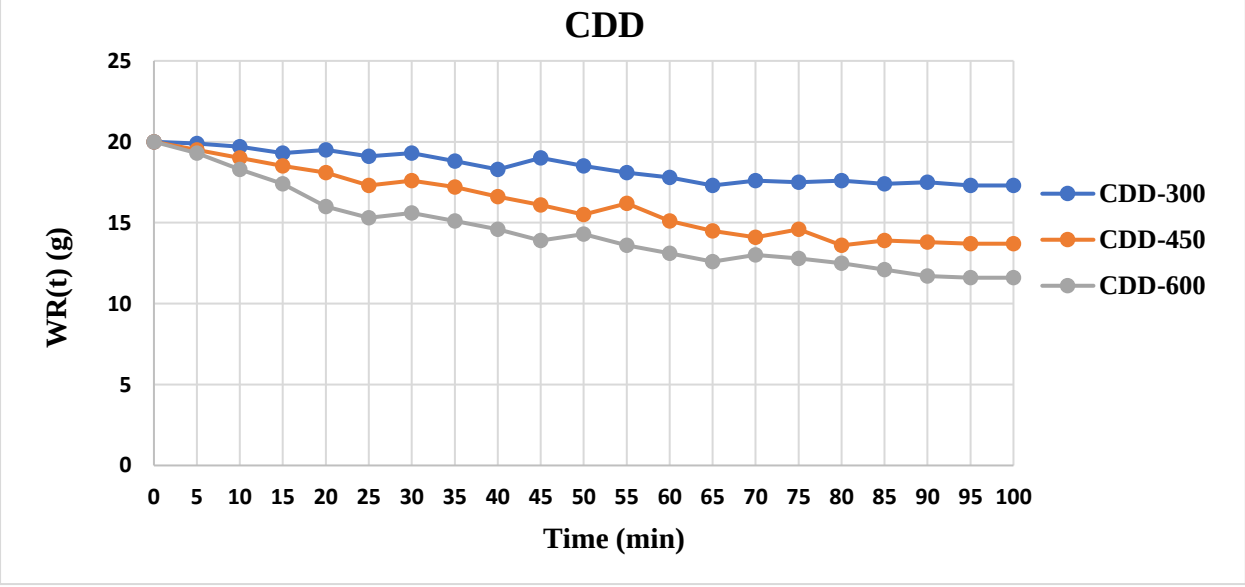
6.5. Pyrolysis kinetics

6.5.1. Weight loss for different feedstocks:

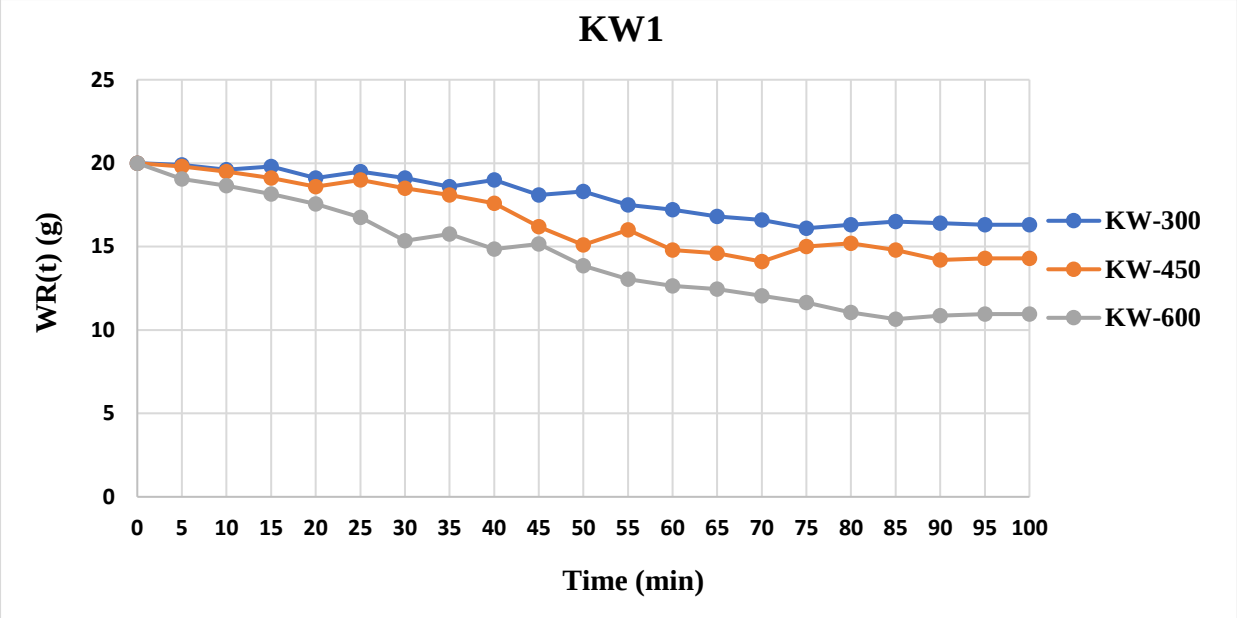
The weight for cow dung (CD), cow dung digestate (CDD), kitchen waste1 (KW1) and kitchen waste digestate1 (KWD1) has been studied in pyrolysis process. The fraction of weight residue had been plotted against time in the temperature range of 300-600°C.



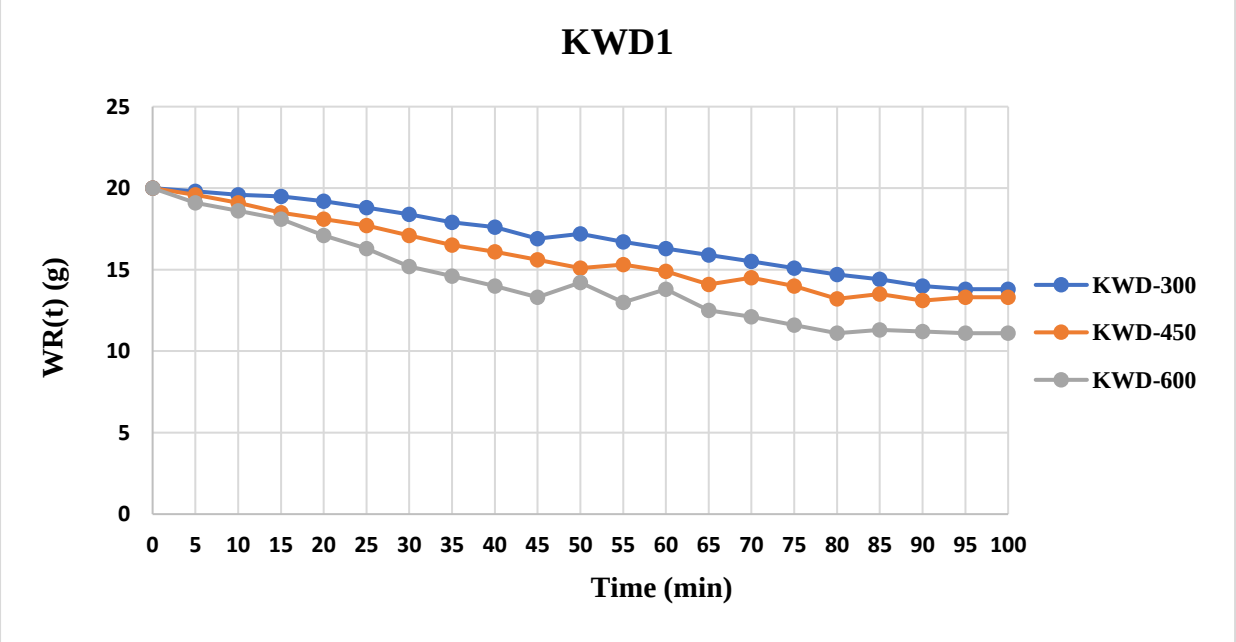
(a)



(b)



(c)

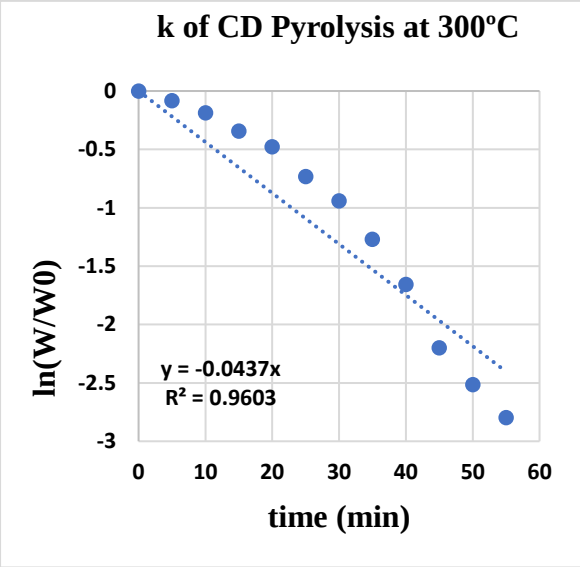


(d)

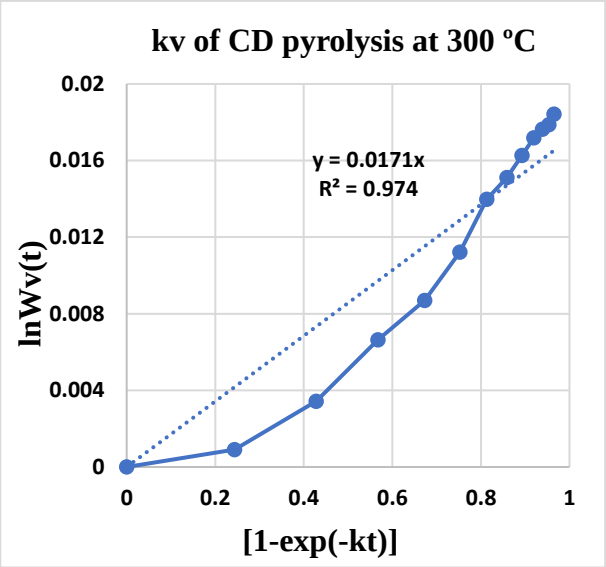
Figure 6.4. Weight residue WR(t) vs Time plots of (a) CD, (b) CDD, (c) KW1, (d) KWD1

As the temperature was increased from 300 to 600 °C, more weight loss was observed.

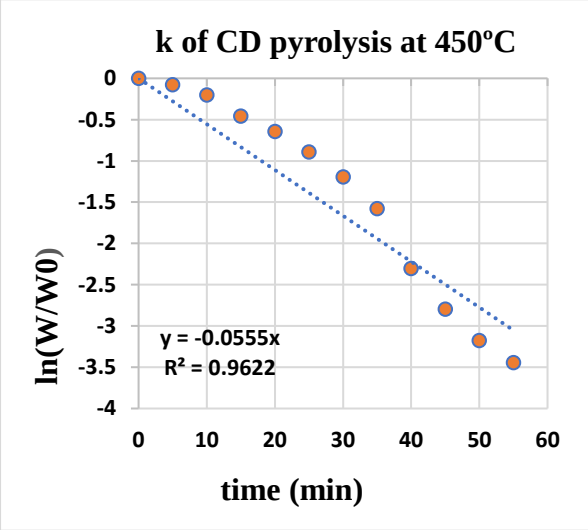
6.5.2. Determination of rate constants (k, k_v and k_c) of feedstocks:



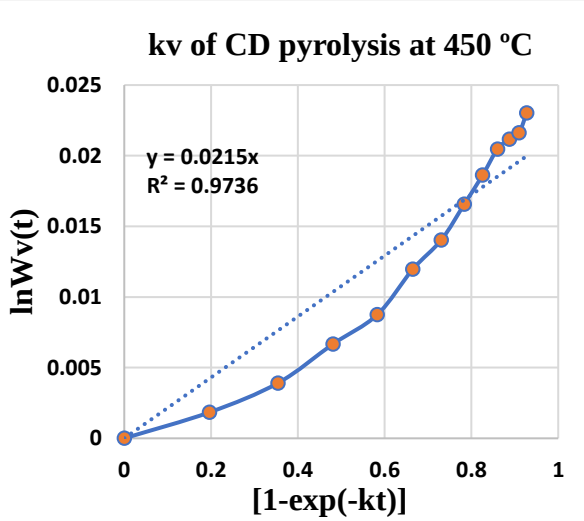
(a)



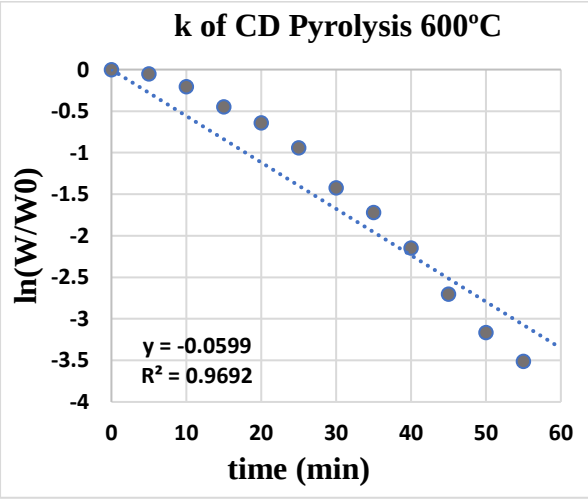
(b)



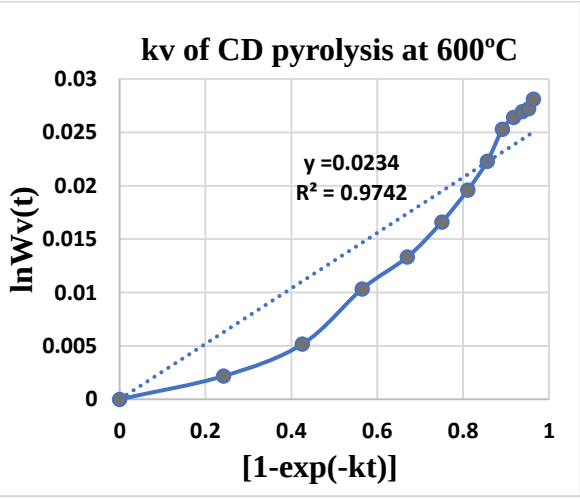
(c)



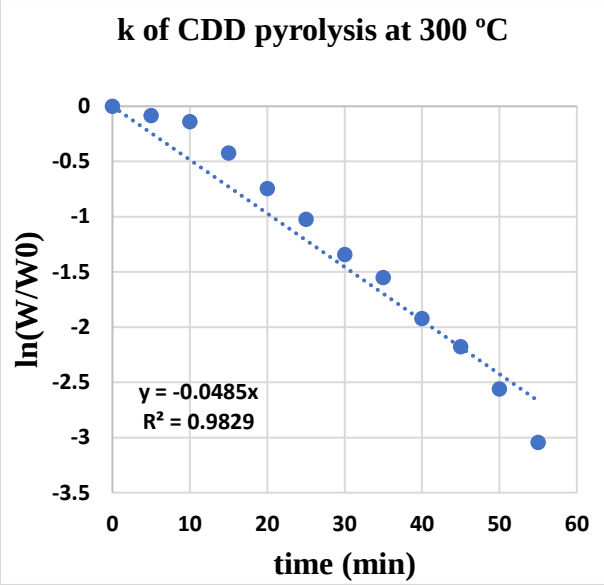
(d)



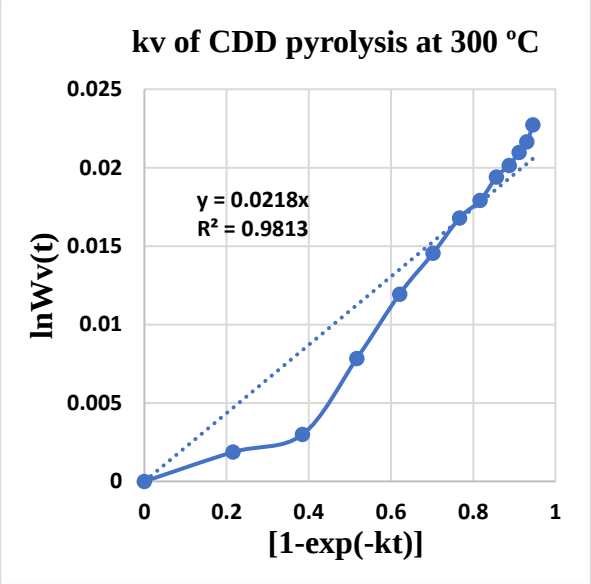
(e)



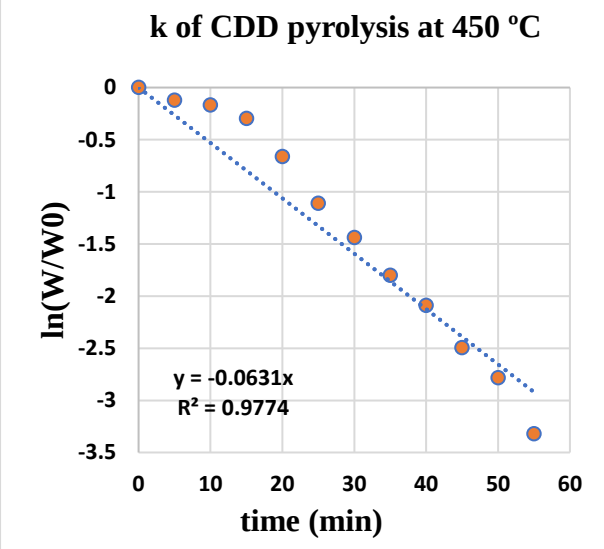
(f)


k of CDD pyrolysis at 300 °C
ln(W/W0)
time (min)
y = -0.0485x
R² = 0.9829

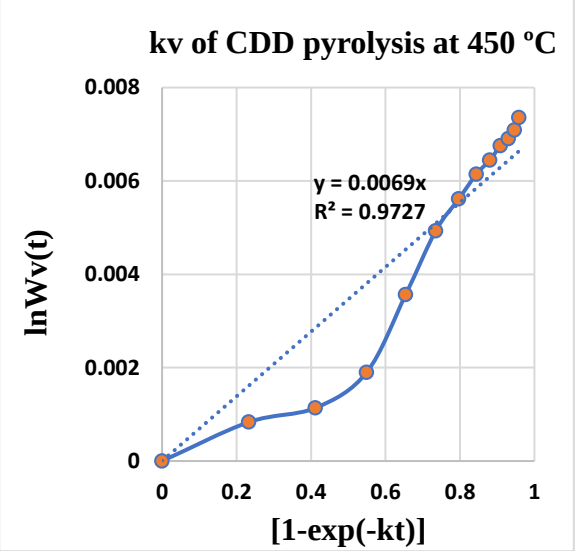
(g)


kv of CDD pyrolysis at 300 °C
lnWv(t)
[1-exp(-kt)]
y = 0.0218x
R² = 0.9813

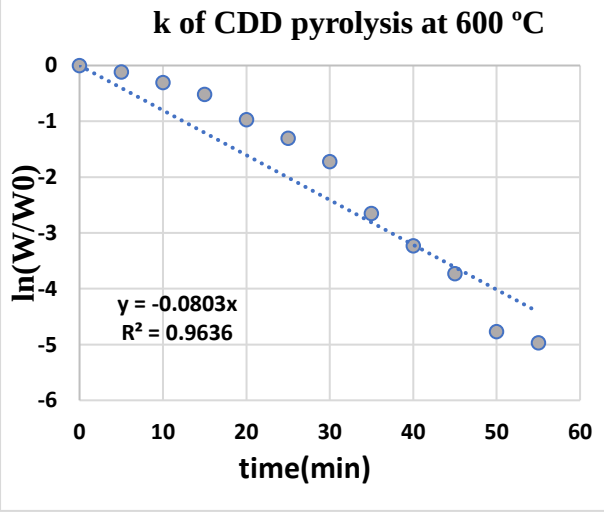
(h)


k of CDD pyrolysis at 450 °C
ln(W/W0)
time (min)
y = -0.0631x
R² = 0.9774

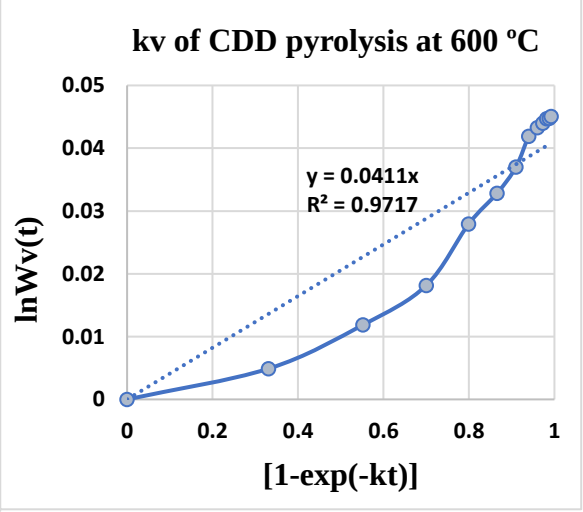
(i)


kv of CDD pyrolysis at 450 °C
lnWv(t)
[1-exp(-kt)]
y = 0.0069x
R² = 0.9727

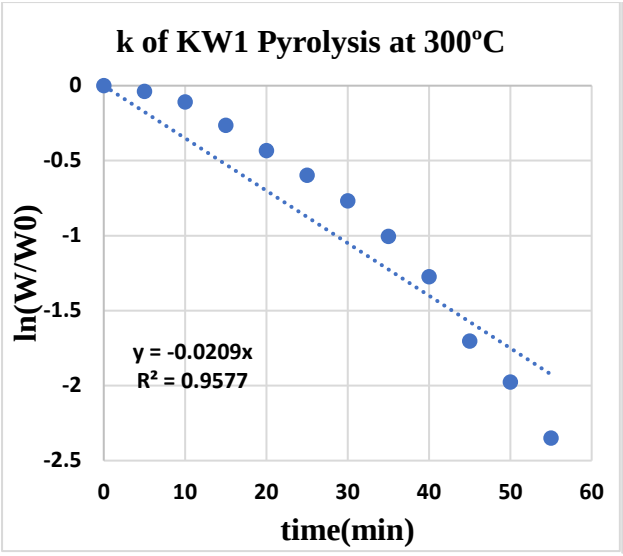
(j)


k of CDD pyrolysis at 600 °C
ln(W/W0)
time(min)
y = -0.0803x
R² = 0.9636

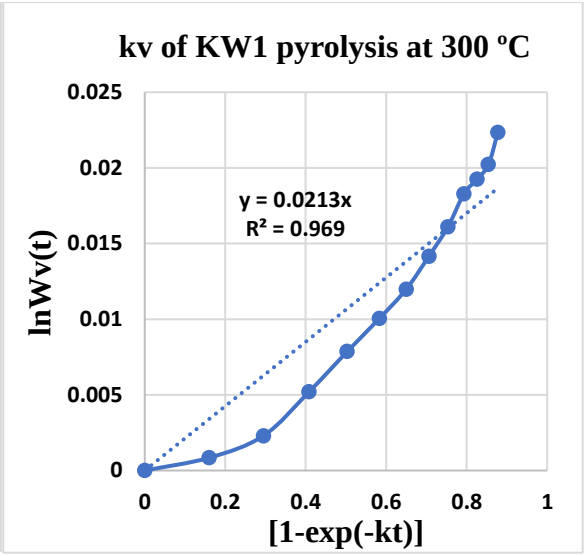
(k)


kv of CDD pyrolysis at 600 °C
lnWv(t)
[1-exp(-kt)]
y = 0.0411x
R² = 0.9717

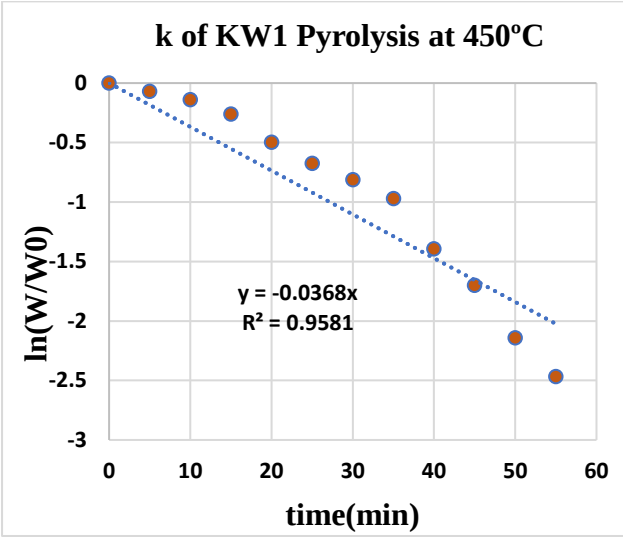
(l)


k of KW1 Pyrolysis at 300°C
ln(W/W0)
time(min)
y = -0.0209x
R² = 0.9577
0
-0.5
-1
-1.5
-2
-2.5
0
10
20
30
40
50
60

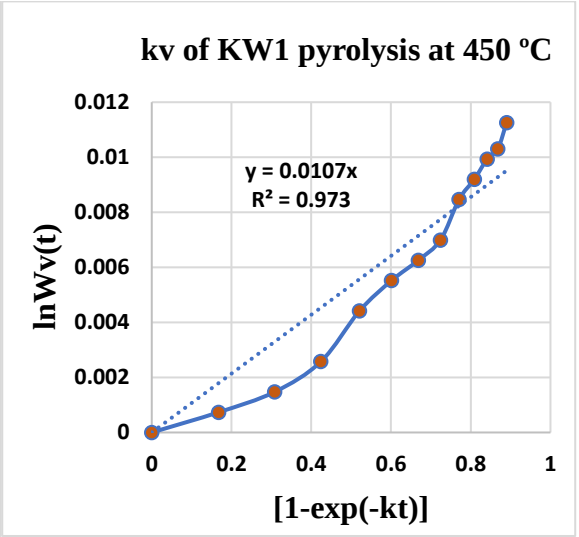
(m)


kv of KW1 pyrolysis at 300 °C
lnWv(t)
[1-exp(-kt)]
y = 0.0213x
R² = 0.969
0.025
0.02
0.015
0.01
0.005
0
0
0.2
0.4
0.6
0.8
1

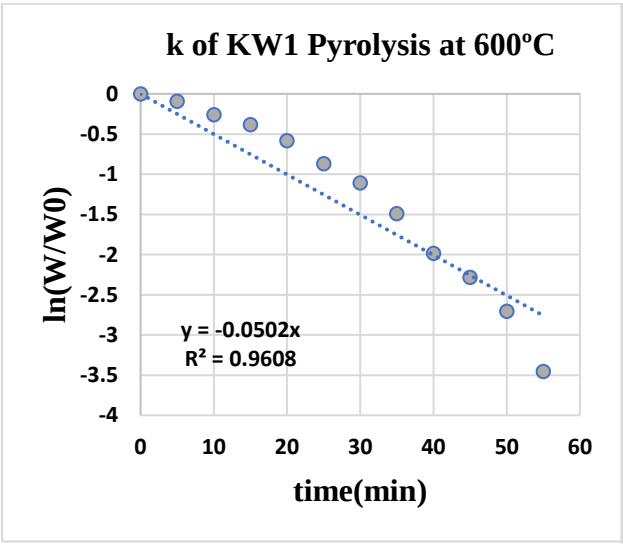
(n)


k of KW1 Pyrolysis at 450°C
ln(W/W0)
time(min)
y = -0.0368x
R² = 0.9581
0
-0.5
-1
-1.5
-2
-2.5
-3
0
10
20
30
40
50
60

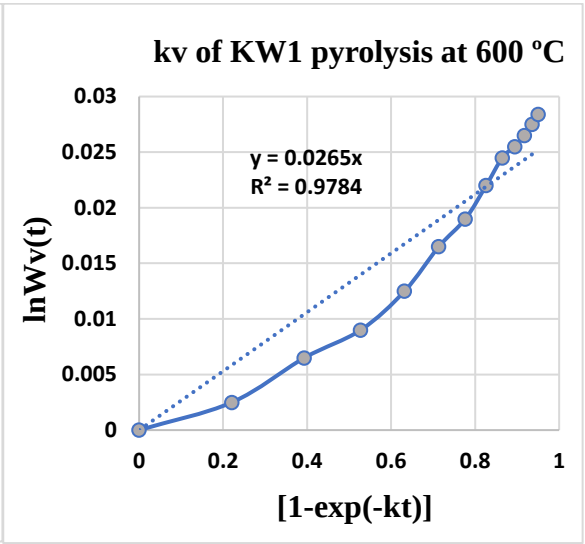
(o)


kv of KW1 pyrolysis at 450 °C
lnWv(t)
[1-exp(-kt)]
y = 0.0107x
R² = 0.973
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.2
0.4
0.6
0.8
1

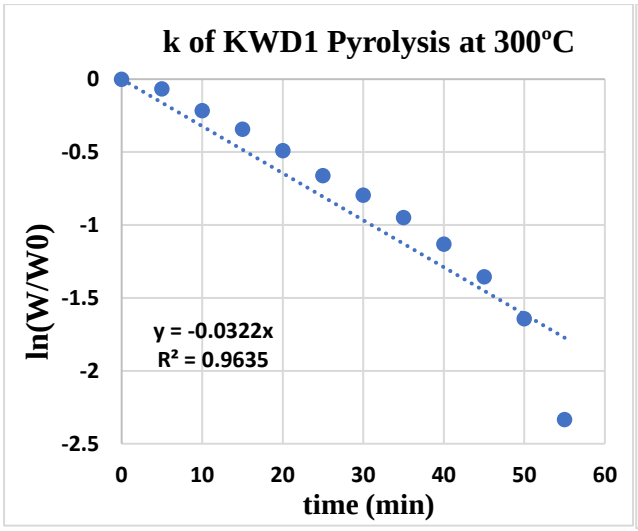
(p)


k of KW1 Pyrolysis at 600°C
ln(W/W0)
time(min)
y = -0.0502x
R² = 0.9608
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
0
10
20
30
40
50
60

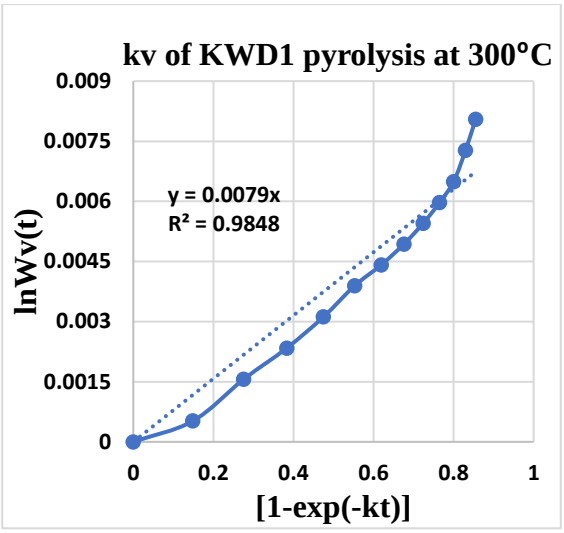
(q)


kv of KW1 pyrolysis at 600 °C
lnWv(t)
[1-exp(-kt)]
y = 0.0265x
R² = 0.9784
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.2
0.4
0.6
0.8
1

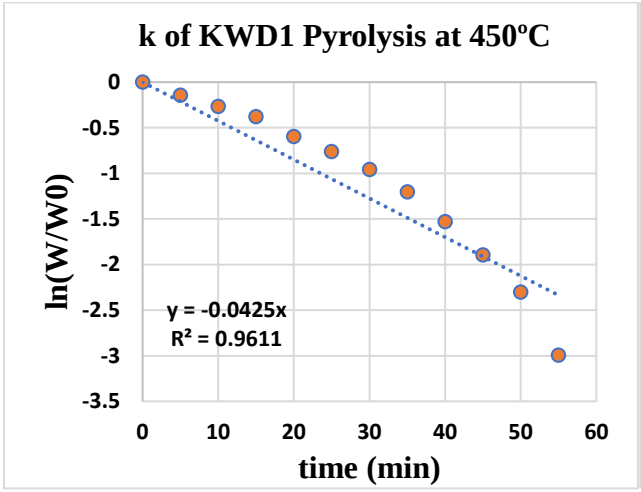
(r)



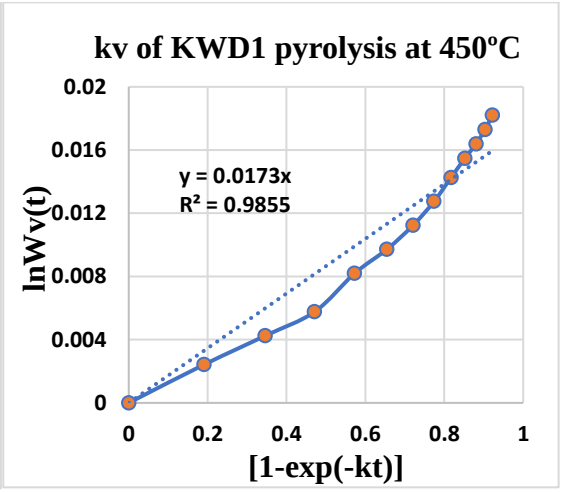
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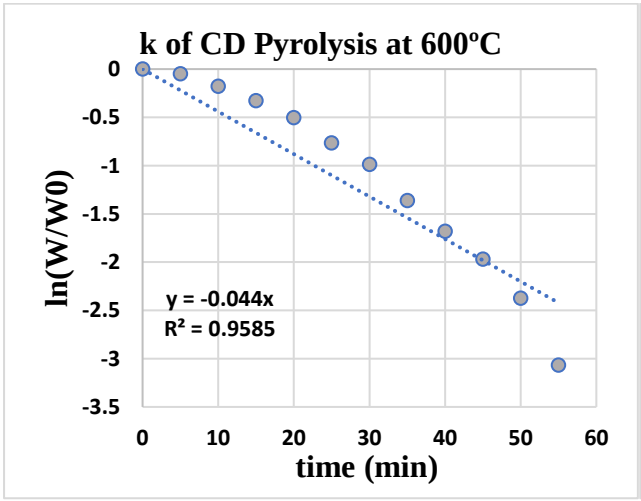
(t)



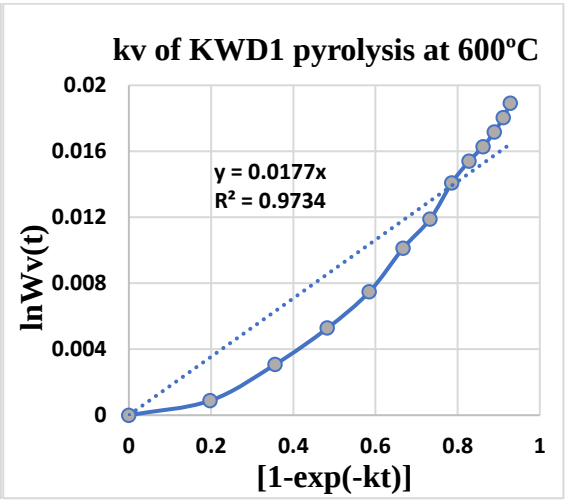
(u)



(v)



(w)



(x)

Figure 6.5. Plot ln(W/W0) vs Time at 300,450 and 600°C0f (a), (c), (e) for CD; (g), (i), (k) for CDD; (m), (o), (q) for KW1;(s), (u), (w) for KWD1. Plot lnWv(t) vs time at 300, 450 and 600°C of (b), (d), (f) for CD; (h), (j), (l) for CDD; (n), (p), (r) for KW1; (t), (v), (x) for KWD1.

To find out the rate constant (k) the data of $\ln(W/W_0)$ was plotted against time for CD, CDD, KW1 and KWD1, the rate constants at 300, 450 and 600°C were determined from the respective slopes of the straight lines (Table 6.9). Similarly, the values of rate constant, k_v were determined at 300, 450 and 600°C by plotting $\ln W_v(t)$ vs [1-exp(-kt)]. The values of k_c at 300, 450 and 600°C were obtained by subtracting the values of k_v from k.

Table 6.9. Values of rate constants

Feed Stocks	Temp (°C)	Rate constants (min^{-1})		
		k	k_v	k_c
CD	300	0.0437	0.0171	0.0266
	450	0.0555	0.0215	0.0340
	600	0.0599	0.0234	0.0365
CDD	300	0.0485	0.0189	0.0296
	450	0.0631	0.0312	0.0319
	600	0.0803	0.0465	0.0338
KW1	300	0.0209	0.0115	0.0094
	450	0.0368	0.0232	0.0136
	600	0.0502	0.0265	0.0237
KWD1	300	0.0322	0.0140	0.0182
	450	0.0423	0.0173	0.0250
	600	0.0440	0.0177	0.0263

6.5.3. Calculation of Activation Energies as per Arrhenius Law:

The primary kinetics of CD, CDD, KW1 and KWD1 is calculated. The rate constants k, kv and kc are plotted in the logarithmic scale against reciprocal of temperature as per the Arrhenius law using the activation energies. All the rate constants are calculated from the experimental results in the temperature range of 573K to 873K and are superimposed with the predicted rate constants

Arrhenius law is $k = k_0 * e^{-\frac{E}{RT}}$

Where k is rate constant, k_0 is the frequency factor, E is the activation energy, R is universal

gas constant, T is the temperature.

Taking ln both side and get $\ln(k) = \ln\ (k_0) - \frac{E}{R} * \frac{1}{T}$

Plot the graph ln(k) vs 1/T and get frequency factor (k_0) from intercept and from slope get activation energy (E)

Similarly, for k_v, k_c by using Arrhenius law get frequency factor and activation energies in different temperature of different feedstocks.

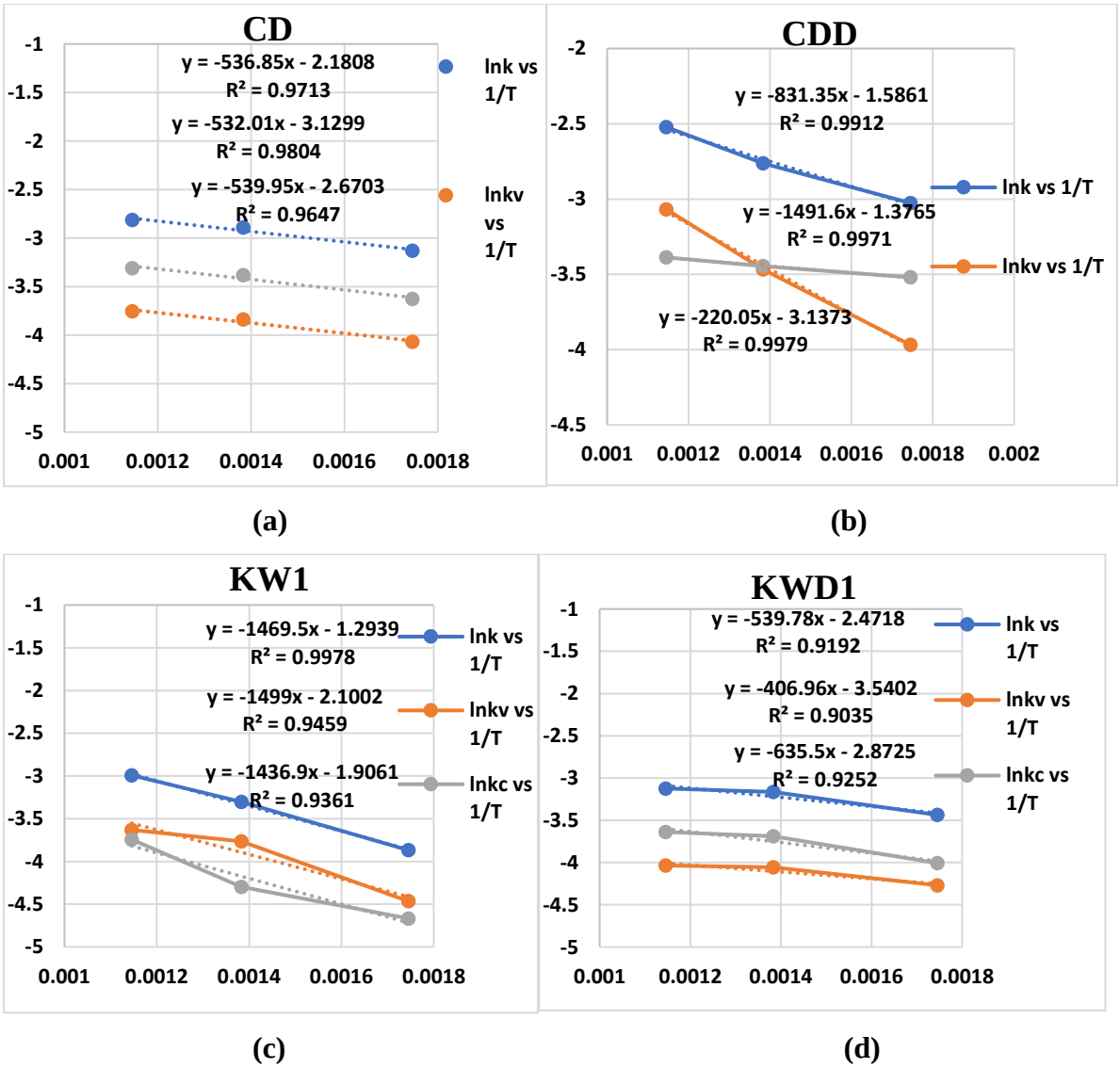


Figure 6.6. lnk vs 1/T, lnkv vs 1/T and lnkc vs 1/T plots of (a) CD, (b) CDD, (c) KW1, (d) KWD1

Table 6.10.

Feedstocks	Reaction rate constants	Frequency factor	Activation Energies (kJ/mol)	R^2 value
CD	k	0.11295	4.46337	0.9713
	k_v	0.043722	4.42313	0.9804
	k_c	0.069231	4.4891	0.9647
CDD	k	0.20472	4.48773	0.9912
	k_v	0.25246	12.4011	0.9971
	k_c	0.0434	1.8294	0.9979
KW1	k	0.2742	12.21	0.9978
	k_v	0.12243	12.4626	0.9459
	k_c	0.14859	11.946	0.9361
KWD1	k	0.08443	4.4877	0.9192
	k_v	0.029	3.3834	0.9035
	k_c	0.05655	5.2835	0.9252

6.6. HTL yields of GRD, KWD1 and CDD

Yields of hydro char, hydro liquid and gas of GRD, KWD1 and CDD was calculated and got better liquid yield for KWD1 was 31%. Gas yields better for CDD of 42%. Maximum char obtained for GRD of 48% yield.

Table 6.11.

Feed Stocks	Process Condition	Yield (%)		
		Hydro Char	Hydro liquid	Hydro Gas
GRD	200 °C, 30 min	48	15	37
KWD1	200 °C, 30 min	44	31	25
CDD	200 °C, 30 min	41	17	42

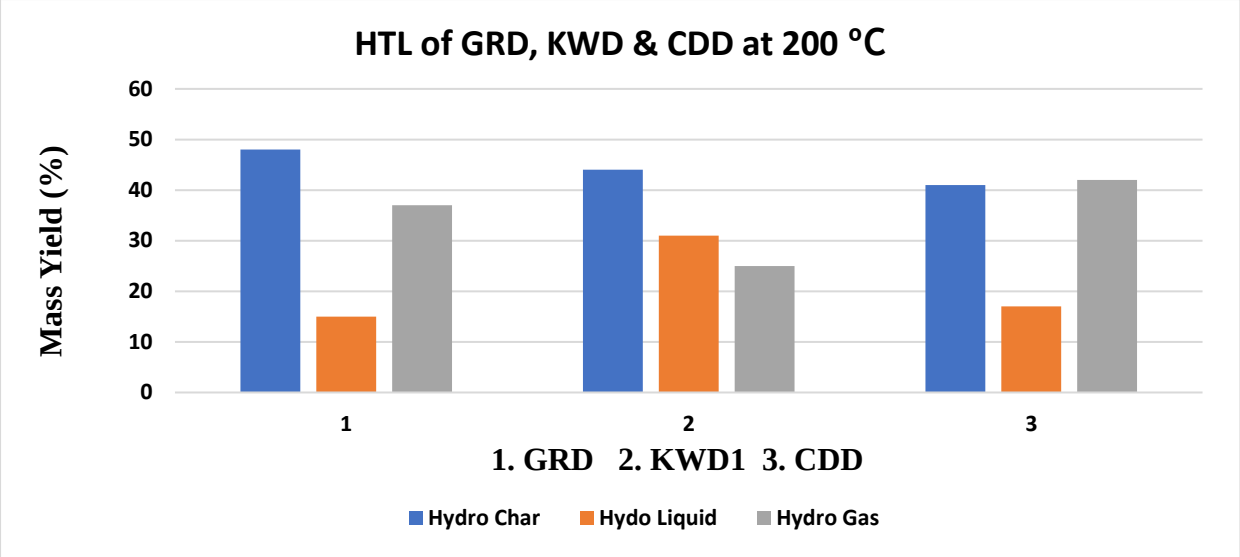


Figure 6.7. Mass yield (%) of different feedstocks at 200ºC (1) GRD, (2) KWD1, (3) CDD1

6.7. Characterization of Pyrochar

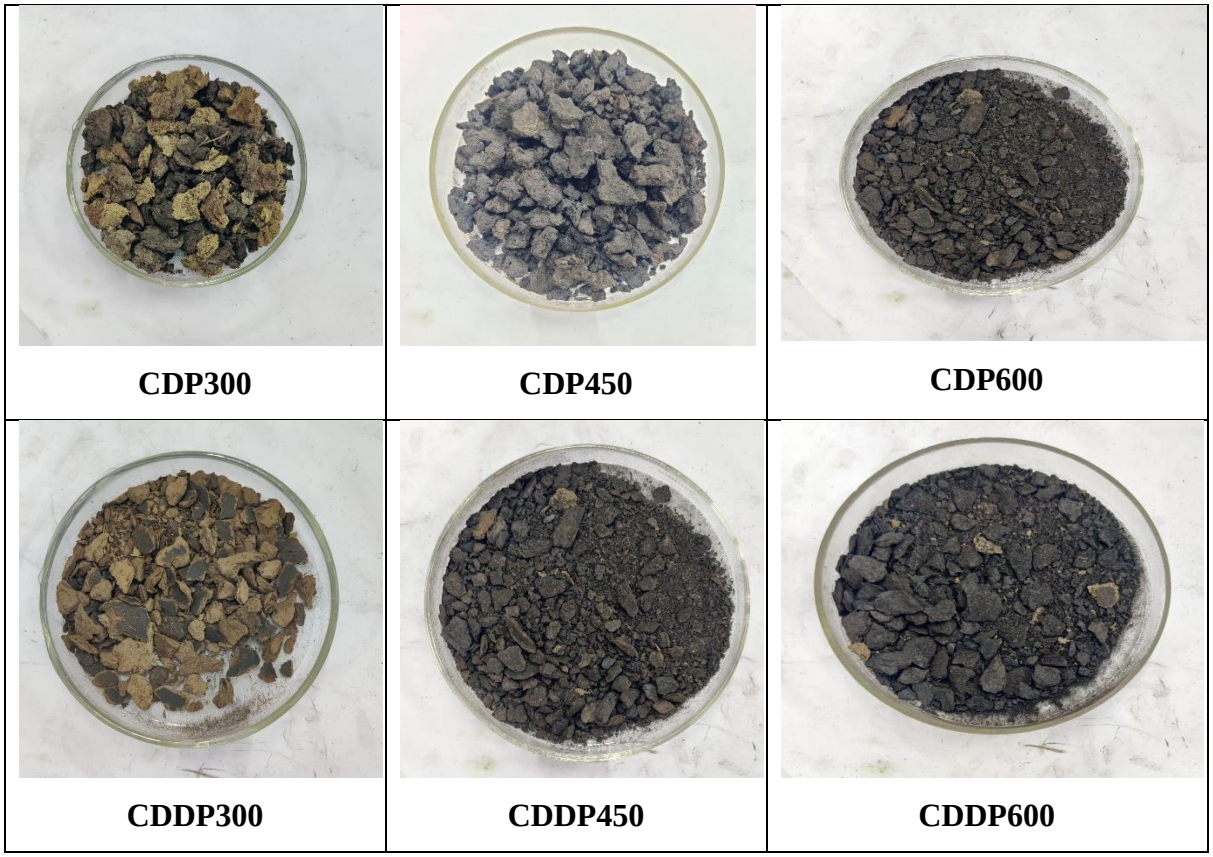


Figure 6.8. Pyrochar at different temperature 300,450 and 600ºC of CD and CDD.

Char quality increased by increasing the temperature from 300 to 600ºC of cow dung and cow dung digestate.

Table 6.12. Ultimate analysis of Pyro char at 300,450 and 600ºC of CD, CDD and Hydro char of CDD.

Feed Stocks	C (mass %)	H (mass %)	N (mass %)	S (mass %)	O (mass %)	H/C	O/C	HHV (MJ/kg)
CDP300	29.98	3.79	1.01	0.158	65.062	0.126418	0.460791	2.79833
CDP450	34.95	2.125	1.22	0.508	61.197	0.060801	0.571106	2.844598
CDP600	38.5	1.974	1.45	0.129	57.947	0.051273	0.6644	4.462429
CDDP300	39.01	4.211	1.81	0.355	54.614	0.107947	0.714286	8.67351
CDDP450	37.14	2.449	1.31	0.123	58.978	0.06594	0.629726	4.489523
CDDP600	38.55	4.536	1.15	0.08	55.684	0.117665	0.692299	8.689563
CDDHC	39.49	5.599	1.74	0.198	52.973	0.141783	0.745474	11.19758

6.7.1 SEM analysis of char

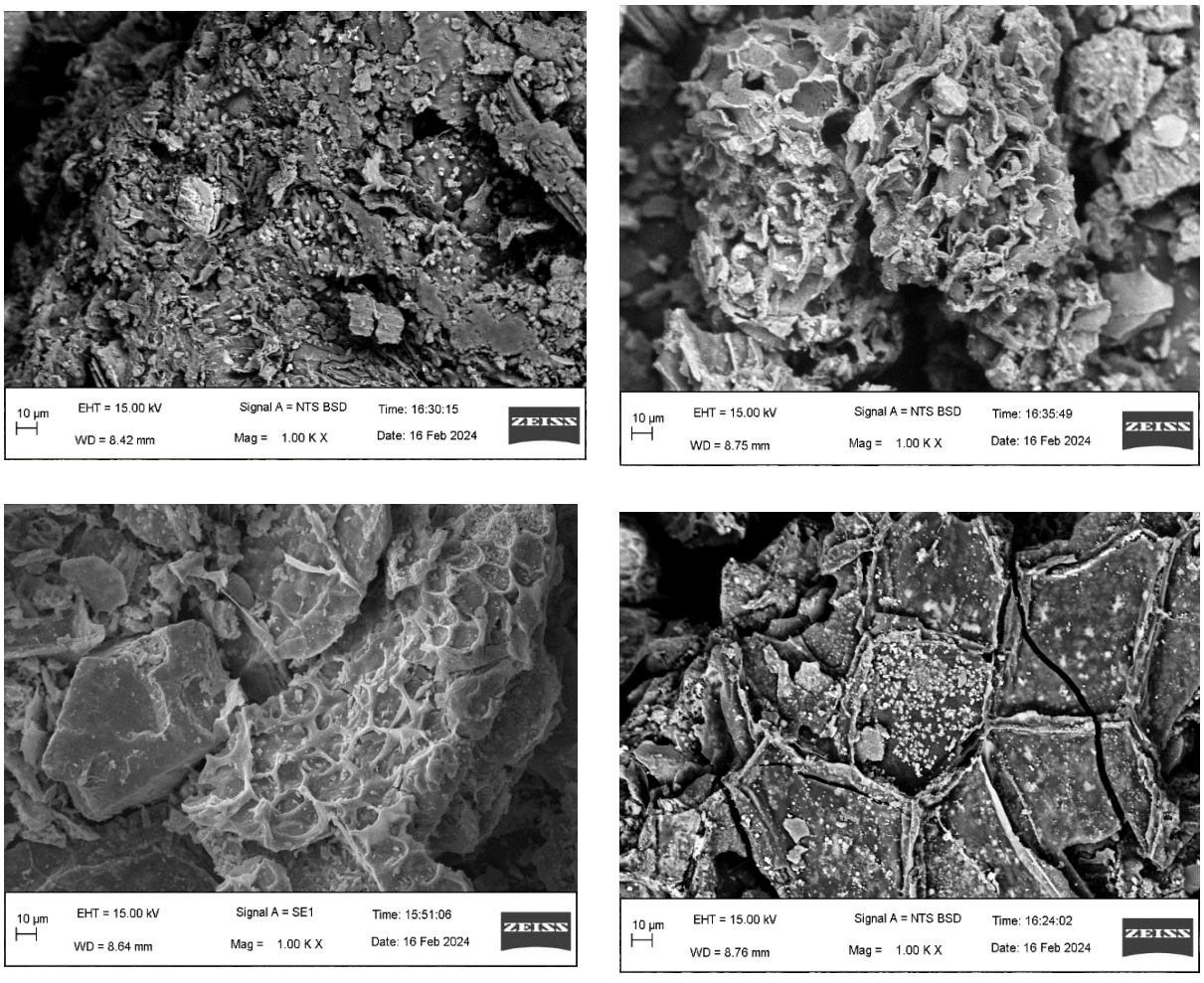


Figure 6.9. SEM images of Hydrochar (top left), Pyrochar at 573K (top left); pyrochar at 723K (bottom left)); pyrochar at 973K (bottom right) derived from KW1.

HTLchar (a) shows porous cracks, PYchar300 (d) shows planer sheet-like structures. PYchar450 (b) and PYchar600 (c) show agglomerated rocky-like structure. The structures have rough textures and are heterogeneous in nature. Melting followed by devolatization and finally vesicle formation can be responsible for the formation of such structures. As temperature gets increased with high heating rate, there is release of various volatile components. Devolylatilization results in morphological changes of bio-char, followed by the formation of high porous surface structure of bio-char samples.

6.8. Characterization of oil

Table 6.13. Ultimate Analysis

Feed Stocks	C (mass %)	H (mass %)	N (mass %)	S (mass %)	O (mass %)	H/C	O/C	HHV (MJ/kg)
GR HTL	59.12	8.2855	1.28	0.3245	30.99	0.1401	0.5241	26.3962
KWP450	65.53	9.777	2.11	0.111	22.472	0.1491	0.3429	32.2335
KWDP450	73.39	9.833	2.30	0.170	14.307	0.1339	0.1949	36.4518

6.8.1. FTIR of Hydro Liquid and Pyro Liquid

Table 6.14. FTIR data of Hydro liquid and Pyro Liquid

Wave No. (cm^{-1})	**Peak's Wave No. (cm^{-1})**	**Group**	**Compound Class**
550-850	806	C-I stretching	Halo compounds
885-895	888	C=C bending	Alkanes
1030-1070	1031	S=O stretching	Sulfoxide
1087-1124	1088	C-O stretching	Aliphatic ether
1200-1270	1224	C-O stretching	Alkyl aryl ether
1310-1390	1361	O-H bending	Phenol
1450	1450	C-H bending	Alkane
1500-1550	1510	N-O stretching	Nitro compound
1626-1662	1662	C=C stretching	Alkene
1705-1725	1705	C=O stretching	Carboxylic acid

1) Peaks represent C-O stretching of ether, O-H bending of phenolic compound, N-O stretching of nitro compounds, C=C stretching of alkene, C=O stretching of aliphatic ketone.
2) No peak for wavenumber higher than 2000 nm, indicating that there is no absorption peak of C–H stretching vibration. The results indicate that the transformer oil comprises saturated carbon components, and does not contain unsaturated carbon components.

6.9. Application of Pyrochar and Hydrochar

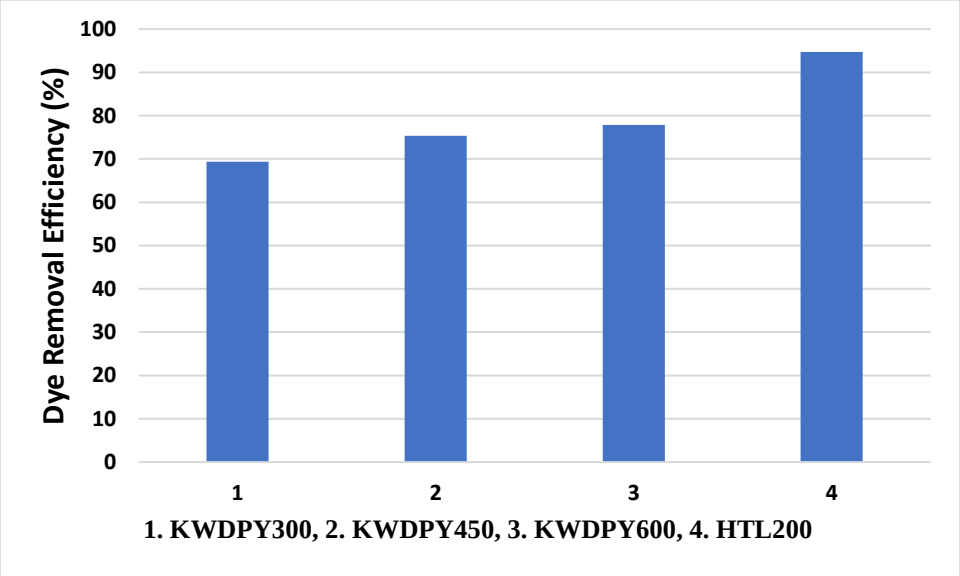
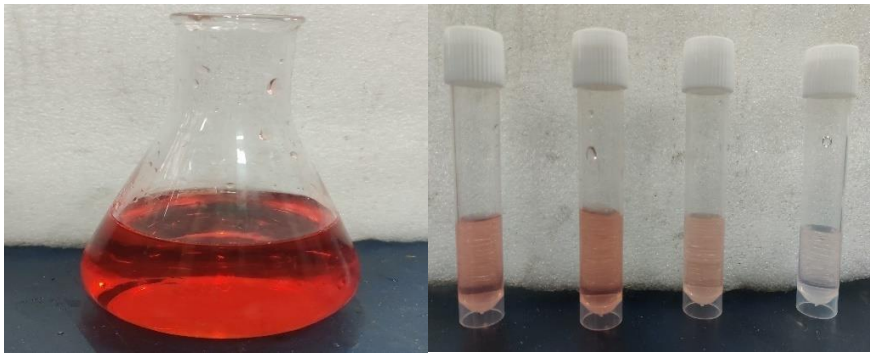


Figure 6.10. Dye removal efficiency of Pyrochar and Hydrochar



(a) **(b)**

Figure 6.11. (a) Congo red dye solution before adding different Pyrochar and Hydrochar, (b) Congo red dye solution after adding different Pyrochar and Hydrochar.

For Congo red dye removal, hydrochar gave better results compared to pyro char.

6.10. Process Modelling in ASPEN PLUS

Moisture, volatile matter, FC and Ash content of Feed were measured experimentally and used as input. Cellulose, hemicellulose and lignin contents were adopted from literature. Lignin and ash content in the biomass were assumed to remain inert during anaerobic digestion reaction. Simulation was run using 0.16667 L/day inflow and 60 days operation time. Total biogas produced was found to be 358.32 mL/gVS, with 53% CH_4 content and 47% CO_2 content. Water was removed from digestate and that data of the dry digestate was used in the feed for Pyrolysis simulation. After validating the simulated result with experimental information, it was assumed that 67% of the biomass was assimilated in AD process and the residual biomass was thermally degraded through pyrolysis at 500°C for 1h residence time. The char, liquid and gas yield were found to be 49.30, 20.86 and 29.84 % respectively and was fitted with the experimental results. This result indicates that further integrated model can be developed using this, and after validating with experiment results found in lab scale, Industrial scale production can also be predicted using ASPEN Plus.

Chapter7

CONCLUSION AND FUTURE SCOPE OF WORK

7.1. Conclusion:

1) Cumulative biogas production (in ml/gVS) of CD, GR, KW1 and KW2 are 172.5, 301.9, 248.6 and 275.6 respectively.

2) Successful mathematical model and process model have been developed.

3) The kinetics for the pyrolysis of CD, CDD, KW1 and KWD1 were determined in the temperature range of300-600ºC. From the kinetic study it is concluded that at each time the weight loss increases with the increase in pyrolysis temperature due to the increase the increase in the rate of pyrolysis.

4) It is observed that the char yield decreases with increase in pyrolysis temperature and gas yield gradually increases with temperature. Maximum yield of pyro-liquid was found at 450°C which is 9.52%, 27%, 19.7% and 25% for Cow Dung, Cow Dung Digestate, Kitchen Waste1andKitchen Waste Digestate1respectively. Maximum yield of char was at 300°C, 67.04%, 86.14%, 69.4% and 75% for cow dung, cow dung digestate, kitchen wate1 and kitchen waste digestate1 respectively. Maximum pyro-gas yield was 47.69%, 39.18%, 46.58 and29.29% for Rice Straw (at 400°C), Jute Stick (at 400°C) and Mustard Straw (at 350°C) respectively. Cow dung digestate gave better oil yield compare to cow dung and also kitchen waste digestate1 gave better performance than kitchen waste1.

5) For hydrothermal liquefaction of grass digestate, cow dung digestate and kitchen waste digestate1 at 200°C liquid yield % was 15%, 17% and 31%. Kitchen waste digestate1 gave better oil yield than others feedstock.

6) AD and pyrolysis of kitchen waste will encourage the concept of circular bioeconomy and reduce carbon footprints.

7) The establishment of integrated system (AD and pyrolysis) will support to create opportunities of better jobs for people. It will also contribute to research and development (R&D) for upgrading the lab-scale studies to pilot and industrial scales.

8) Successful integration of AD and PY will also guide the clean treatment and energy recovery of biomass. The integrated process of anaerobic digestion (AD) and pyrolysis (PY) will eliminate the obstacles of a single AD or PY application.

9) The char, liquid and gas yield were found to be 49.30, 20.86 and 29.84 % respectively, which fitted with the experimental result.Total biogas produced was found to be 358.32 ml/gVS, with 53% CH_4 content and 47% CO_2 content.

10) Application of char for dye removal of congo red hydro char gave better efficiency than pyrovhar.

7.2. Future scope of work:

1. Hydrothermal treatments can play a huge role with respect to digestate valorization, as it requires far less energy compared to pyrolysis, but further studies required.

2. Pyrolysis can convert the whole undegraded lignin part of the digestate. Studies on using energy generated from biogas for pyrolysis can help saving energy of the overall integrated system.

3. Biochar can have several applications. Also, they can be used as additives to AD for process enhancement.

4. Integrated model of PY-AD, AD-PY, AD-HTL, HTL-AD need to be developed.

5. Studies necessary to determine optimize pathways for different feedstocks (both high-moisture and high-lignin containing materials).

6. Further life cycle assessment and technoeconomic assessment need to investigated for industrial scale implementation of the integrated process.

APPENDIX

Nomenclature:

AD	Anaerobic digestion	k	Rate constant (min^{-1})
CELL	Cellulose	kc	Rate constant of char (min^{-1})
CELLA	Cellulose acetate	k_v	Rate constant of volatile (min^{-1})
CD	Cow dung	K_S	Half-velocity constant
CD300	Cow dung at temperature 300ºC	KW1	Kitchen waste1 (summer collection)
CD450	Cow dung at temperature 450ºC	KW2	Kitchen waste2 (winter collection)
CD600	Cow dung at temperature 600ºC	KWD1	Kitchen waste digestate1(summer collection)
CDD	Cow dung digestate	KWD2	Kitchen waste digestate2 (winter collection)
CDD300	Cow dung digestate at temperature 300ºC	LD	Liquid digestate
CDD450	Cow dung digestate at temperature 600ºC	LIG	Lignin
CDD600	Cow dung digestate at temperature 600ºC	LIG-C	Lignin-C
CDDHTL200	Cow dung digestate hydrothermal liquefaction at 200ºC	LIG-H	Lignin-H
CDP300	Cow dung pyrochar at 300ºC	LIG-OH	Lignin-OH
CDP450	Cow dung pyrochar at 450ºC	Ln	Logarithm (natural log)
CDP600	Cow dung pyrochar at 600ºC	LVG	Levoglucosan
CDDP300	Cow dung digestate pyrochar at 300ºC	min	Minute
CDDP450	Cow dung digestate pyrochar at 450ºC	NRTL	Non-random two liquid
CDDP600	Cow dung digestate pyrochar at 600ºC	PID	Process instrumentation diagram
CR	Congo red	Py	Pyrolysis
$C_{reac,i}$	Concentration of reactant i	PY	Pyrolysis
ºC	degree Celsius	PY300	Pyrolysis at temperature 300ºC
E	Activation energy (KJ/mol)	PY450	Pyrolysis at temperature 450°C
$E_{a,sub,i}$	Activation energy of substrate i	PY600	Cow dung at temperature 600°C
FC	Fixed carbon	pH_{LL}	pH lower limit
FS	Feedstocks	pH_{UL}	pH upper limit
FTIR	Fourier transform infrared spectroscopy	reac,i	Reactant i
GR	Grass	R	Universal gas constant (KJ/mol-K)
GRD	Grass digestate	S	Substrate concentration
GRDHTL200	Grass hydrothermal liquefaction at 200ºC	SEM	Scanning electron microscope
HAA	Hydroxy-acetaldehyde	TBMP	Theoretical biomethane pdt

HC	Hydrochar	T	Temperature (in K)
HCE	Hemicellulose	t	Time
HHV	Higher heating value	TS	Total solid
HMFU	5-hydroxymethyl-furfural	UA	Ultimate analysis
HTL	Hydrothermal liquefaction	VS	Volatile solid
HTL200	Hydrothermal liquefaction at 200ºC	Wc(t)	Weight of char at any time during pyrolysis (g)
HTC	Hydrothermal carbonization	W(t)	Weight of the solid reactant at any time during pyrolysis (g)
$k_{react,i}$	Rate constant of reactant i	Wv(t)	Weight of volatile at any time during pyrolysis (g)
$k_{sub,o}$	Pre-exponential factor of substrate	μ	Growth rate of microorganism and
k_0	Frequency factor	μ_{max}	Maximum growth rate of microorganism

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