Studies on Catalytic Pyrolysis of Raw Lignocellulosic Waste and Non-catalytic Pyrolysis of Bio-decarboxylated Lignocellulosic Waste

Thesis

Submitted By

Shalini Das

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[Class Roll No. 001410302002]

[Reg. No. 128878 of 2014-2015]

Under the Guidance of ***Prof. (Dr.) Ranjana Chowdhury***

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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 2014-2016**.** All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are fully authentic to this work.

Name: Shalini Das

Examination Roll Number: **M4CHE1602**

Thesis Title: ***Studies on Catalytic Pyrolysis of Raw Lignocellulosic Waste and Non-catalytic Pyrolysis of Bio-decarboxylated Lignocellulosic Waste.***

Signature:

Date:

CERTIFICATE

*This is to certify that the thesis entitled "***Studies on Catalytic Pyrolysis of Raw Lignocellulosic Waste and Non-catalytic Pyrolysis of Bio-decarboxylated Lignocellulosic Waste***" has been carried out by Shalini Das in partial fulfilment of the requirements for the degree 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 other university for the award of any degree or diploma.*

Prof. (Dr.) Chandan Guha
Head of Department and Professor,
Chemical Engineering Department
Jadavpur University.

Prof (Dr.) Ranjana Chowdhury
Project Supervisor,
Professor& former Head,
Chemical Engineering Department
Jadavpur University.

Prof. Sivaji Bandyopadhyay
Dean of Faculty and Engineering
Technology
Jadavpur University.

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Shalini Das
Department of Chemical Engineering
Jadavpur University

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ABSTRACT

Under the present investigation, pyrolysis of locally collected waste banana pseudo-stem has been conducted in the temperature range of 673K to 1173K in a semi-batch pyrolyzer. The effects of pyrolysis temperature on product yields have been studied in detail. The effects of using different catalysts namely, alumina, zinc oxide, sodiumaluminosilicate, potassium chloride and sodium chloride, on the product yield and de-oxygenation of pyro-oil have also been investigated. The weight loss history of the banana stem (by both conventional process and thermogravimetric analysis) and the lumped kinetics for the pyrolysis of untreated and catalytically treated banana stem have been determined in the pyrolysis temperature range and it has been found that the experimental results are according to the predictions of Arrhenius law.

The prediction of dynamic trends of unreacted banana stem, volatiles and char using lumped kinetics haven been determined under the present study and the multi-component lumped kinetics using kinetic parameters of cellulose, hemicellulose and lignin available in the literature have been compared.

KCl has been observed to be the best among all catalysts with respect to both the yield and quality of pyro-oil. A suitable strain of microorganism, Baker's yeast (*S. cerevisiae*) has been selected for bio-decarboxylation of raw banana stem. The effect of bio-decarboxylation time on the characteristics of chemical bonds in banana stem and on the yield of pyro-oil has been studied using FTIR spectroscopy. From the FTIR analysis it has been observed that bio-decarboxylation of banana stem took place during its treatment with Baker's yeast and the concentration of carboxylic acid decreased with the increase in incubation time of banana stem with yeast. The optimum condition for the maximum pyro-oil yield from the pyrolysis of yeast treated banana stem has been observed to be 48h incubation time at an incubation temperature of 37ºC. From CHN analysis it has been observed that the oxygen content of the pyro-oil obtained from pyrolysis of yeast treated banana stem was lowest (54.57 wt%)compared to that of the pyro-oil obtained from untreated and KCl treated banana stem (66.63 wt%) , thus improving the quality and stability of the pyro oil, the most.

Chapter 1

INTRODUCTION

1.1 Energy Crisis

Burgeoning advancement of global climate change induced by the emission of noxious green house gases (GHGs) from the excessive fossil fuel usage as the primary energy source has already striked the alarming limits. Energy is the fundamental building block for the continuous progress of the society and industrial civilisation. Rapid energy consumption is based on the fossil fuel and other types of fuels. In the recent decade, there has been a rapid increase in the energy demand worldwide. This necessitated a paradigm shift towards the development and potential utilisation of environmentally benign sources of renewable fuels. Renewable sources of fuel are also known as alternative energy sources or non-conventional sources of energy. Alternative energy is defined as that kind of energy which does not utilise fossil fuel. The alternative energies are eco-friendly causing negligible pollution.

1.2 WTE (Waste to Energy) Conversion

Waste to energy (WTE) conversion has gained considerable importance globally as a feasible solution to multiple associated issues including;

1) The growing demand for alternative and renewable energy resources

2) Reduction of the extreme reliance on the fossil fuels

3) Eventual reduction of GHG emission and

4) Efficient abatement of environmental pollution.

Transportation sector is the chief consumer of liquid fossil fuel resources and consequent GHG emission worldwide. Therefore, this sector is a prime target of the scientific communities worldwide to look for the alternative options of renewable liquid fuels and its efficient application in an eco-friendly way. Utilisation of an abundantly available renewable resource for the generation of the liquid fuels can only make this whole concept a sustainable one. In this regard, lignocellulosic biomass is the most suitable option as potential feedstock for both bio-chemical and thermo-chemical WTE processes.

The technologies used for conversion of biomass to energy are:

1) Biological/biochemical :
    a) Fermentation
    b) Anaerobic digestion

2) Thermochemical :
    a) Gasification
    b) Liquefaction
    c) Pyrolysis

1.2.1 Fermentation:

Fermentation is a microbial metabolic process that converts simple sugars to acids, gases or alcohol. Yeast and bacteria are the most commonly used microbes for industrial fermentations. Fermentation is also used to produce a specific chemical product utilizing the bulk growth of microorganisms on a growth medium. Fermentation takes place in the lack of oxygen and by this process energy production of the cell takes place.

1.2.2 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.

1.2.3 Gasification:

Gasification is a process for conversion of fossil fuel into various gases like carbon monoxide, carbon dioxide and hydrogen. The reaction temperature is high, and it takes place without combustion. The valuable gaseous product is called syngas which is used as a fuel. The energy generated by this process is considered to be a potential source of renewable energy.

The advantage of gasification is that using the syngas is a more effective process than that of direct combustion of the fuel. The raw material for the process of gasification is lignocellulosic waste which is degradable and easily available at minimum cost. Syngas can be directly combusted to produce methanol and hydrogen. Gasification being a high-temperature process helps in purification of the gas by the removal of corrosive materials like potassium and chloride. The process of gasification has found wide application in the industries for electricity generation.

1.2.4 Liquefaction:

Liquefaction of gases is a process for physical conversion of a gas into a liquid (condensation).The process is used for scientific, industrial and commercial purposes. Liquefaction is used for the analysis of the fundamental properties of gas molecules like intermolecular force, for gas storage (LPG) and in refrigeration and air conditioning. In this technology the gas is liquefied in the condenser releasing the heat of vaporization and then gets evaporated in the evaporator. The liquefaction of gases uses compression and expansion to obtain high pressure and low temperature. Ammonia is widely used as an industrial refrigerant, but nowadays, it is mostly replaced by other compounds derived from petroleum and halogens.

1.2.5 Pyrolysis:

Pyrolysis is a thermochemical decomposition of organic material at high temperature in the absence of oxygen or any halogen. It is an irreversible process and it involves both change of chemical composition and physical phase. Pyrolysis has been derived from the Greek words: pyro meaning "fire" and lysis meaning "separating". Pyrolysis of lignocellulosic wastes produces gaseous and liquid products leaving a solid residue behind, rich in carbon content named as char.

Fig 2.1.Pyro- Char

Fig 2.2.Pyro-Oil

Fig 2.3.Pyro-Gas

1.2.5.1 Industrial applications of pyrolysis:

1. The process is used in the industries for the production of renewable energy (pyro-oil) from lignocellulosic biomass.
2. The biomass gets converted to syngas and biochar.
3. The biochar is used to increase the fertility of soil.
4. In the chemical industries pyrolysis is widely used for the production of charcoal, activated carbon, methanol and coke from coal.
5. The process is used for conversion of ethylene dichloride into vinyl chloride for the manufacture of PVC.
6. To convert the waste into eco-friendly disposable substances.
7. Pyrolysis is also used in the manufacturing of nanoparticles.
8. It is used as a tool for chemical analysis.
9. It also plays a prominent role in baking and grilling.

1.2.5.2 Advantages of pyrolysis:

1) Pyrolysis produces a value-added marketable product (electricity).
2) Reduces greenhouse gas emissions and enhances the disposal of waste.
3) Minimises the risk of health hazards.
4) Lowers odour and water pollution.
5) The process is flexible.
6) Yields of different products may be modified by just changing the temperature of pyrolysis. Generally at low temperature (300-500ºC) we obtain high yield of solid, at medium range (500-800ºC) the liquid yield is more and at temperature (>800ºC) gasification takes place the most.

1.2.5.3 Disadvantages of pyrolysis:

1) High oxygen content of pyro-oil.

2) Its tendency for polymerization affecting the properties of oil.

3) Causes difficulty to handle the mixed feed by the process of pyrolysis.

4) Pyrolysis is an evolving technology till date.

Among all these conversion processes described above, pyrolysis is considered to be one of the most promising technologies for liquid oil production, with solid char and gases as valuable by-products.

On a comparative note, presently, thermo-chemical WTE processes like pyrolysis and gasification are considered better than the bio-chemical processes like fermentation and anaerobic digestion for efficient conversion of recalcitrant lignocellulosic materials at a much faster rate.

1.2.5.4 Societal Impacts of Pyrolysis:

1. This technology provides jobs and opportunities for skilled people.
2. Effective way of waste cleanup benefitting the society as well as public health.
3. Enhances the use of local feedstocks.
4. Provides power and fuels.
5. Also provides charcoal to enhance the fertility of soil enriching its organic matter.

Pyrolysis converts the raw waste into energy rich fuels by heating the bio-waste under controlled conditions. Pyrolysis involves heating of waste materials to high temperatures (between 300ºC and 900ºC) in the absence of oxygen producing liquid pyro-oil as the main product and solid pyro-char and pyro-gas as the by-products.

The pyro-gas can be used as a fuel to generate electricity. The pyro-liquid can be used as a fuel for automobiles, feedstock for gasification and feedstock for valuable chemicals.The pyro-char can be used as an adsorbent or as a nutrient additive to improve soils.

1.3 Catalytic pyrolysis:

Catalytic pyrolysis is a process through which deoxygenation reaction occurs through simultaneous dehydration and decarboxylation in the presence of suitable catalysts. It is one of the most effective thermochemical conversion techniques for lignocellulosic waste which generates fuel that caters to the increasing energy demand worldwide over the past few years. The selection of a suitable catalyst and process conditions play an important role in determining the overall outcome of a catalytic pyrolysis process. The main objective of catalytic pyrolysis is to reduce the oxygen content of the oil in order to increase the quality of the pyro-oil. The small schematic of the catalytic pyrolysis is shown below.

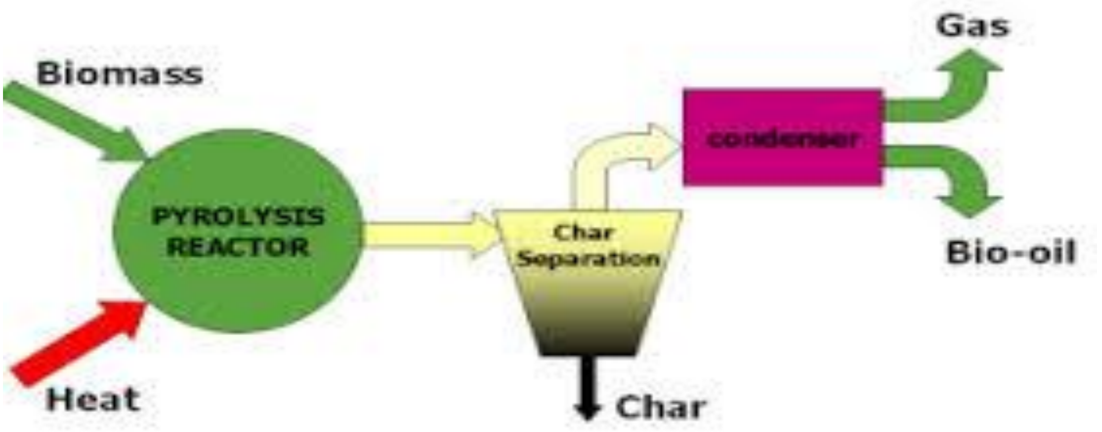


Fig 2.4: Schematic of catalytic pyrolysis

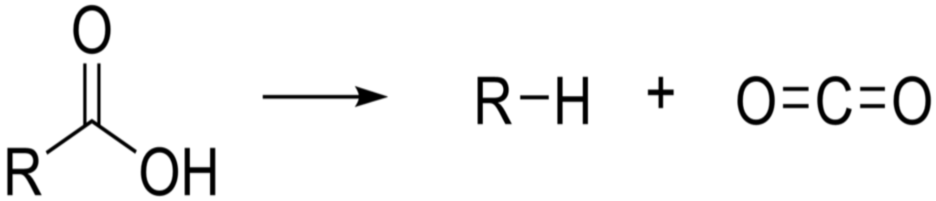
1.3.1 Advantages of catalytic pyrolysis:

1. This process can be applied for lessening the adverse physical and chemical properties of bio-oil.
2. Catalytic fast pyrolysis is a more effective process for oxygen removal from the bio-oil in the form of water and results in lower yields of the organic fraction.

3. In catalytic pyrolysis, the chemical characteristics of the bio-oil is shifted from its polar composition towards the characteristics of petroleum-derived fuels.
4. Catalytic pyrolysis reduces the operating cost while used for atmospheric processing.
5. The temperature maintained for this process is similar to those used in the production of bio-oil.

1.4 Decarboxylation:

Decarboxylation is a chemical reaction that removes a carboxyl group (-COOH), replaces it with a proton and releases carbon dioxide (CO_2). The chemical reaction by which a carbon atom, in the form of carbon dioxide, detaches itself from an organic molecule is called a decarboxylation reaction. It refers to the reaction of carboxylic acids, displacing a carbon atom from a carbon chain. Enzymes catalyzing decarboxylation reaction are known as decarboxylases. For decarboxylation to take place in chemical route, heating is required because the reaction is less favourable at low temperatures and yields are highly sensitive to the operating conditions.



Equation 1: Equation demonstrating decarboxylation process

However, there are many microorganisms that can also decarboxylate compounds through their metabolic pathways. Biochemical decarboxylation does not require severe temperature condition and hence the energy is saved.

1.4.1 Pretreatment of pyrolysis feedstock through biodecarboxylation:

One of the main drawbacks of pyro-oil generated through pyrolysis of lignocellulosics is the high oxygen content. If the lignocellulosic biomass is pre-treated through decarboxylation, the oxygen content of biomass itself is reduced due to the removal of oxygen rich carboxylic group. As a consequence the oxygen content of pyro-oil generated from the pyrolysis of decarboxylated biomass is expected to decrease.

1.5 Selection of feedstock:

India is the largest producer of bananas in the world. India produces huge amount of bananas but along with that a lot of lignocellulosic wastes are generated which poses a disposal threat to the society. Out of all the different parts of bananas the pseudo-stem accounts for the highest amount of generated wastes. This rejected bio-waste is used to feed the cattle and also as soil fertilizer. Since they are being generated in such a large quantity, their availability is in huge abundance at a nominal market price. These lignocellulosic wastes are rich in carbon content and can be utilized as an alternative energy source by “Waste to Energy Conversion” techniques. Since there is no commercial use for these bio-wastes they are available in the market at minimal price. For all these reasons, waste banana pseudo-stem has been selected as the raw-material for pyrolysis.

Chapter 2

LITERATURE SURVEY

An extensive literature review was carried out covering the areas of catalytic pyrolysis and decarboxylation of biomass.

Sr. No.	Name of author and year of publication	Description of the Study
1.	**K. Kyaw and C. Hmwe (*2015*)**	They studied the effect of various catalysts on fuel oil pyrolysis process of mixed plastic wastes. The pyrolysis of plastic wastes was carried out in a fixed bed reactor in the temperature range of 305K to 653K. The catalysts used were Shwedaung clay, Mabisan clay, Bentonite clay, Dolomite and synthetic catalyst, zinc oxide. The highest yield of pyro-oil (67.06%) was obtained from the plastic waste pyrolysis by using Mabisan clay within the temperature range of 493K to 643K for 90 mins. They concluded that natural catalysts should be used as they possess good cracking efficiency and they analyzed the pyrolysis fuels by FTIR.
2.	**Romeroa et al. (*2015*)**	They presented a preliminary experimental study on biofuel production by deoxygenation of Jatropha oil. The feedstock used in the study was Jatropha. The catalysts used for the catalytic pyrolysis of the feedstock were alumina and hydrotalcite. An inert atmosphere was maintained inside the pyrolyzer reactor throughout the experiment with the help of nitrogen. The catalytic pyrolysis was conducted at 350 and 400°C. Deoxygenation of the liquid pyro-oil through decarboxylation of feedstock was accomplished. The liquid product yield obtained after

		pyrolysis was quite high. After analysing the pyro-oil using FTIR spectroscopy, the results showed that the oxygen content of the pyro-oil decreased significantly. The quality of the pyro-oil obtained from the pyrolysis of feedstock with hydrotalcite for a reaction time of 6 h was more effective than that obtained with alumina. The liquid bio-fuel was found to contain high proportion of hydrocarbons (around 83%). The main product ie. the pyro-oil showed very good heating value (around 44 MJ/kg) and a lower viscosity compared to the other one. The gases, carbon dioxide and carbon monoxide were identified as the principal compounds in the product pyro-gas using Gas Chromatography analysis (GC). The analysis validated the fact that oxygen was removed mainly through decarboxylation reaction.
3.	**Aramideh et al. (*2015*)**	They presented a study on the numerical simulation of biomass fast pyrolysis in an auger reactor. A multistep pyrolysis reaction mechanism was proposed by the researcher to study the degradation of the different components (cellulose, hemicellulose and lignin) of lignocellulosic feedstock. The instantaneous degradation of the components of the lignocellulosic material from virgin to active biomass was studied. They also studied the trends of the formation of the products namely tar, char and syngas. The fast pyrolysis process was conducted in a fluidized bed reactor. Computational fluid dynamics (CFD) simulation of the fast pyrolysis of feedstock was carried out and the average residence time of the reactants in the reactor was obtained. A rotating frame was taken as reference to develop a model for the auger reactor. It was observed that the residence time of the feedstock inside the reactor played an important factor in the product yields. A parametric study was also conducted to obtain the optimum operating conditions for the maximum tar production. The predicted product yields matched well with the experimental results. It was also concluded from the modelling that higher nitrogen inlet rate favoured the tar production. On the other hand, if the biomass feed rate was higher, then the amount of unreacted biomass was more, thus reducing the yield of tar.

4.	**Sarkar et al. (*2014*)**	They presented a review on Mathematical Modeling of a Semibatch Pyrolyser for Sesame Oil Cake. They studied the kinetics parameters for the decomposition of solid reactant along with the formation of the by-products (volatiles and char) with the help of a lumped parameter model under isothermal conditions varying the temperature between 673K and 1173K. They also determined the pyrolysis kinetics under non-isothermal conditions using the Distributed Activation Energy Model (DAEM). They also determined the activation energy and frequency factors using TGA analysis of the sesame oil cake at different heating rates (5-25K/min). The model equations was solved numerically and validated by comparing the simulated and experimental data of the exit concentration of the pyro-oil and the different components of pyro-gas like CH_4, CO, CO_2 and H_2.
5.	**A. Sarkar & R. Chowdhury (*2014*)**	They studied the Catalytic Pyrolysis of Mustard Press Cake with NaCl. They conducted catalytic and non-catalytic experiments with mustard press cake as the feedstock in a long semi-batch pyrolyzer varying the temperature from 673K to 1173K. They maintained the inert atmosphere purging nitrogen gas into the pyrolyzer. They determined the kinetic rate constants of the volatile and the char by-products along with the activation energies and the pre-exponential factors. Catalytic pyrolysis was done in three different temperatures of 673K, 773K and 873K and at three different concentrations of NaCl (5-15%). The product yields and the activation energy of the catalytic and non-catalytic pyrolysis were compared. Higher yields of pyro-gas and lower yields of pyro-oil and pyro-char was observed in the case of catalytic pyrolysis. The activation energy for catalytic pyrolysis was found to be low than that of non-catalytic pyrolysis, hence enhancing the overall pyrolysis rate in the presence of the catalyst.

6.	**Abdullah et al. (*2014*)**	They presented a study on characterization of banana (*Musa* spp.) pseudo-stem and fruit-bunch-stem as a potential renewable energy resource. Both the banana pseudo-stem and fruit-bunch-stem were characterized through different analyses like proximate, ultimate and thermal analyses in order to determine their feasibility to be used as potential feedstocks. The higher and the lower heating values were also determined for both the feedstocks. The moisture content, carbon and ash content were reported in the study. The percentage content of the three constituents of the lignocellulosic material namely, cellulose, hemicellulose and lignin were also determined by chemical analysis for both the feedstocks. The kinetics of the samples was studied by Thermogravimetric Analysis (TGA). It was analyzed in the study that the chemical composition and behaviour of the banana pseudo-stem was similar to that of the other lignocellulosic materials. The characterization of both the feedstocks revealed quite a difference in terms of chemical composition and behaviour. The lignocellulosic content for banana pseudo-stem and fruit-bunch-stem was very high. The degradation of both the feedstocks occurred around 430ºC. Finally it was concluded that from the physical, chemical and thermal analyses the feedstocks were much similar to other biomass used to a renewable source of energy. The feedstocks were also eco-friendly minimising the negative impact on the environment.

7.	**Paasikallio et al. (*2013*)**	They presented a review on studies of the effect of reaction temperature on bio-oil physical properties and chemical composition. The feedstock taken for study is the forest thinning which was subjected to different pyrolysis conditions to obtain liquid, gas and solid products. The catalysts used for this experiment were two different types of ZSM-5. Initially experiments were carried out in a fluidized bed reactor at 475°C for comparing the effectiveness of the two catalysts. The catalyst with higher activity was finally used for the experimental run conducted at a temperature of 400°C to 550°C. Both

		the catalytic and non-catalytic experiments were carried on in the reactor. The catalyst was characterized and significant changes were noticed both in the physical (pH, viscosity etc.) and chemical properties of the liquid product namely bio-oil. The pyrolysis temperature had a pronounced effect on the changes in physical and chemical properties of the bio-oil. Catalytic upgrading was considered to improve the physical and chemical properties of the liquids to convert them into eco-friendly and marketable liquid fuel. Kinetic studies were performed by thermogravimetric analysis (TGA). The bio-oil yield decreased for catalytic pyrolysis process than that of non-catalytic one but the oxygen content was much lowered in the pyro-oil obtained after catalytic pyrolysis of the feedstock, thus improving the physical properties of the bio-oil. GC-MS (Gas Chromatography coupled with Mass Spectrometry) was also conducted for further analysis of the pyro-oil.
8.	**Prasad et al. (*2013*)**	They presented a review on thermal and catalytic pyrolysis of Karanja seed to produce liquid fuel. Karanja seed was considered to be a potential feedstock for the process of pyrolysis. Thermal pyrolysis of the feedstock was carried out in a semi batch reactor at a range of temperature and the optimum temperature was found out to be 550 ºC for the maximum liquid oil yield (55.17 wt %). The liquid oils obtained from both thermal and catalytic pyrolysis were characterized in order to see the effect of pyrolysis on their physical properties. Three different catalysts such as CaO, Alumina and Kaolin were used for the pyrolysis process. The different feed to catalytic ratios (2:1, 4:1 and 8:1) were considered as a parameter to obtain the optimum feed to catalyst ratio (8:1) where the liquid oil yield was maximum. The catalysts Alumina and Kaolin were found to be more effective than CaO in terms of pyro-oil yield. The pyro-oil yield was comparatively greater in case of catalytic pyrolysis than that of thermal pyrolysis. On further analysis of pyro-oil proved that the usage of catalysts improved the physical properties like pH and chemical composition of the pyro-

		oil. The calorific value of the pyro-oil was found to have enhanced after catalytic pyrolysis.
9.	**Prasad et al. (*2013*)**	They presented a study on comparison of yield and fuel properties of thermal and catalytic Mahua seed pyrolytic oil. Mahua seed was considered to be a potential feedstock for the process of pyrolysis. The characterization of the Mahua seed was done. The catalyst used for the experimental run was CaO. Non-catalytic pyrolysis of the feedstock was carried out in a reactor at a range of temperature and the optimum temperature was found out to be 525ºC for the maximum liquid oil yield. Hence, catalytic pyrolysis of the feedstock was carried out at 525 ºC at which the pyro-oil yield was maximum (40.71 % wt). The liquid oils obtained from both non-catalytic and catalytic pyrolysis were characterized in order to see the effect of pyrolysis on their physical properties. The different feed to catalytic ratios (2:1, 4:1 and 8:1) were considered as a parameter to obtain the optimum feed to catalyst ratio (2:1) where the liquid oil yield was maximum. The amount of catalyst needed was high in this pyrolysis process. The pyro-oil yield was comparatively greater in case of catalytic pyrolysis than that of non-catalytic one. On further analysis of pyro-oil proved that the usage of catalysts improved the physical properties like pH and decreased the viscosity of pyro-oil. There was also a pronounced change in the chemical composition of the pyro-oil. The heating value of the pyro-oil was found to have enhanced after catalytic pyrolysis. GC-MS (Gas Chromatography coupled with Mass Spectrometry) was done to identify the organic functional groups that were present in the liquid pyro-oil. Catalytic pyrolysis improved the quality of the pyro-oil.
10.	**Fernandes et al. (*2012*)**	They studied slow pyrolysis of banana waste: leaves and pseudostem. They characterized the banana waste through different analyses namely proximate and ultimate analyses, thermogravimetric analysis (TGA) and differential thermal analysis. They carried out the pyrolysis process in a batch reactor upto the temperature of 773K. The

		experimental run consisted of 60 minutes for each batch while an inert atmosphere was maintained inside the pyrolyzer. The pyrolysis products were analysed by different instruments viz. the pyro-gas fraction was analyzed by gas chromatography (GC), the pyro-oil by gas chromatography coupled with mass spectroscopy (GC-MS) and pyro-char by scanning electron microscopy (SEM) X-ray fluorescence. The characteristic of slow pyrolysis of banana waste was found that the highest mass yield was of pyro-char followed by that of pyro-oil and pyro-gas. The gases generated were mainly CH_4, CO, CO_2. They concluded that banana waste had the potential for fuel production via slow pyrolysis.
11.	**Bulushev et al. (*2011*)**	They presented a review on catalysis for conversion of biomass to fuels via pyrolysis and gasification. Synthesis gas was produced by the catalytic steam-reforming of biomass. This product namely, syngas could be further treated to give transportation fuels using the catalysis process. The bio-oil produced from the non-catalytic pyrolysis of feedstock could be catalytically upgraded to produce various fuel additives. Catalytic upgrading was performed following two pathways, one at lower temperature where esterification took place and the other at higher temperature where gasification and hydrotreating processes were conducted. Zeolites with different porous structures were used for catalytic pyrolysis of biomass. Upgrading of bio-oil was also possible because of the catalytic pyrolysis of the lignocellulosic material.
12.	**French et.al (*2009*)**	They presented a review on catalytic pyrolysis of biomass for biofuels production. Bio-oils obtained from the biomass pyrolysis had the potential to be used as a fuel in semi-commercial plants for power generation using boilers or turbines but the bio-oils needed suitable treatments in order to upgrade their oil quality to be useful for transportation fuel. The gaseous by-product namely, pyro-gas could be upgraded catalytically using zeolites. The objective was to reduce oxygen content of the product in order to improve its quality, hence

		improving its efficiency and converting them to hydrocarbons in order to increase its fuel value. In this study a set of commercial and laboratory-synthesized catalysts were used for the pyrolysis process. Three different types of biomass like cellulose, lignin, and wood were selected as the feedstocks. The feedstocks were pyrolyzed in quartz boats along with the catalysts. The batch experiments were conducted at temperature range of 400°C to 600°C. The catalyst-to-biomass ratio was 5–10 by weight. The product, gas composition was analyzed using Molecular-beam mass spectrometry (MBMS). The maximum yield of the product was obtained using nickel, cobalt, iron, and gallium-substituted ZSM-5. Over a period of time during the experiments, coke got deposited on the surface of the catalyst, therefore, reducing the deoxygenation activity.
13.	**Bilba et al. (*2007*)**	They presented a review on study of banana and coconut fibres botanical composition, thermal degradation and textural observations. Four different types of fibres were chosen for feedstock for the experiments. They were leaf and trunk fibres from the banana tree and husk and fabric from the coconut tree. The botanical and chemical properties of the four different fibres were analyzed before preparation of the insulating material that could be used for various construction purposes. Pyrolysis temperature was used as a parameter for this study. The temperature for pyrolysis was varied in the range of 200ºC to 700ºC. The solid pyro-char obtained from the pyrolysis of the fibres were analyzed by several analyses like SEM (Scanning Electron Microscopy) and Fourier Transform Infra Red (FTIR) spectroscopy. Rapid decomposition of the banana fibres was observed with the increase in the pyrolysis temperature.
14.	**Bandyopadhyay et al. (*1999*)**	They presented a review on Thermal Deactivation Studies of Coconut Shell Pyrolysis. They determined the pyrolysis kinetics of coconut shell which was being pre-dried under the sun and then in an oven for 48 h at 373K. The pyrolysis was done varying the temperature from

		523K to 1023K by captive sample technique maintain an inert atmosphere inside the pyrolyzer. Five deactivation models were proposed in the paper to describe the behavior of the system.
15.	**Papachristos et al. (*1987*)**	They presented a paper on upgradation of low-rank solid fuels with catalyzed decarboxylation under very mild conditions. Low rank coal, with high oxygen content, was used as the pyrolysis feedstock for the experiments. In this study the oxygen content of the pyro-oil obtained from the pyrolysis of coal was reduced through decarboxylation reaction. It was analyzed that the main organic functional group present in lignite and peat was that of carboxyl group. Carboxyl group was present mostly in low rank coals like lignite peat, whereas, it was not much present in high rank coals like bituminous coal. Carboxyl group was the main source of oxygen for lignite and peat. Hence, via decarboxylation reaction the oxygen content of the pyro-oil was lowered thereby, improving the properties of the liquid pyro-oil.

Chapter 3

AIMS & OBJECTIVES

1. To characterize the pyrolysis feedstock (banana stem) by proximate and ultimate analyses.
2. To perform the pyrolysis reaction in a semi-batch reactor under non-isothermal conditions.
3. To determine the lumped kinetics for the pyrolysis of banana stem in the temperature range of 400-900ºC.
4. To determine the kinetics of catalytic pyrolysis in the temperature range of 400-900ºC.
5. Comparison of prediction of dynamic trends of unreacted banana stem and pyro-products, namely, volatiles and char using lumped kinetics determined under the present study and the multi-component lumped kinetics [Aramideh et al. (*2015)*], using kinetic parameters of cellulose, hemicellulose and lignin available in the literature.
6. To select a suitable microorganism for decarboxylation of banana stem.
7. To study the effect of bio-decarboxylation time on the characteristics of chemical bonds in banana stem and on the yield of pyro-oil.
8. To determine the pyrolysis kinetics of bio-decarboxylated banana stem.
9. To compare the yield and quality of pyro-oil generated through the catalytic and non-catalytic pyrolysis of banana stem with those obtained from pyrolysis of optimally bio-decarboxylated banana stem.

Chapter 4

MATERIALS & METHODS

4.1 Materials:

4.1.1 Feedstock Used: Waste banana pseudo-stem

The banana pseudo-stem was purchased from the local vegetable market of Jadavpur. The samples were cut into small pieces, then they were dried under the sun for few days and finally put in the oven at 60ºC for further drying in order to remove the moisture as required for the process of pyrolysis and then milled to produce the samples of approximately 10-20 mm in size. The contents of cellulose, hemicellulose and lignin in banana pseudo-stem are 44, 17.5 and 37.3 wt% respectively [Abdullah et al. (2014)].

Fig 4.1: Dried Banana Pseudo-stem

Fig 4.2: Banana Pseudo-stem after sizing

4.1.2 Catalysts Used:

a) Aluminium Oxide [Al_2O_3],
b) Zinc Oxide [ZnO],
c) Sodium Chloride [$NaCl$],
d) Potassium Chloride [KCl] and
e) Sodium Aluminosilicate [$NaAl(SiO_3)_2$]

All the catalysts were purchased from SRL, India. The catalysts were calcined at 120ºC for 2 hrs in muffle furnace at the beginning of the experiments. In each experiment 10% (w/w) of catalyst with respect to the mass of pyrolysis feedstock was used.

4.1.3 Microorganism for biodecarboxylation:

Baker's yeast (*Saccharomyces cerevisiae*) was purchased from local market and was used for biodecarboxylation of banana stem.

4.2. Experimental set-up for pyrolysis:

The different components for the experimental set-up are:

a. PID temperature controller:

PID temperature controller (Honeywell DC-1040), manufactured by G.B. Enterprises, was used to maintain the isothermal condition for the pyrolyzer. The heating rate was maintained at 10ºC/min.

Fig 4.3: PID Temperature Controller

b. Furnace:

The furnace, manufactured by Bhattacharya & Co., was tubular and a weighing machine was placed on top of it.

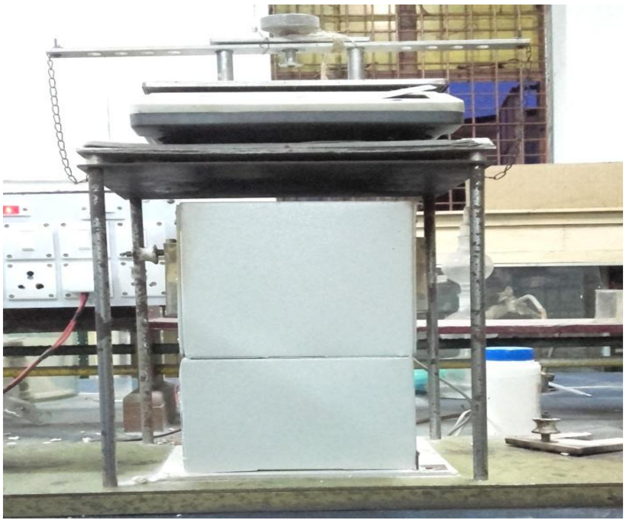


Fig 4.4: Furnace with the weighing machine on the top

c. Nitrogen Cylinder:

The nitrogen cylinder, manufactured by Prakash Traders, was used to maintain an inert atmosphere inside the pyrolyzer.

d. Water bath:

The water bath, manufactured by S.C. Dey & Co., was connected to the condenser. The cooling circulating water inside the condenser was maintained at 15ºC by the water bath.

Fig 4.5: Water Bath

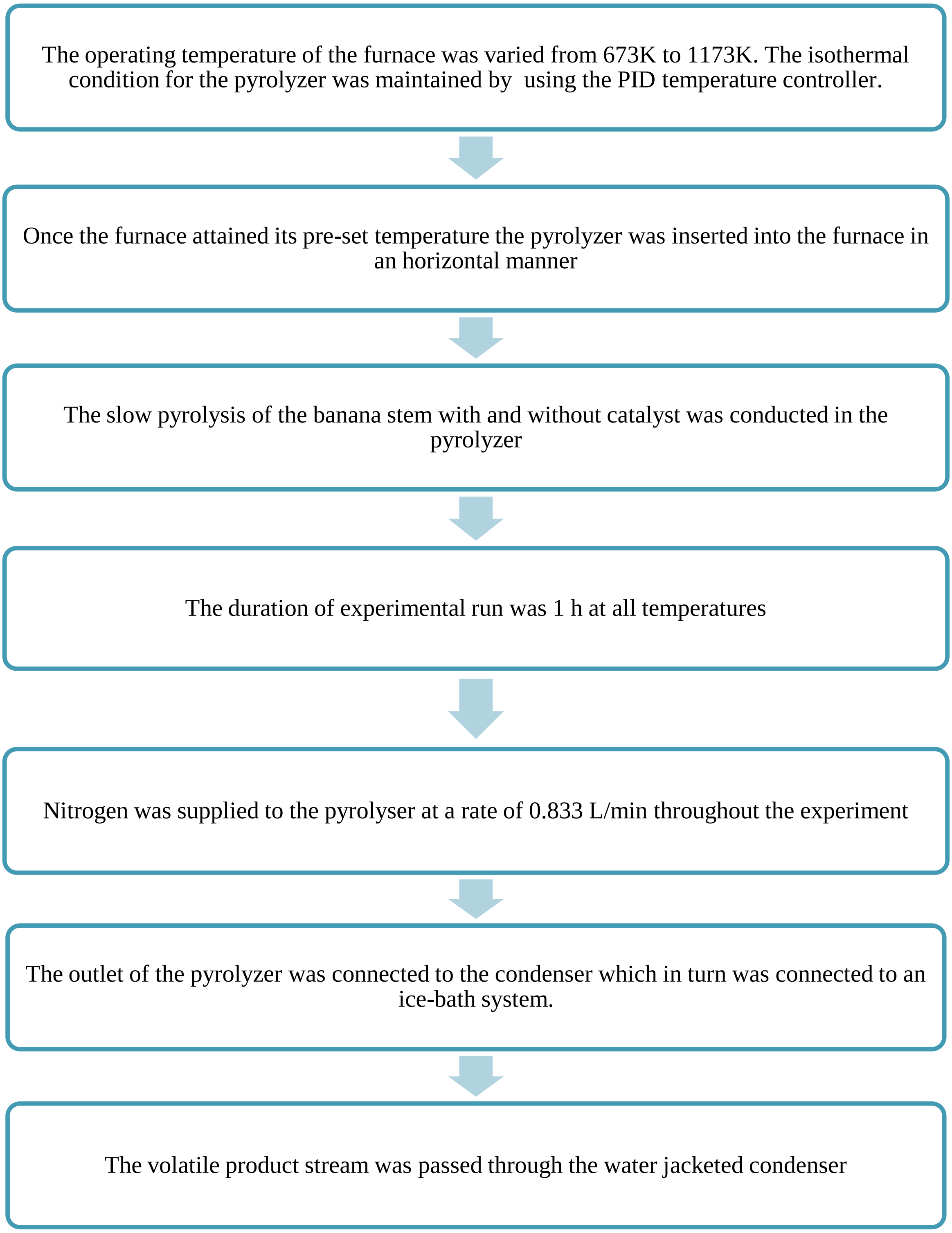
e. Pyrolyzer reactor :

The semi-batch pyrolyzer (sample holder) , manufactured by S.C. Dey & Co., was 50 mm in diameter and 640 mm long, cylindrical and made up of stainless steel. It operated isothermally.

Fig 4.6: Experimental set-up for pyrolysis

4.3 Experimental Procedure:

The following protocol has been followed for the catalytic and non-catalytic pyrolysis experiments.



The operating temperature of the furnace was varied from 673K to 1173K. The isothermal condition for the pyrolyzer was maintained by using the PID temperature controller.

Once the furnace attained its pre-set temperature the pyrolyzer was inserted into the furnace in an horizontal manner

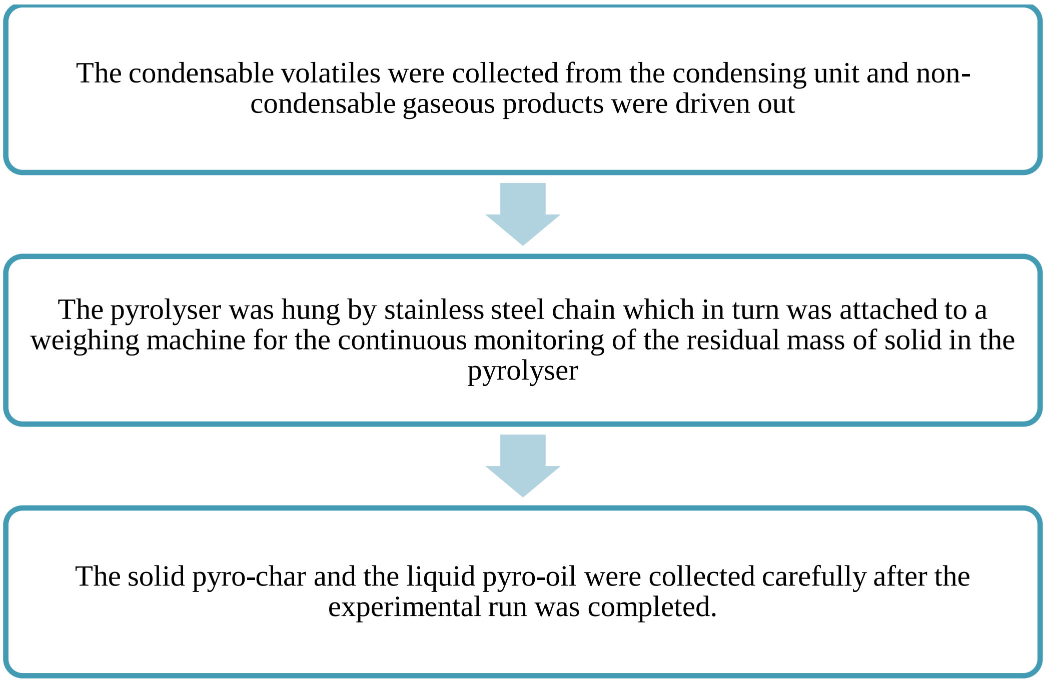
The slow pyrolysis of the banana stem with and without catalyst was conducted in the pyrolyzer

The duration of experimental run was 1 h at all temperatures

Nitrogen was supplied to the pyrolyser at a rate of 0.833 L/min throughout the experiment

The outlet of the pyrolyzer was connected to the condenser which in turn was connected to an ice-bath system.

The volatile product stream was passed through the water jacketed condenser



The condensable volatiles were collected from the condensing unit and non-condensable gaseous products were driven out

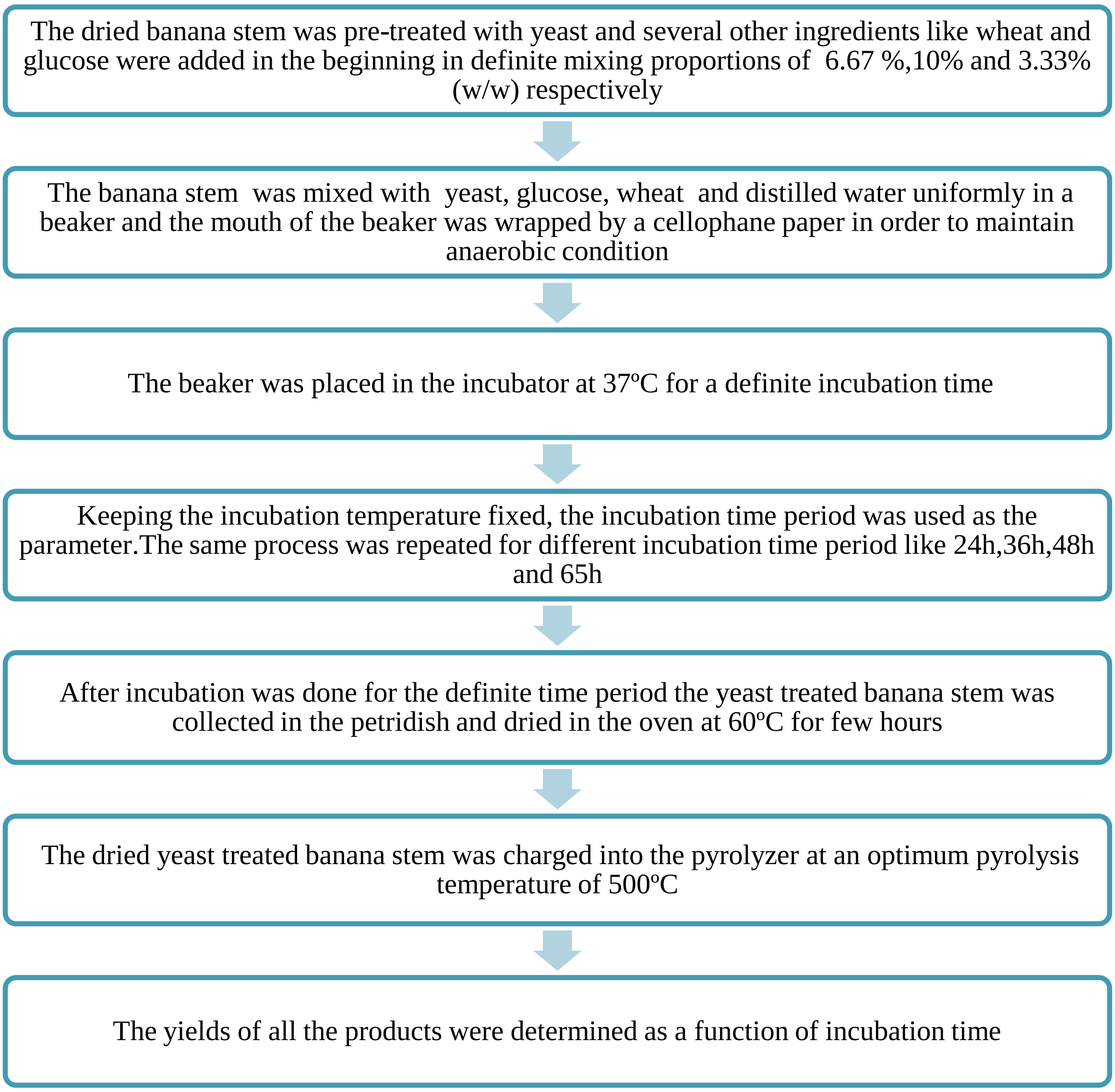
The pyrolyser was hung by stainless steel chain which in turn was attached to a weighing machine for the continuous monitoring of the residual mass of solid in the pyrolyser

The solid pyro-char and the liquid pyro-oil were collected carefully after the experimental run was completed.

The same protocol was also followed for the pyrolysis of bio-decarboxylated banana stem.

4.3.1 Pre-treatment of banana stem with yeast

Pretreatment of banana stem using baker’s yeast was done according to the following protocol.



The dried banana stem was pre-treated with yeast and several other ingredients like wheat and glucose were added in the beginning in definite mixing proportions of 6.67 %,10% and 3.33% (w/w) respectively

The banana stem was mixed with yeast, glucose, wheat and distilled water uniformly in a beaker and the mouth of the beaker was wrapped by a cellophane paper in order to maintain anaerobic condition

The beaker was placed in the incubator at 37ºC for a definite incubation time

Keeping the incubation temperature fixed, the incubation time period was used as the parameter.The same process was repeated for different incubation time period like 24h,36h,48h and 65h

After incubation was done for the definite time period the yeast treated banana stem was collected in the petridish and dried in the oven at 60ºC for few hours

The dried yeast treated banana stem was charged into the pyrolyzer at an optimum pyrolysis temperature of 500ºC

The yields of all the products were determined as a function of incubation time

4.4 Computation using MATLAB:

The simultaneous ODE equations for the prediction of dynamic trends of unreacted banana stem, volatiles and char using lumped kinetics determined under the present study and the multi-component lumped kinetics [Aramideh et al. (*2015)*] using kinetic parameters of cellulose, hemicellulose and lignin available in the literature, were solved using MATLAB R2013a software by using ODE45 method.

4.5 Instrumental Analysis:

The proximate and ultimate analyses or raw and untreated banana stem were done using the following methods and instruments

Table4.1: Details of the instruments used in the project

Analysis	Method	Name of the equipment	Name of the company
Moisture content	ASTM D-4442	Hot Air oven	Bhattacharya & Co.
Ash content	ASTM E-1755-01	Muffle Furnace	Bhattacharya & Co.
Volatile matter	ASTM D-4209	Muffle Furnace	Bhattacharya & Co.
Calorific Value	ASTM E-711-87	Bomb Calorimeter	JOEL JSEM 5200 (Japan)
Ultimate Analysis (CHNO)	-----	CHN Analyser	Perkin Elmer

4.5.1 Liquid product analysis:

4.5.1.1 CHN Analysis:

The pyro-oil obtained after pyrolysis of the untreated and treated (both catalytic and bio-route) feedstock were analyzed elementally using a CHN Analyzer (Perkin Elmer make with model number 2400). For this analysis the technical help was provided by Indian Association for the Cultivation of Science, Kolkata.

Fig 4.7: Ultimate analysis instrumental set up (CHN Analyzer)

4.5.2 Solid sample analysis:

4.5.2.1 FTIR Analysis:

The FTIR analysis of the untreated and yeast treated banana pseudo-stem at different incubation time periods (24h, 36h and 48h) were conducted using FTIR Analyzer of SHIMATZU Make, Japan with model number IR-Prestige-21.The various characteristic functional groups of the solid samples were identified by this analysis. For this analysis the technical help was provided by School of Material Science and Nanotechnology, Jadavpur University, Kolkata.

Fig 4.8: Fourier Transform Infra Red laboratory setup

4.5.2.2 Thermogravimetric analysis (TGA):

The kinetics of the untreated and yeast treated banana pseudo-stem at incubation time of 48h were studied at two different heating rates of 10 and 20ºC/min using a Thermogravimetric analyser of PerkinElmer make, Singapore with model Pyris Diamond TG/DTA. For this analysis the technical help was provided by Metallurgical & Material Engineering Department, Jadavpur University, Kolkata.

Fig 4.9: Thermogravimetric Analyzer

Chapter 5

THEORETICAL ANALYSIS

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) 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 (Bradbury et al. 1979)

5.1 Kinetics of Primary Pyrolysis (Scheme 1):

A scheme (Scheme 1) was proposed by Bandyopadhay et al. (*1999*) for the reaction pathway of the pyrolysis of biomass. This reaction scheme is described below:

$$\text{Banana Stem} \longrightarrow \text{Active Complex} \begin{cases} \xrightarrow{k_v} \text{Volatiles} \\ \xrightarrow{k_c} \text{Char} \end{cases} \qquad \text{----(1)}$$

The weight loss profile of the solid reactant W with time is given by:

$$-\frac{dW}{dt}=(k_v+k_c)W \qquad \text{----(2)}$$

Let, $k_v + k_c = k$

Therefore,

$$-\frac{dW}{dt}=kW \qquad \text{----(3)}$$

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

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

$$= k_v W_0 \exp(-kt) \qquad \text{----(4)}$$

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

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

$$= k_c W_0 \exp(-kt) \qquad \text{----(5)}$$

Equation (3), (4) and (5) have been solved analytically with the following initial conditions:

$$W(t \to 0) = W_0, W_v(t \to 0) = W_{v0}, W_c(t \to 0) = W_{c0} \qquad \text{----(6)}$$

The solutions under isothermal conditions are as follows:

$$W(t) = W_0 \exp(-kt) \qquad \text{----(7)}$$

$$W_v(t) - W_{v0} = (\frac{k_v}{k}) W_0 [1 - \exp(-kt)] \qquad \text{----(8)}$$

$$W_c(t) - W_{c0} = (\frac{k_c}{k}) W_0 [1 - \exp(-kt)] \qquad \text{----(9)}$$

Under isothermal condition:

$$\frac{W_c(t) - W_{c0}}{W_v(t) - W_{v0}} = \frac{k_c W}{k_v W}$$

$$= \frac{k_c}{k_v}$$

$$= \frac{W_c(t \to \infty) - W_{c0}}{W_v(t \to \infty) - W_{v0}} \qquad \text{----(10)}$$

Assuming that at a pyrolysis temperature (above 633K) the residue obtained at infinite time is entirely comprised of char we can write,

$$W_c(t \to \infty) = W_R(t \to \infty)$$

And, $W_v(t \to \infty) = W_0 - W_R(t \to \infty)$ ----(11)

Therefore:

$$\frac{W_c(t) - W_{c0}}{W_v(t) - W_{v0}} = \frac{W_R(t \to \infty) - W_{c0}}{W_0 - W_R(t \to \infty)}$$

or $W_c(t) - W_{c0} = \dfrac{W_R(t \to \infty) - W_{c0}}{W_0 - W_R(t \to \infty)} * (W_v(t) - W_{v0})$ ----(12)

At any time t, the weight of the unreacted reactant is given by:

$$W(t) = W_0 - (W_v(t) - W_{v0}) * [1 + \frac{W_R(t \to \infty) - W_{c0}}{W_0 - W_R(t \to \infty)}] \qquad \text{----(13)}$$

Regression analysis of equations (7), (8) and (9) gives the values of the rate constants k, k_v, k_c respectively, at different temperatures.

Kinetic parameters have been determined for the catalytic and non-catalytic pyrolysis of banana stem. The kinetics of pyrolysis of bio-treated banana stem has also been determined using the same procedure.

5.2 Multistep Reaction Mechanism (Scheme 2) based on the constituents of the feedstock:

Another reaction scheme for the pyrolysis of banana stem (Scheme 2) has been attempted on the basis of the constituents (cellulose, hemicellulose and lignin) of the banana stem [Aramideh et al. (*2015*)].

According to the model

Dry Banana stem = α Cellulose + ß hemicellulose + γ lignin ----(14)

where α, ß and γ are the mass fraction of cellulose, hemicellulose and lignin respectively in banana stem.

Therefore,

$\alpha + ß + \gamma = 1$ ----(15)

According to the model, the virgin biomass is converted to active state and then the active biomass gets decomposed into pyro-oil, char and syngas (non–condensable gases) following the competitive reaction steps as described below. Some pyro-oil also gets cracked into syngas depending on the residence time of the feedstock and pyrolysis temperature.

$$\begin{tikzcd}
 & & \text{Syngas(g)} + \text{Char(s)} \\
\text{Cellulose} \arrow[r, "k_{C1}"] & (\text{Active Complex})_{\text{cellulose}} \arrow[ur, "k_{C3}"] \arrow[dr, "k_{C2}"'] & \\
 & & \text{Pyro} - \text{oil} \arrow[uu, "k_{C4}"']
\end{tikzcd}$$

----(16)

$$\begin{tikzcd}
 & & \text{Syngas(g)} + \text{Char(s)} \\
\text{Hemicellulose} \arrow[r, "k_{H1}"] & (\text{Active Complex})_{\text{hemicellulose}} \arrow[ur, "k_{H3}"] \arrow[dr, "k_{H2}"'] & \\
 & & \text{Pyro} - \text{oil} \arrow[uu, "k_{H4}"']
\end{tikzcd}$$

----(17)

$$\begin{tikzcd}
 & & \text{Syngas(g)} + \text{Char(s)} \\
\text{Lignin} \arrow[r, "k_{L1}"] & (\text{Active Complex})_{\text{lignin}} \arrow[ur, "k_{L3}"] \arrow[dr, "k_{L2}"'] & \\
 & & \text{Pyro} - \text{oil} \arrow[uu, "k_{L4}"']
\end{tikzcd}$$

----(18)

All reactions are assumed to be of 1st order.

$k = A \exp(-E / RT)$ ----(19)

The mass balance equations are as follows:

Cellulose:

$$\frac{dW_C}{dt} = -k_{C1} W_C$$

----(20)

Hemicellulose:

$$\frac{dW_H}{dt} = -k_{H1} W_H$$

----(21)

Lignin:

$$\frac{dW_L}{dt} = -k_{L1}W_L \qquad \text{----(22)}$$

Active cellulose:

$$\frac{dW_{AC}}{dt} = k_{C1}W_C - k_{C2}W_{AC} - k_{C3}W_{AC} \qquad \text{----(23)}$$

Active hemicellulose:

$$\frac{dW_{AH}}{dt} = k_{H1}W_H - k_{H2}W_{AH} - k_{H3}W_{AH} \qquad \text{----(24)}$$

Active lignin:

$$\frac{dW_{AL}}{dt} = k_{L1}W_L - k_{L2}W_{AL} - k_{L3}W_{AL} \qquad \text{----(25)}$$

Pyro-oil:

$$\frac{dW_T}{dt} = k_{C2}W_{AC} + k_{H2}W_{AH} + k_{L2}W_{AL} - k_4W_T \qquad \text{----(26)}$$

Syngas:

$$\frac{dW_S}{dt} = (1-Y_C)k_{C3}W_{AC} + (1-Y_H)k_{H3}W_{AH} + (1-Y_L)k_{L3}W_{AL} + (1-Y_T)k_4W_T \qquad \text{----(27)}$$

Char:

$$\frac{dW_{ch}}{dt} = Y_C k_{C3}W_{AC} + Y_H k_{H3}W_{AH} + Y_L k_{L3}W_{AL} \qquad \text{----(28)}$$

MATLAB (R2013a) was used to solve the simultaneous ODE equations using ODE45 method.

Chapter 6

RESULTS AND DISCUSSIONS

6.1 Characterization of banana stem:

6.1.1 Proximate and Ultimate Analyses:

- The moisture, volatile and ash contents of the waste banana pseudo-stem are determined through proximate analysis. The moisture content is determined using standard method ASTM D-4442 in a conventional hot air oven.
- The volatile matter is determined using standard method ASTM D-4209 and the ash content using standard method ASTM E-1755-01 in a conventional muffle furnace.
- The fixed carbon is determined by subtracting the sum of the others (moisture, volatile and ash) from total sample. All the analyses arre repeated thrice and the results are tabulated below.

Table6.1: Proximate Analysis of waste banana pseudo-stem

Proximate Analysis	Moisture Content	Volatile Matter	Ash Content	Fixed Carbon
(% w/w)	15	76	6.85	2.15

- The carbon, hydrogen and nitrogen content of the untreated raw feedstock are determined in the PerkinElmer CHN/O 2400 Analyzer. The oxygen content is determined by the difference of the sum of the other elements (carbon, hydrogen and nitrogen) from the total sample.

Table6.2: Ultimate Analysis of waste banana pseudo-stem

Ultimate Analysis	Carbon	Hydrogen	Nitrogen	Oxygen
(% w/w)	40.40	6.02	0.11	53.47

- The calorific value is determined to be 18.5 MJ/kg using standard Bomb calorimeter (ASTM E-711-87).

6.2 Determination of the lumped kinetics for the non-catalytic and catalytic pyrolysis of banana stem

6.2.1Weight loss history for untreated banana stem:

The weight loss history for untreated banana stem has been studied in two ways, first by the conventional pyrolysis process and secondly by analyzing banana stems using TGA (Thermogravimetric Analysis) at two heating rates of 10 and 20ºC/min.

6.2.1a. Weight loss history of untreated banana stem by conventional pyrolysis:

The weight of the unreacted reactant at any time and at any temperature was calculated by weighing the condensable part of the volatile obtained from the experiment. The amount of residue was calculated from the expression below.

$$W(t)=W_0-(W_v(t)-W_{v0})*[1+\frac{W_R(t\rightarrow\infty)-W_{c0}}{W_0-W_R(t\rightarrow\infty)}]$$

The percentage (%) of weight residue had been plotted against time in the temperature range of 573K-1173K.

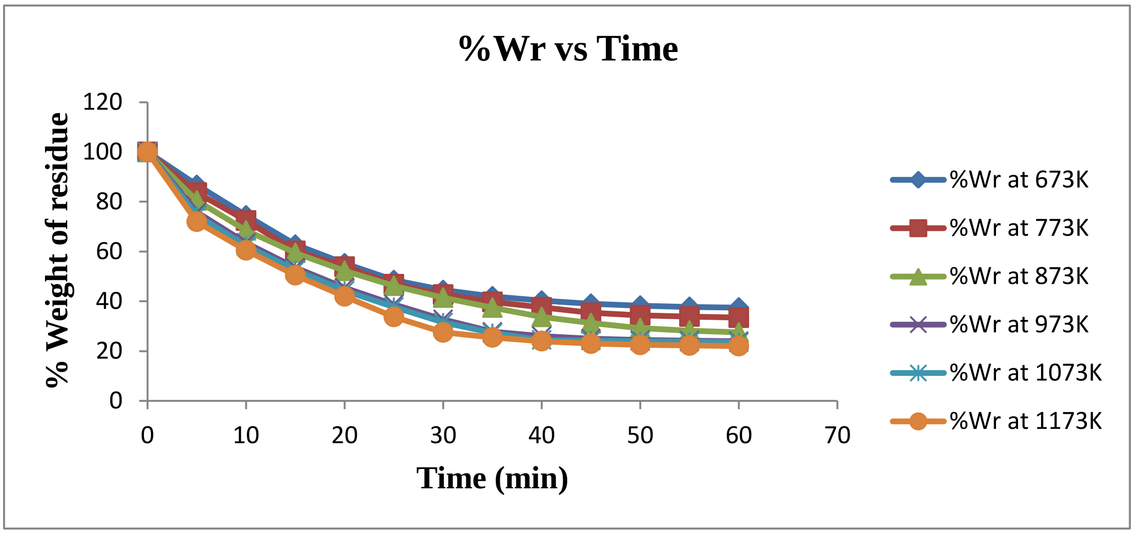


Fig 6.1: Comparative curve of % Wt residue to Time (untreated banana stem)

From figure 6.1 it is observed that there is a gradual weight loss of the banana stem as it is pyrolyzed to produce volatiles and char with the increase in temperature over a time period of 1h. At each time the weight loss is increasing with the increase in pyrolysis temperature due to the increase of rate of pyrolysis.

6.2.1b.Weight loss history of untreated banana stem by TGA:

Thermogravimetric Analysis (TGA) is an instrumental technique to study the fundamental kinetic characteristics of biomass pyrolysis. In the thermogravimetric analysis, the untreated banana stem is exposed to a heating program at two heating rates 10ºC/min and 20ºC/min and the weight loss is simultaneously recorded over the temperature range from room temperature to 900ºC. TGA is performed on a Perkin Elmer make (Singapore) model (Pyris Diamond TG/DTA). Nitrogen atmosphere (150ml/min) is used in this analysis. Platinum crucible is used with alpha alumina powder as reference.

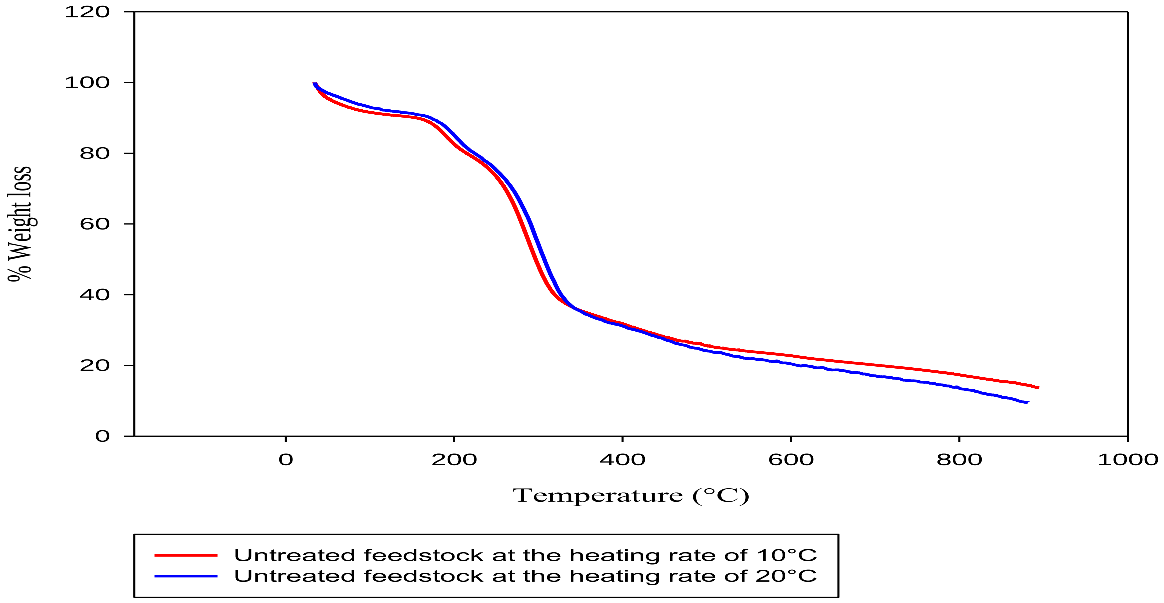


Fig 6.2: TGA curves of the pyrolysis process of the untreated banana stem at two heating rates of 10 and 20°C/min

From the analysis of the plots in the figure 6.2, it is clear that there are three distinct zones of the weight loss profile with temperature at both the heating rates, first one up to 150°C, second one from 150°C to 350°C and the third one from 350°C to 800°C. The first one may signify the loss of moisture loss, second one may be the main pyrolysis zone for cellulose and hemi-cellulose and the third one may be the pyrolysis zone for the lignin part. The pyrolysis reaction may include decarboxylation, depolymerisation and cracking from the temperature of 150ºC (Abdullah et al. 2014). Heat may have propagated through the banana stem and removed the inherent moisture at about 150ºC. At this heating rate thermal degradation of the banana stem may have initiated at about 150ºC and the rate may be maximum between 300ºC and 350ºC. Between the temperature of 400ºC and 450ºC devolatilisation of the banana stem may be completed leaving a residue behind of around 35 wt%.It is observed that the effect of heating rate on the weight loss profile for the untreated banana stem is not much pronounced.

6.2.2 Weight loss history for banana stem treated with different catalysts:

The banana stem is treated with five different catalysts namely Potassium Chloride (KCl), Zinc Oxide (ZnO), Sodium Chloride (NaCl), Alumina (Al_2O_3) and Sodiumaluminosilicate [$NaAl(SiO_3)_2$] and the amount of residue is calculated from the same expression as described for the untreated banana stem . The percentage (%) of weight residue is plotted against time in the temperature range of 573K-1173K for all the different catalysts respectively.

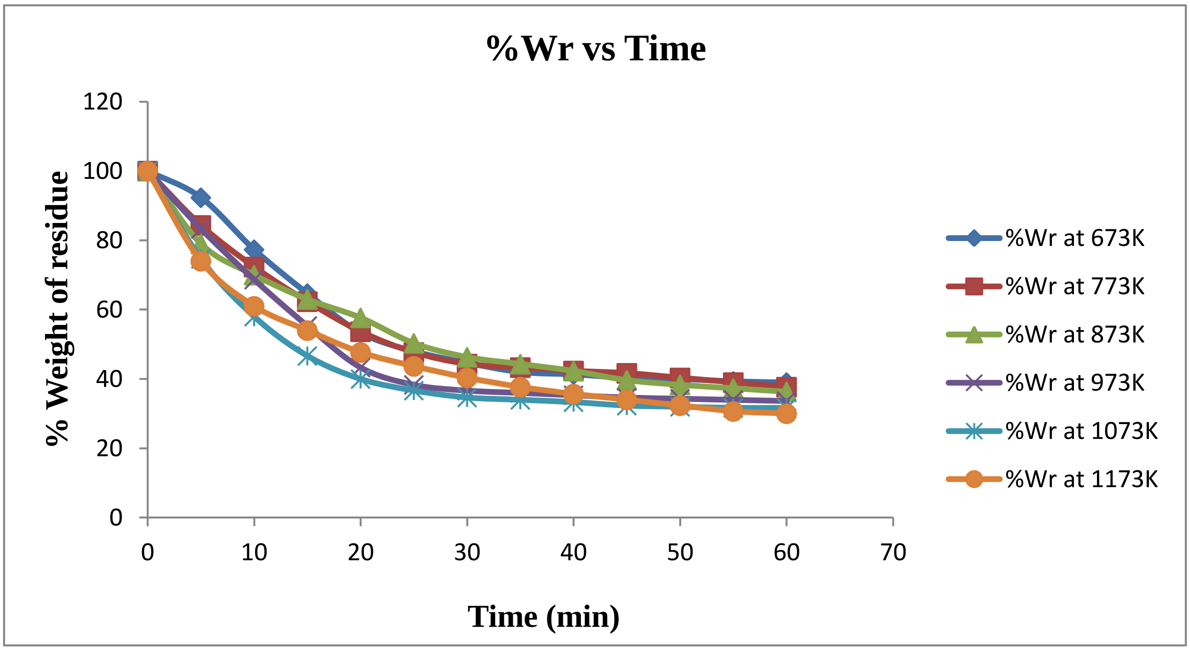


Fig 6.3a: Comparative curve of % Wt residue to Time (Banana stem with catalyst Alumina)

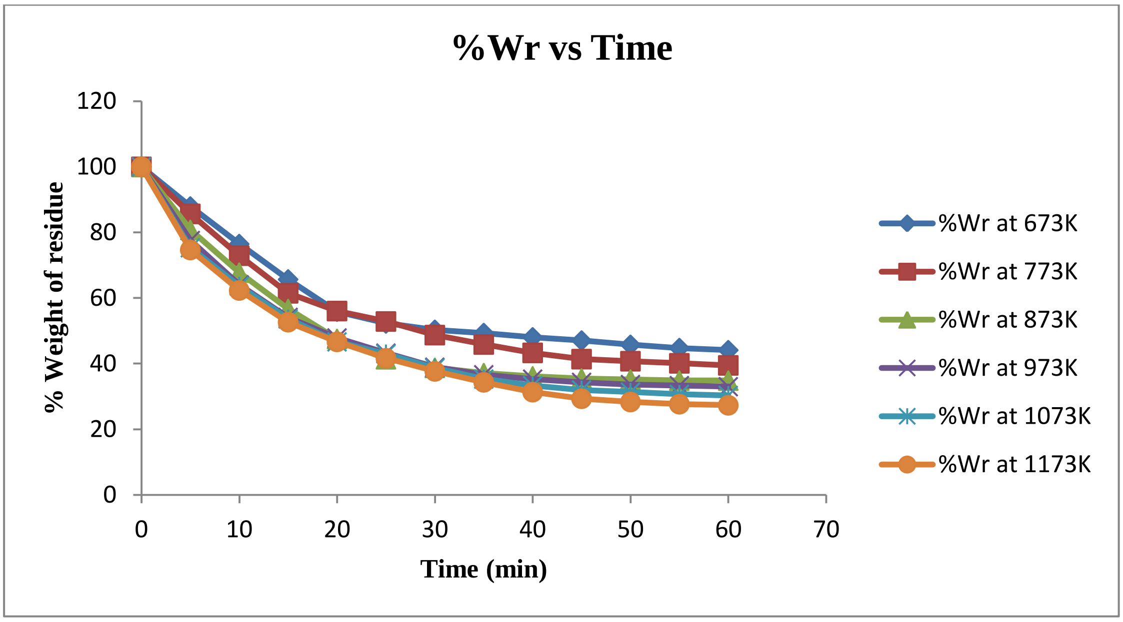


Fig 6.3b: Comparative curve of % Wt residue to Time (Banana stem with catalyst KCl)

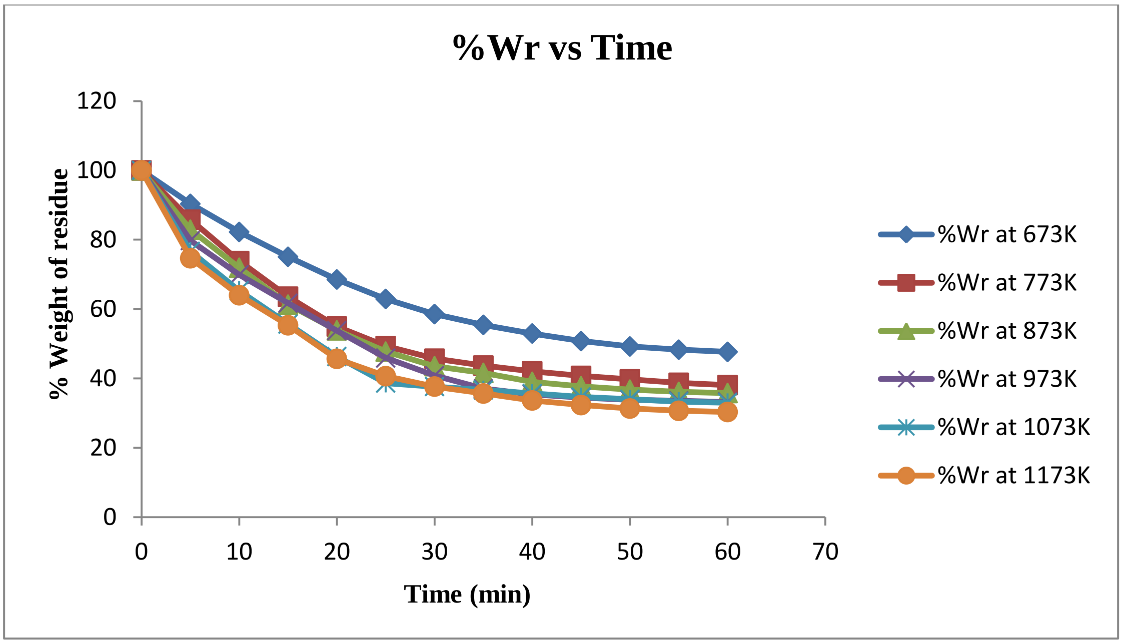


Fig 6.3c: Comparative curve of % Wt residue to Time (Banana stem with catalyst NaCl)

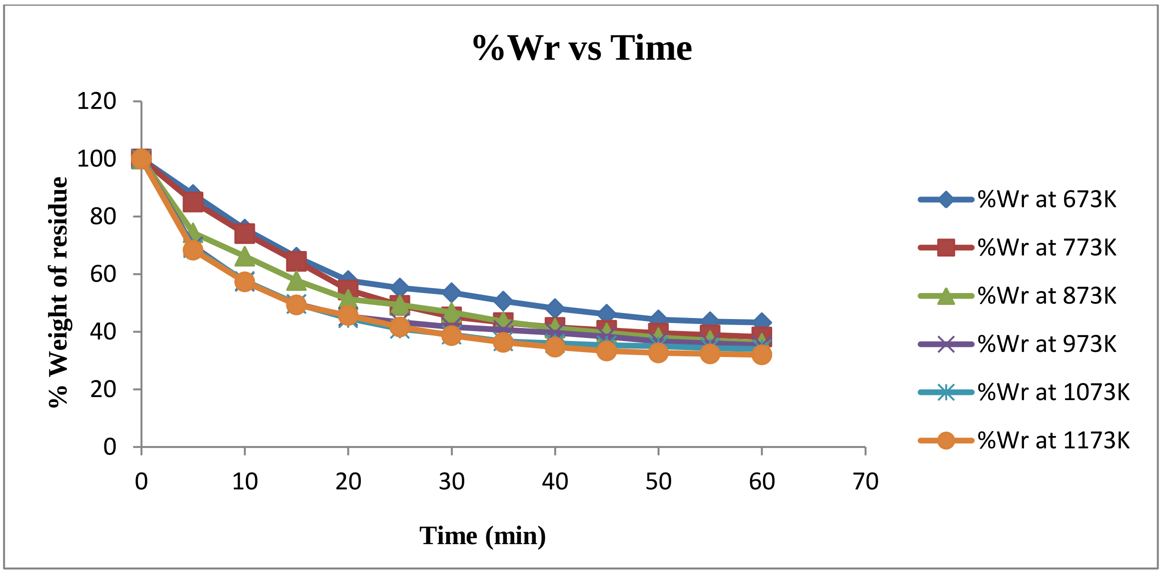


Fig 6.3d: Comparative curve of % Wt residue to Time (Banana stem with catalyst ZnO)

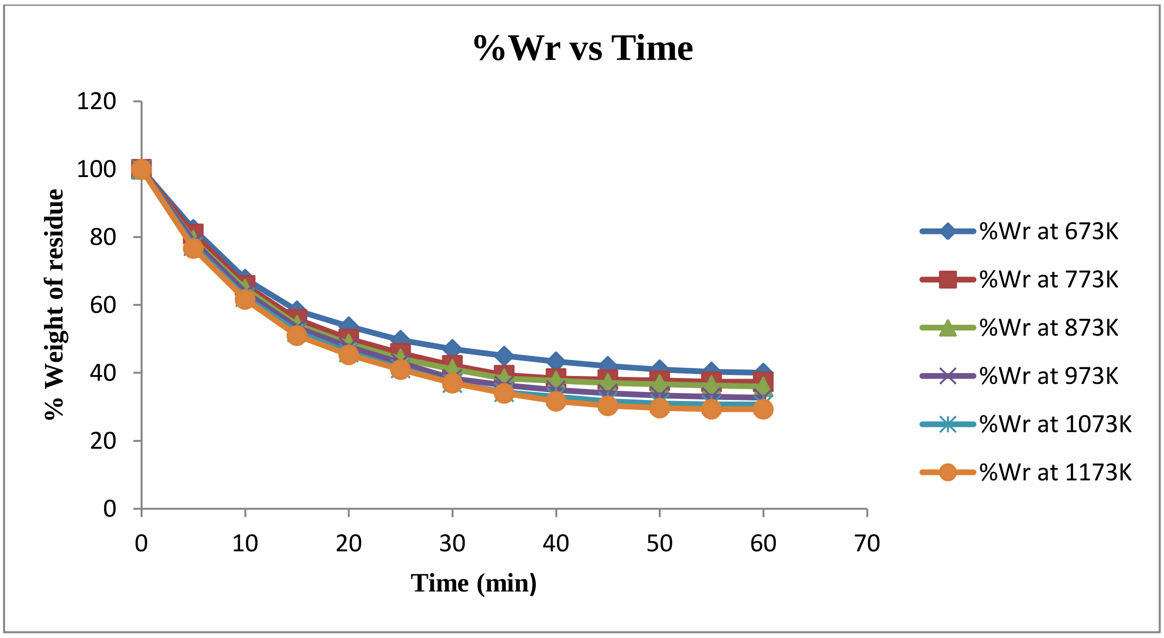


Fig 6.3e: Comparative curve of % Wt residue to Time (Banana stem with catalyst [$NaAl(SiO_3)_2$])

From the figures 6.3a to 6.3e, it is observed that there is a gradual weight loss of the catalytically treated banana stems as it is pyrolyzed to produce volatiles and char with the increase in temperature over a time period of 1h. At each time the weight loss is increasing with the increase in pyrolysis temperature due to the increase of rate of pyrolysis. Among all the catalytically treated banana stems, it is observed that the greatest weight loss took place for the banana stem treated with catalyst KCl. Hence it is evident that KCl is more effective than the other catalysts, increasing the rate of pyrolysis the most.

6.3 Calculation of Activation Energies and Frequency Factors as per Arrhenius Law:

W_v, W_c and weight loss percentage of the untreated and catalytically treated banana stem are calculated from the experimental results. The rate constants k, k_v and k_c at different pyrolysis temperature (673K-1173K) are determined from the graph $\Delta W/\Delta t$ or $\Delta Wv/\Delta t$ or $\Delta Wc/\Delta t$ vs Wt_{avg} respectively for all the different types of samples. The activation energy (E) and frequency factor (A) of k, kv and kc are determined from the experimental results.

6.4 Reaction kinetics for pyrolysis of untreated and catalytically treated banana stem:

The primary kinetics for the untreated and catalytically treated banana stem 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 and frequency factors reported in Table3. All the rate constants are calculated from the experimental results in the temperature range of 673K to 1173K and are superimposed with the predicted rate constants.

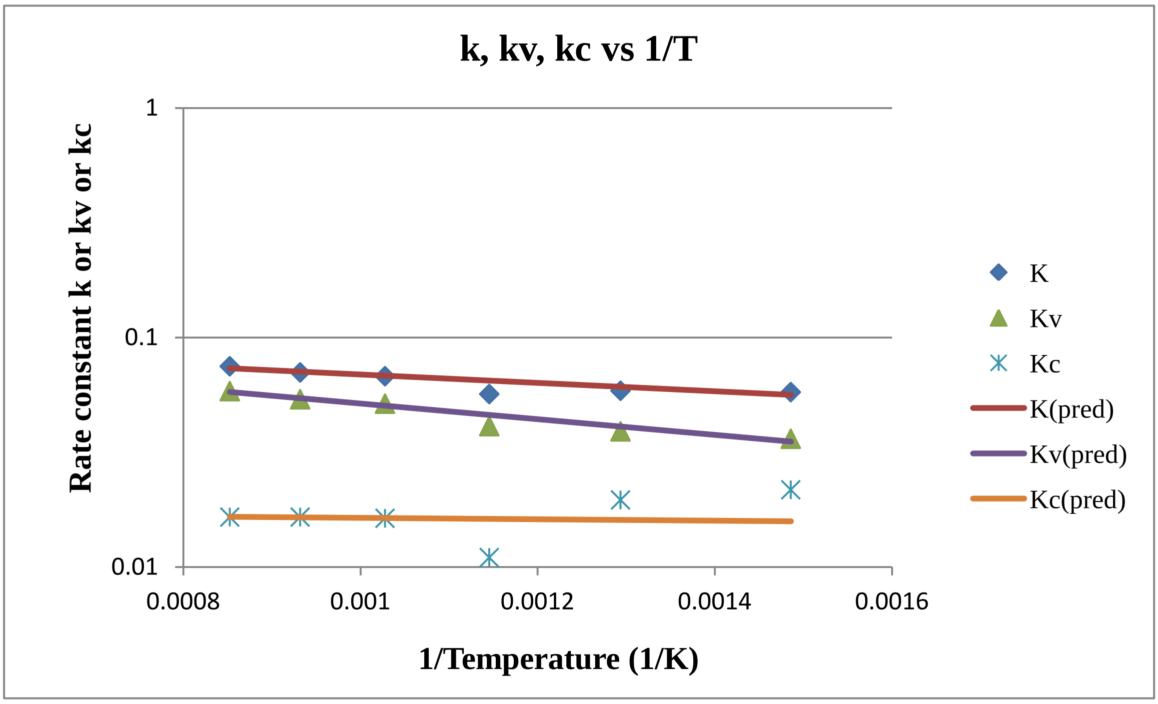


Fig 6.4a k, kv, kc vs. 1/T plot in a semi-logarithmic scale for untreated banana stem

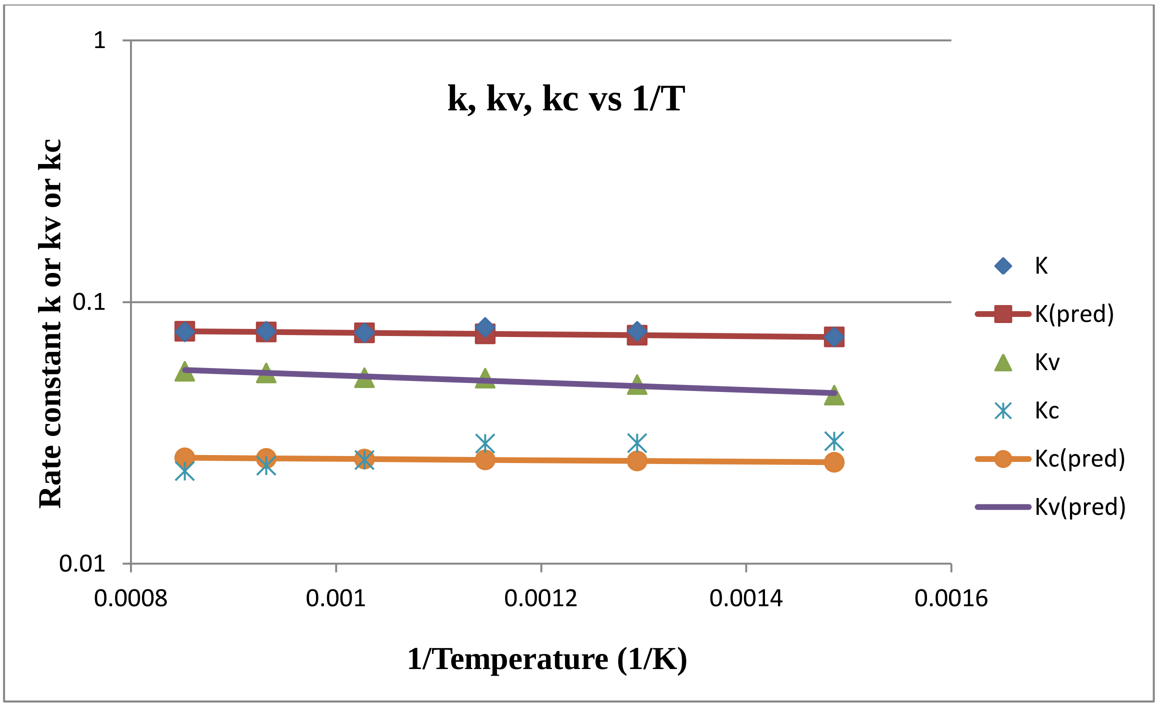


Fig 6.4b: k, kv, kc vs. 1/T plot in a semi-logarithmic scale for banana stem treated with [$NaAl(SiO_3)_2$]

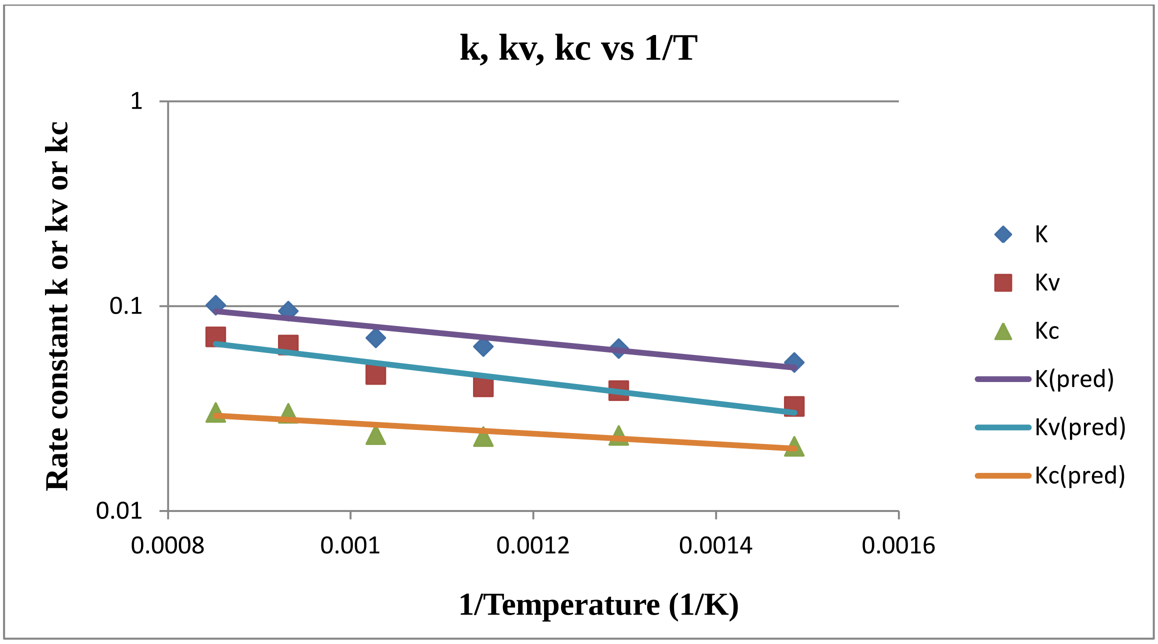


Fig 6.4c: k, kv, kc vs. 1/T plot in a semi-logarithmic scale for banana stem treated with Alumina

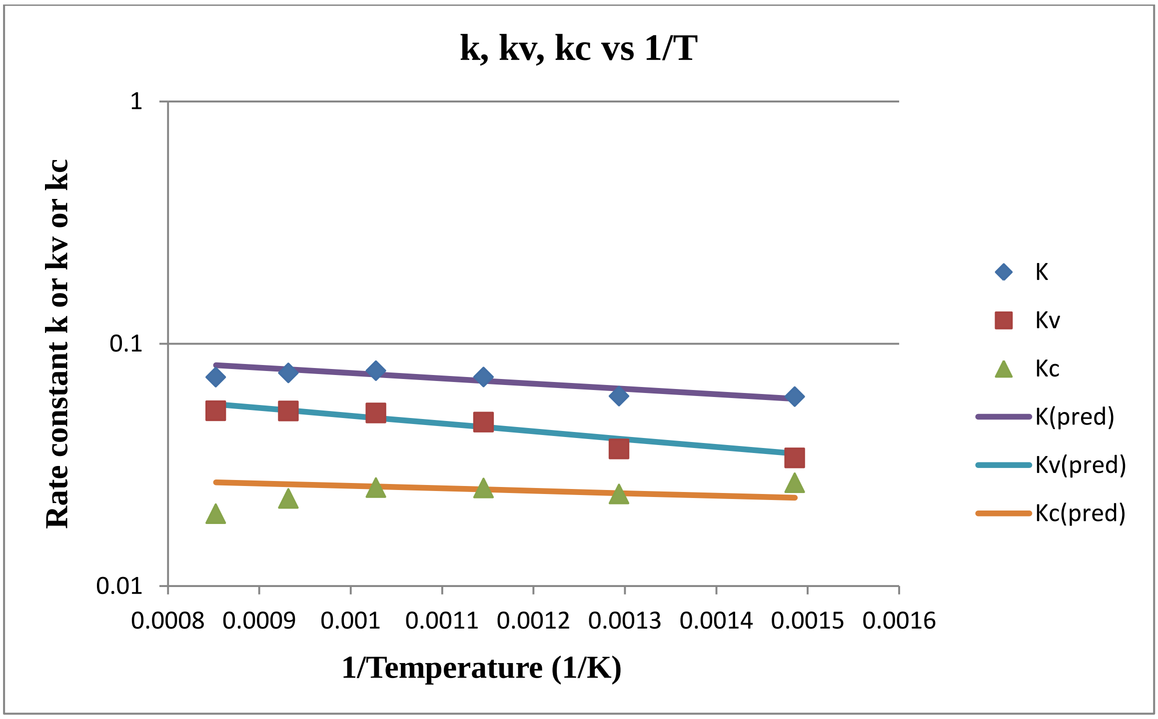


Fig 6.4d: k, kv, kc vs. 1/T plot in a semi-logarithmic scale for banana stem treated with KCl

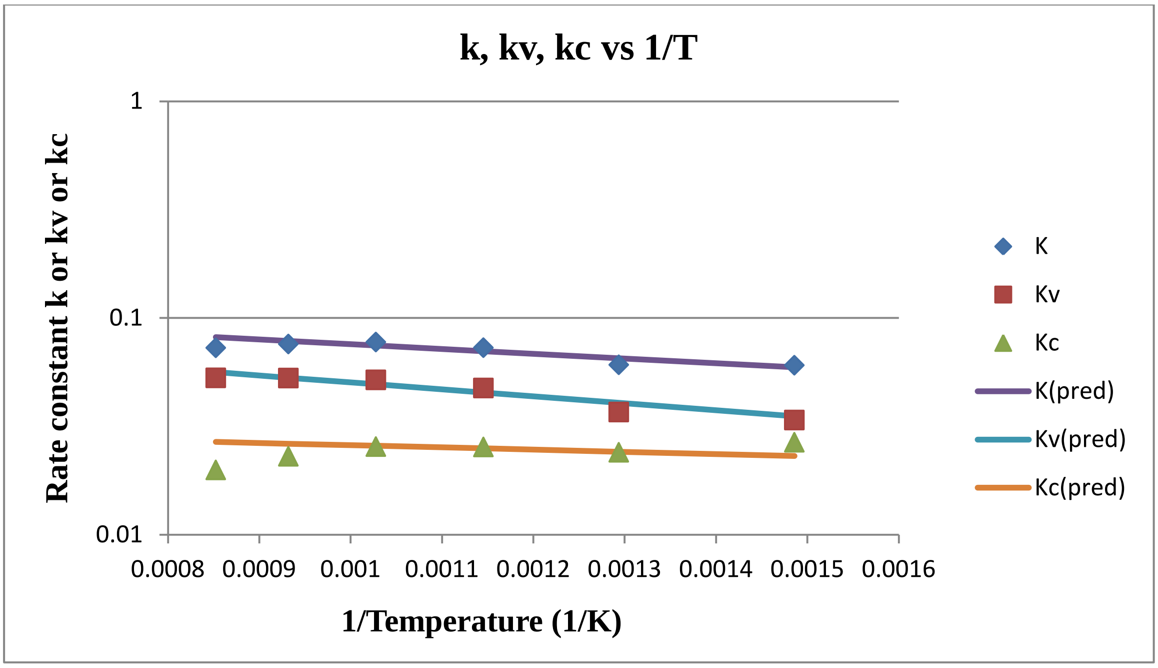


Fig 6.4e: k, kv, kc vs. 1/T plot in a semi-logarithmic scale for banana stem treated with NaCl

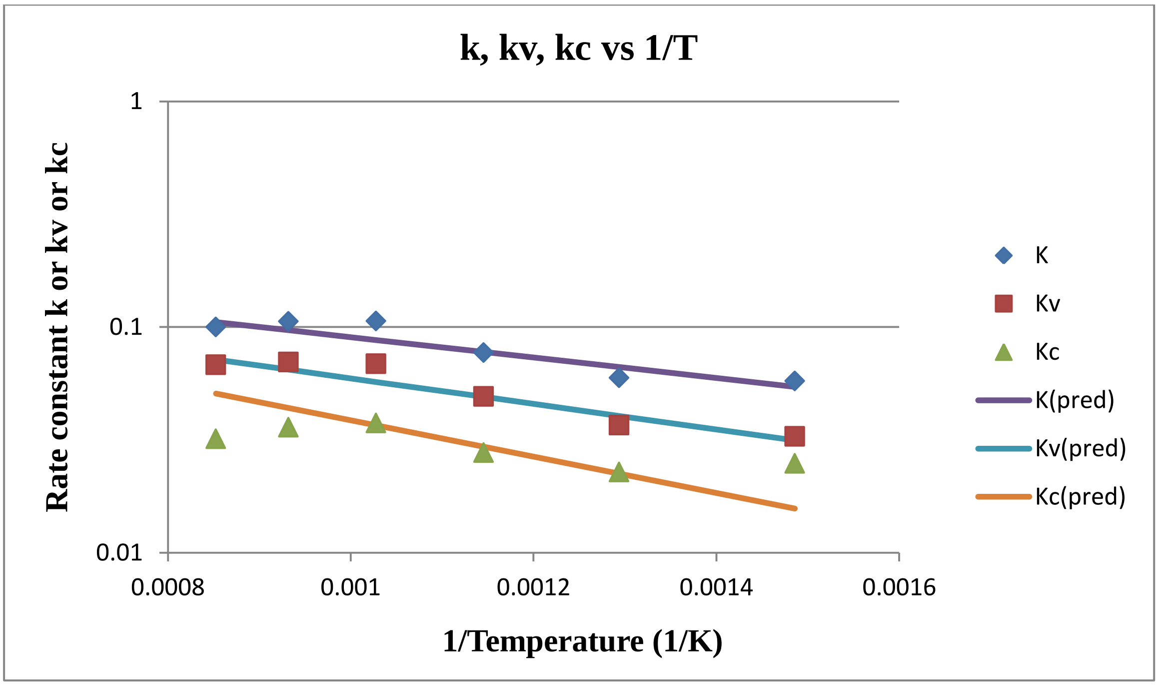


Fig 6.4f: k, kv, kc vs. 1/T plot in a semi-logarithmic scale for banana stem treated with ZnO

From the figures 6.4a to 6.4f, it is observed that the plots for the different rate constants for the untreated and catalytically treated banana stem follow linear nature and hence the Arrhenius equation for the dependence of rate constants on pyrolysis temperature is valid. The values of activation energies and frequency factors are provided in the Table 3.

Table6.3:Calculated activation energies and frequency factors as per Arrhenius law

Type of Feedstock	Reaction rate constant	Activation Energy (kJ/mol)	Frequency Factor (1/min)
Untreated banana stem	k kv kc	0.10499 0.113223 0.017573	3.502023 6.541871 0.594858
Banana stem + Alumina	k kv kc	0.22135 0.18506 0.04791	8.30801392 10.1505626 4.83633694
Banana stem + KCl	k kv kc	0.125281 0.105981 0.032726	4.205055 6.190022 1.949966
Banana pseudo-stem + NaCl	k kv kc	0.182501 0.117796 0.035668	7.583116 7.722542 2.79683
Banana stem + ZnO	k kv kc	0.255738 0.21797 0.246424	8.683973 10.86058 15.44907
Banana stem + Sodiumaluminosilicate	k kv kc	0.082695 0.072093 0.026772	0.654553 2.651168 0.515135

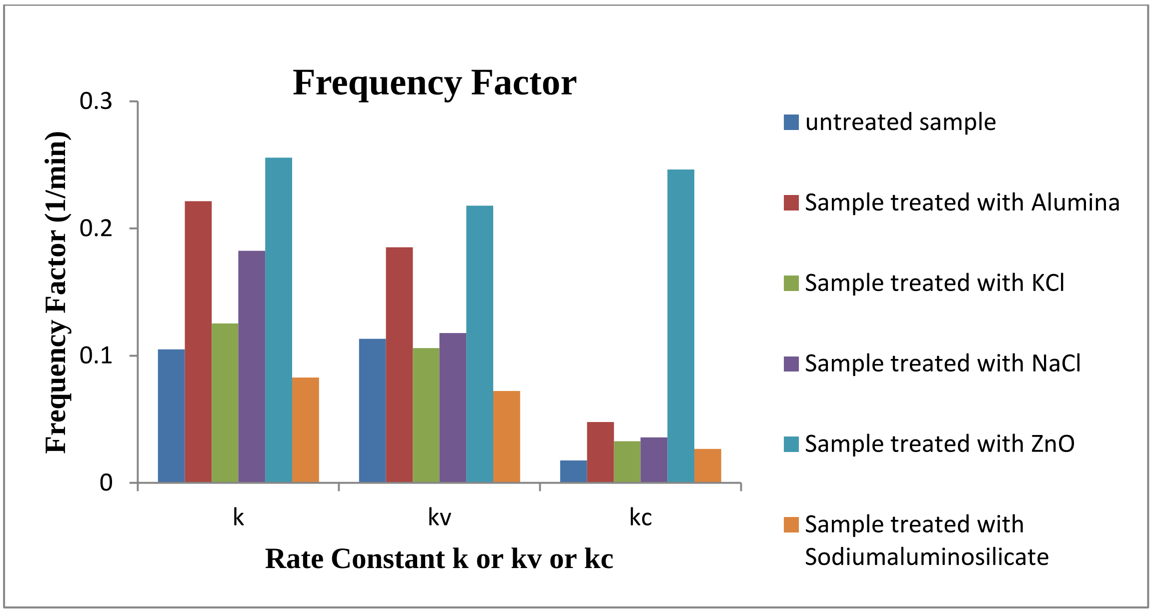


Fig 6.5: Comparison of frequency factors

In the figure 6.5 a comparative study of the other kinetic parameter, frequency factor for the different pyrolysis reactions for untreated and catalytically treated banana stem is done.

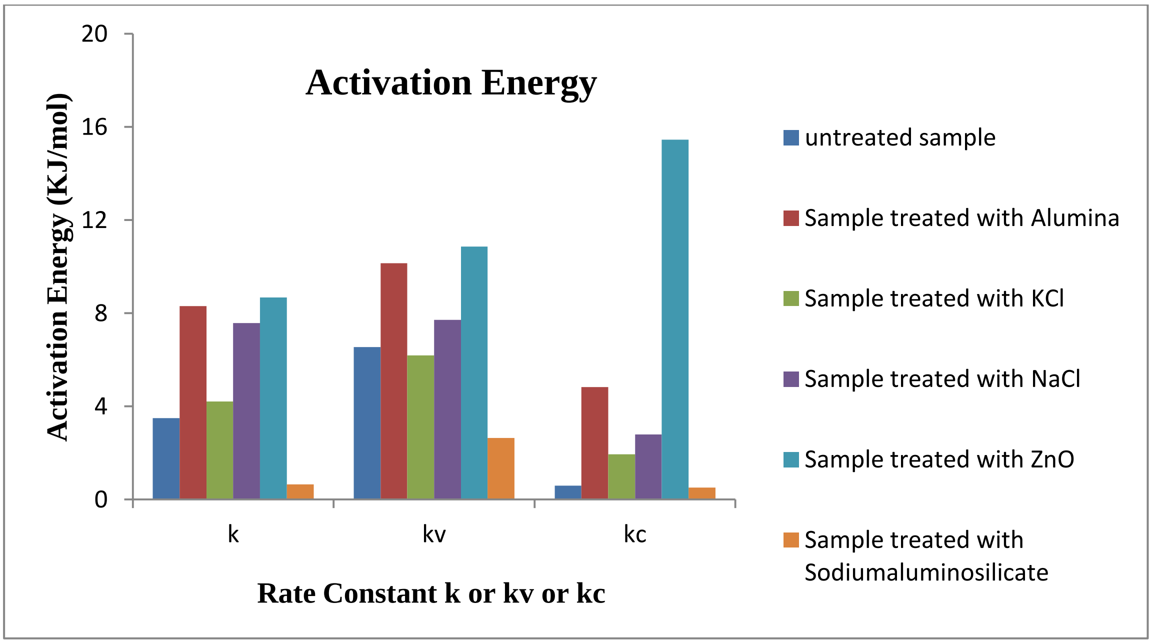


Fig 6.6: Comparison of activation energies

In the figure 6.6, a comparative study of the kinetic parameter, activation energy for the different pyrolysis reactions for untreated and catalytically treated banana stem is done. It is observed that the activation energy is the greatest for the pyrolysis reaction of banana stem treated with ZnO. On the other hand, the activation energies are less for the pyrolysis reactions for both KCl and [$NaAl(SiO_3)_2$] treated banana stem. From the literature survey it is known that [$NaAl(SiO_3)_2$] is a good catalyst for gasification [Wang et al. (2015)]. KCl also acts as an effective catalyst for the pyrolysis of banana stem under the presently studied temperature range.

6.5 Comparison of prediction of dynamic trends of unreacted banana stem, volatiles and char using optimized input parameters through MATLAB R2013a software:

Two schemes are compared to study the dynamic trends of unreacted banana stem, volatiles and char. Scheme 1 is proposed by Bandyopadhay et al. (*1999*) for the series-parallel reaction pathway of the pyrolysis of biomass where all the volatiles are lumped to form a single volatile product and similarly solids are lumped to form char. Scheme 2 is proposed by Aramideh et al. (*2015)* for the lumped, multi-component multi-step reaction mechanism.

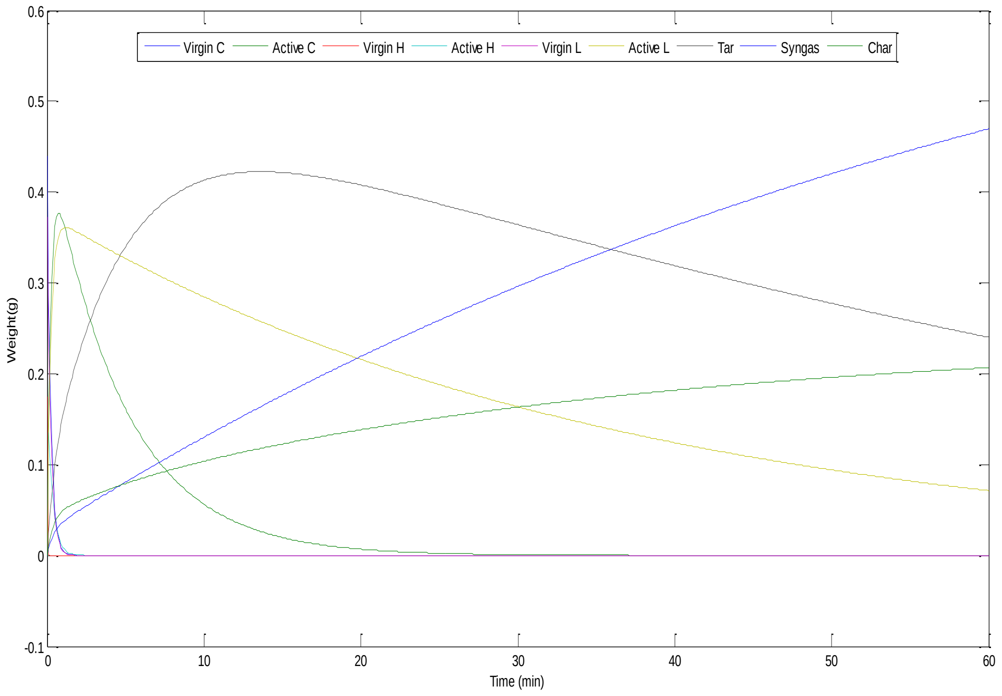


Fig 6.7: The dynamic trends of unreacted banana stem and the volatiles and char formation curves generated in MATLAB R2013a at 400ºC.

Figure 6.7 shows the curves generated in MATLAB R2013a (using simultaneous ODE 45 method) by solving the mass balance equations as formulated from the kinetic scheme described in the theoretical analysis.

From figure 6.7 the dynamic trends of unreacted banana stem and formation of the pyrolysis products namely, char and the volatiles at 400ºC are observed.

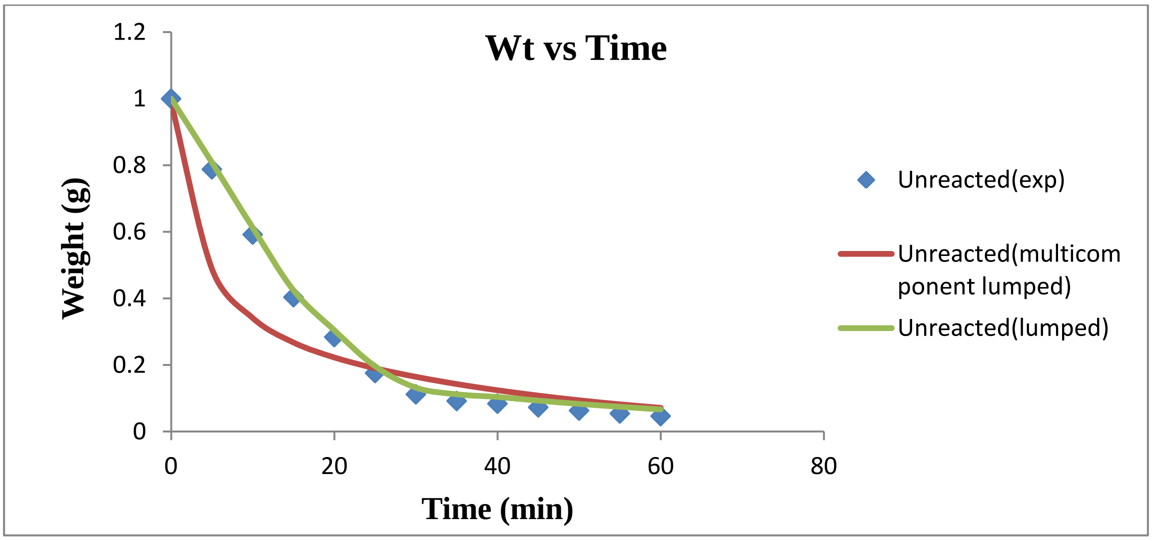


Fig: 6.7a: Comparative study of the experimental, lumped and multicomponent lumped trends of the unreacted banana stem from the pyrolysis process at 400ºC

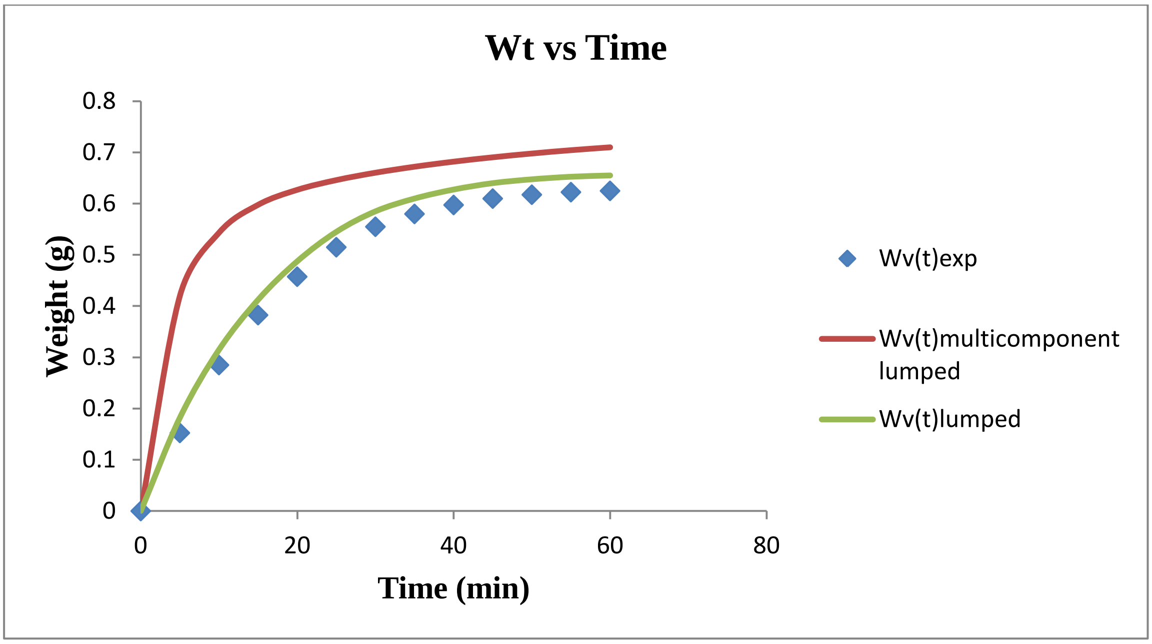


Fig 6.7b: Comparative study of the experimental, lumped and multicomponent lumped trends of the volatile formation from the pyrolysis process at 400°C

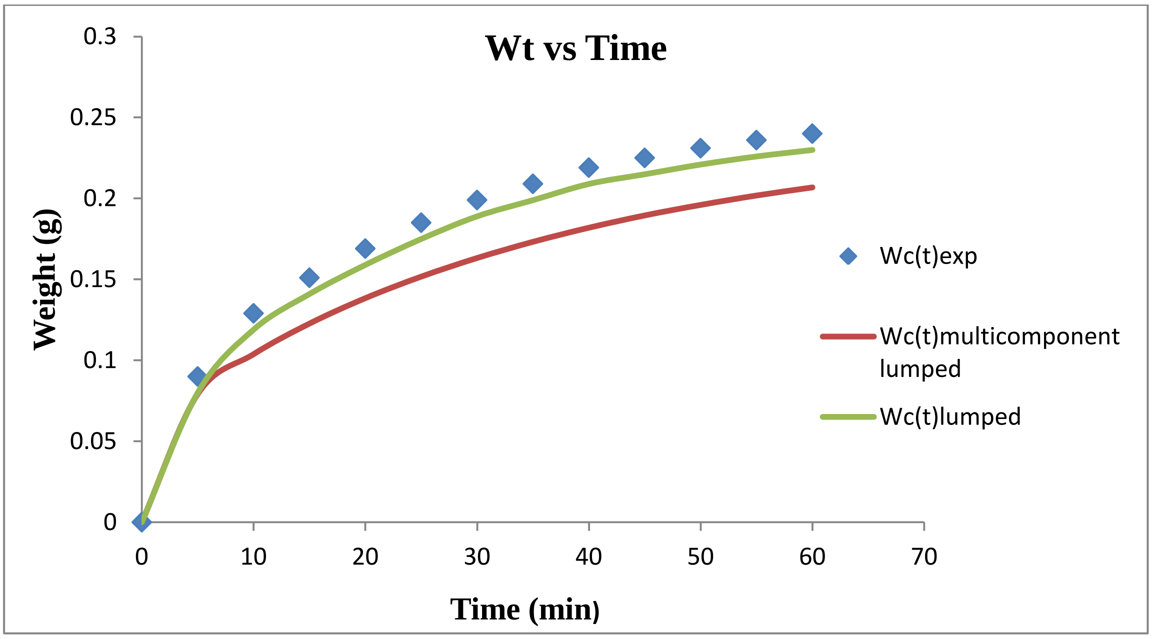


Fig 6.7c: Comparative study of the experimental, lumped and multicomponent lumped trends of the char formation from the pyrolysis process at 400°C

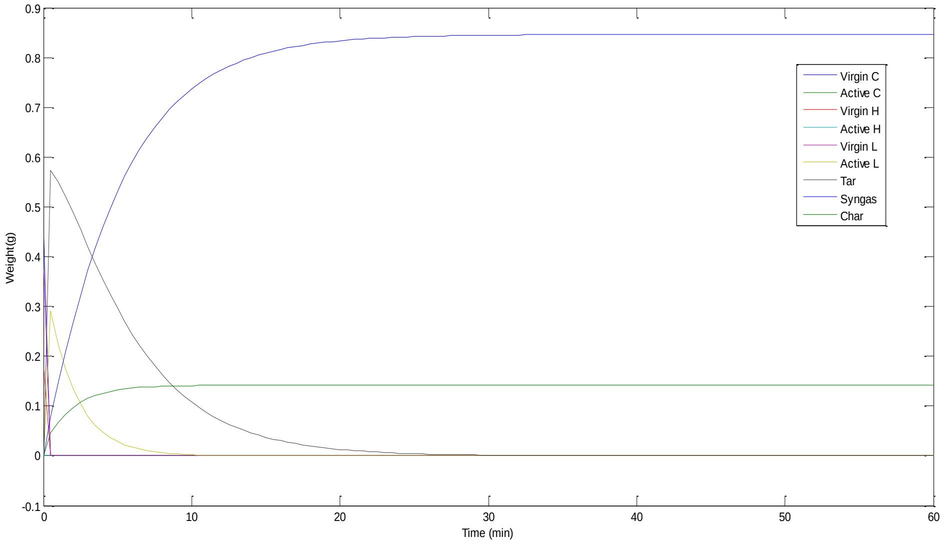


Fig 6.8: The dynamic trends of unreacted banana stem and the volatiles and char formation curves generated in MATLAB R2013a at 500ºC.

From figure 6.8 it is observed that at 500ºC, after the pyrolysis of the banana stem, the volatiles and char formation reached their state of saturation after 20 minutes and 10 minutes respectively.

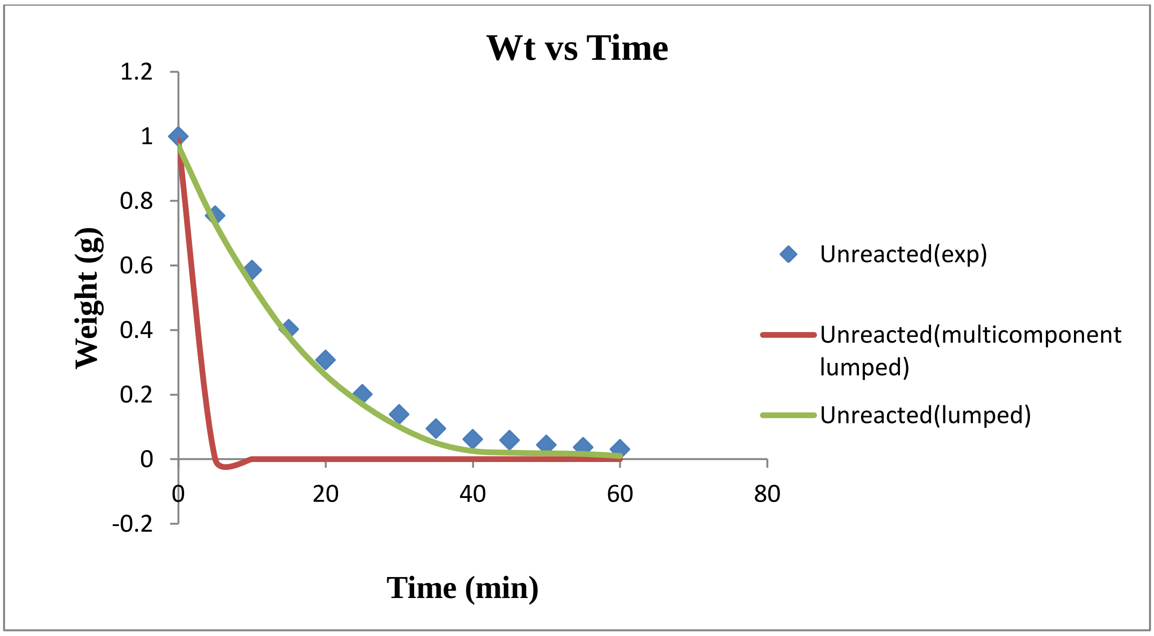


Fig 6.8a: Comparative study of the experimental, lumped and multicomponent lumped trends of the unreacted banana stem from the pyrolysis process at 500ºC

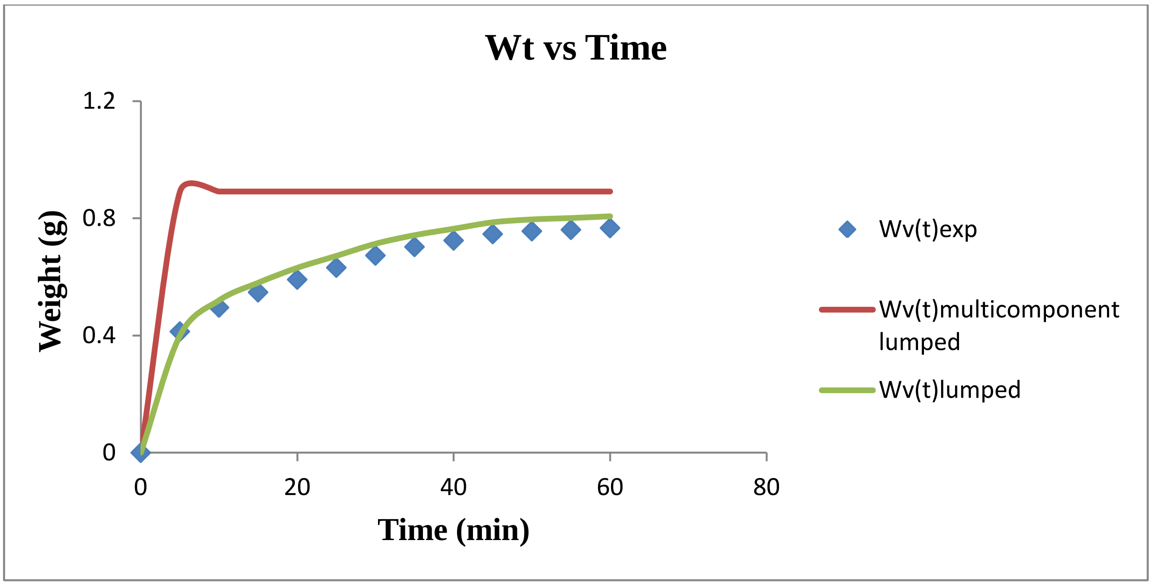


Fig 6.8b: Comparative study of the experimental, lumped and multicomponent lumped trends of the volatile formation from the pyrolysis process at 500°C

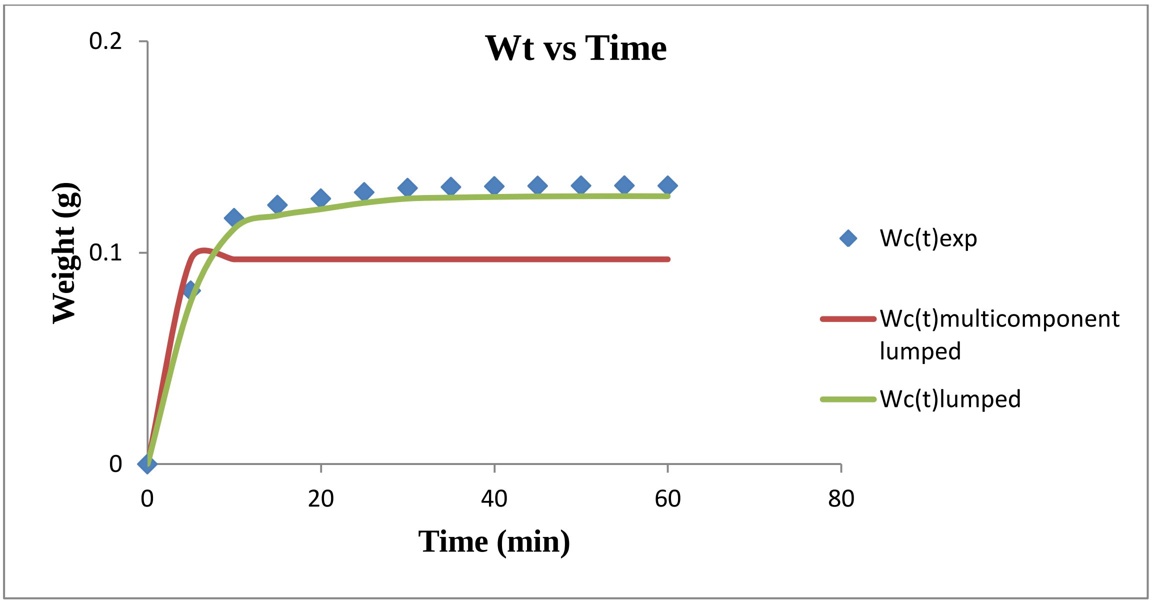


Fig 6.8c: Comparative study of the experimental, lumped and multicomponent lumped trends of the char formation from the pyrolysis process at 500°C

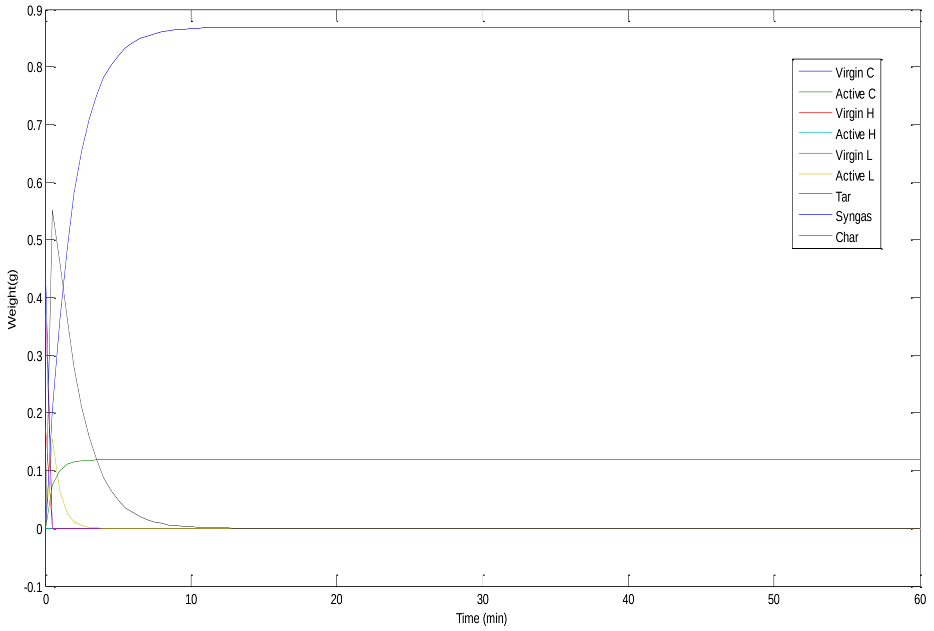


Fig 6.9: The dynamic trends of unreacted banana stem and the volatiles and char formation curves generated in MATLAB R2013a at 550°C

From figure 6.9 it is observed that at 550ºC, after the pyrolysis of the banana stem, the volatile and char formation reached their state of saturation after 10 minutes and 5 minutes respectively.

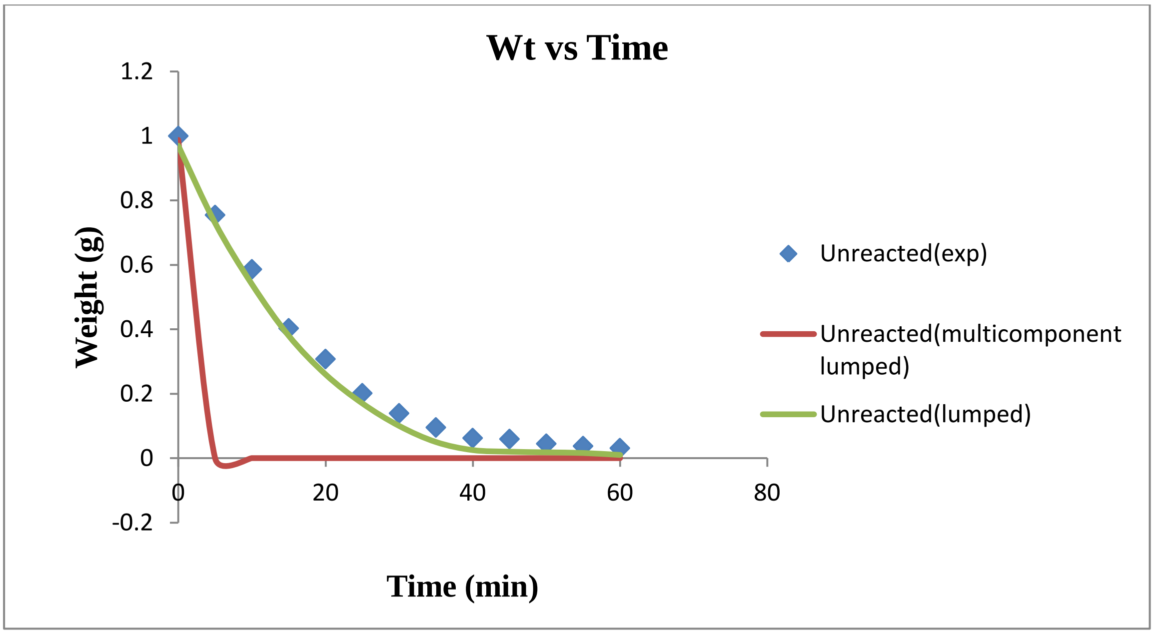


Fig 6.9a: Comparative study of the experimental, lumped and multicomponent lumped trends of the unreacted banana stem from the pyrolysis process at 550°C

From the figures 6.8a and 6.9a it is observed that there is no change in patterns for the unreacted banana stem at the pyrolysis temperature of 500ºC and 550ºC as state of saturation is reached after 5 minutes.

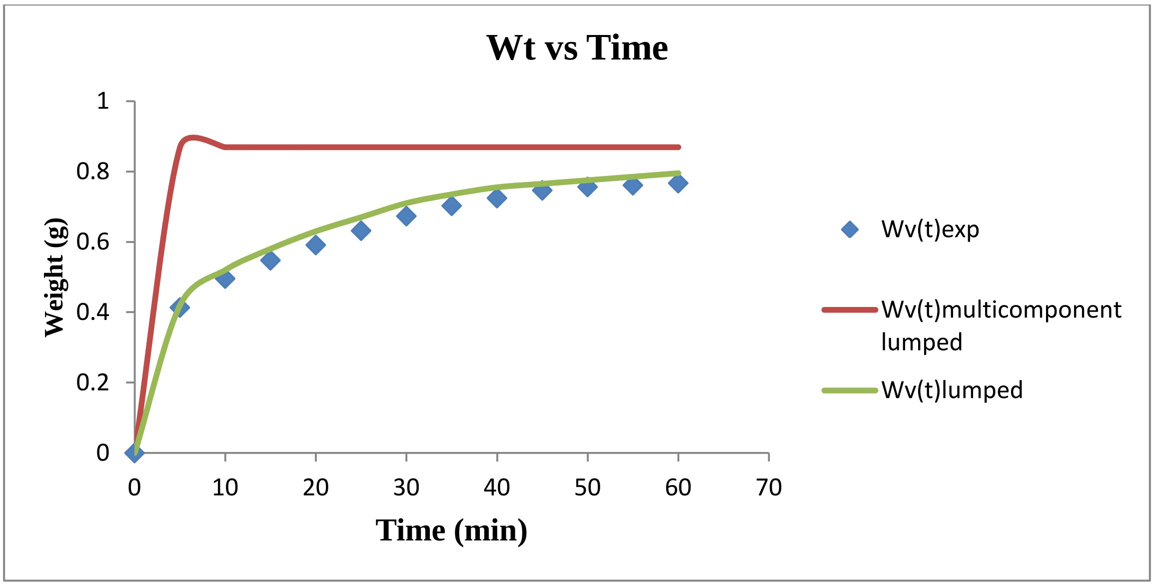


Fig 6.9b: Comparative study of the experimental, lumped and multicomponent lumped trends of the volatile formation from the pyrolysis process at 550ºC

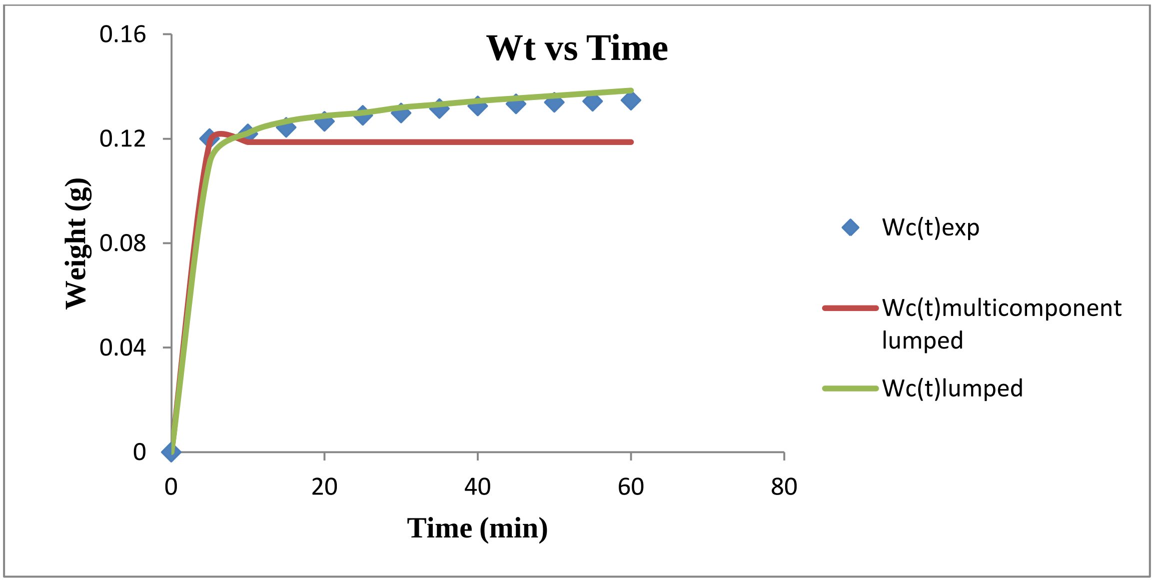


Fig 6.9c: Comparative study of the experimental, lumped and multicomponent lumped trends of the char formation from the pyrolysis process at 550ºC

From the figures 6.7a to 6.7c, 6.8a to 6.8c and 6.9a to 6.9c it is observed that the experimental results are in good agreement with the lumped model but there is a difference between the prediction of multicomponent lumped model and the experimental data. This may be due to the fact that the pyrolysis of cellulose, hemicellulose and lignin are not fully non-interactive. The understanding of interactions between individual products of pyrolysis of different components namely cellulose, hemicellulose and lignin may reveal the exact reason for the deviation of experimental results from the multicomponent lumped model.

6.6 Optimum time for bio-treatment of banana stem:

6.6.1 Pyro-oil yield from yeast treated banana stem:

In order to determine the optimum time for bio-treatment, incubation time (h) has been varied from 24 to 65 hours maintaining the incubation temperature at the optimum temperature of growth of Baker’s yeast, i.e., 37°C.

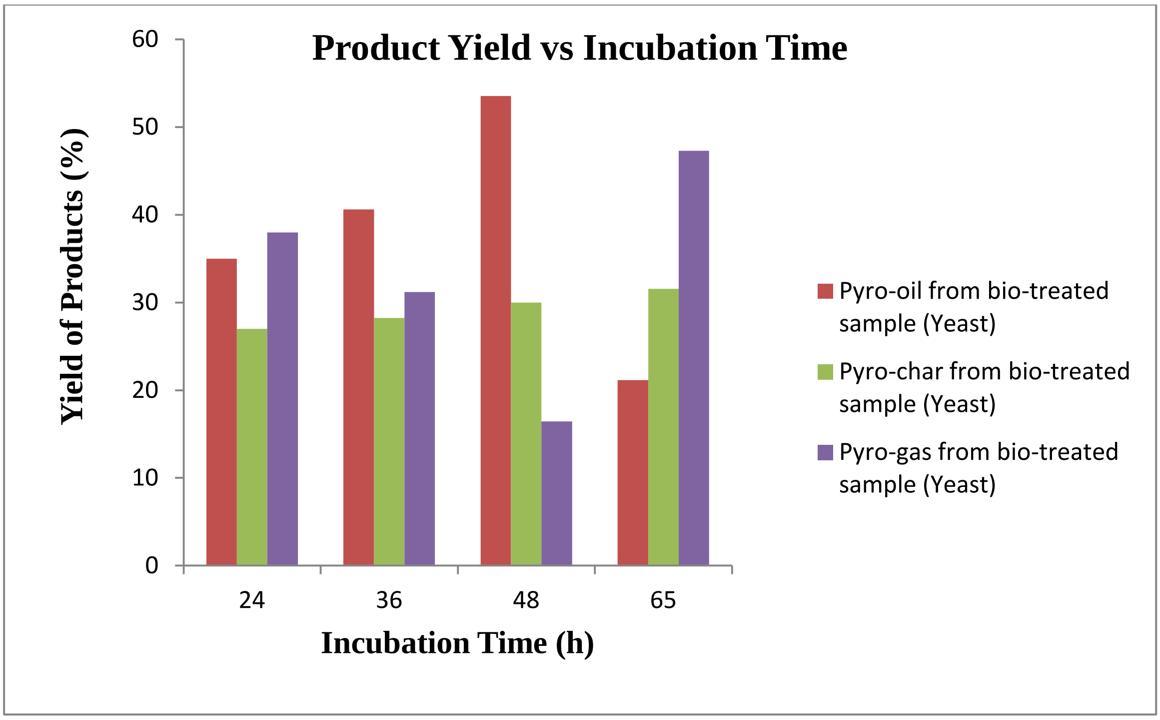


Fig 6.10: Yield of products from yeast-treated banana stem (%) at different incubation time (h) (pyrolysis temperature: 500°C)

From the figure 6.10 it is observed that the variation of incubation time (h) has a very pronounced effect on the product yields of the pyrolysis process at 500 °C. From the analysis of the figure 6.10 it is seen that the optimum condition for the maximum pyro-oil yield from the pyrolysis of yeast treated banana stem is 48h incubation time at an incubation temperature of 37ºC. At the optimum condition, the pyro-oil yield is 53.54 wt %. The pyro-char yield increases gradually with the increase in incubation time from 24h to 65h. At the optimum incubation time (48h) the pyro-gas yield is minimum (16.46 wt %).

6.6.2 FTIR Analysis:

FTIR Spectroscopy, model IR-Prestige-21 SHIMATZU make, Japan, is used to identify various characteristic functional groups present in the untreated banana stem and the bio- treated banana stem varying the incubation time from 24h to 48 h.

Table6.4: Characteristic IR absorption frequencies for the indicated organic functional groups present in the treated and untreated banana stem.

Functional group	Type of Vibration	Characteristic Absorptions (1/cm)
Alcohol		
O-H	stretch, H-bonded	3200-3600
O-H	stretch, free	3500-3700
C-O	stretch	1050-1150
Alkane		
C-H	stretch	2850-3000
-C-H	bending	1350-1480
Alkene		
=C-H	stretch	3010-3100
=C-H	bending	675-1000
C=C	stretch	1620-1680
Alkyl Halide		
C-F	stretch	1000-1400
C-Cl	stretch	600-800
C-Br	stretch	500-600
C-I	stretch	500
Alkyne		
C-H	stretch	3300
$-C\equiv C-$	stretch	2100-2260

Amine		
N-H	stretch	3300-3500
C-N	stretch	1080-1360
N-H	bending	1600
Ether		
C-O	Stretch	1000-1300

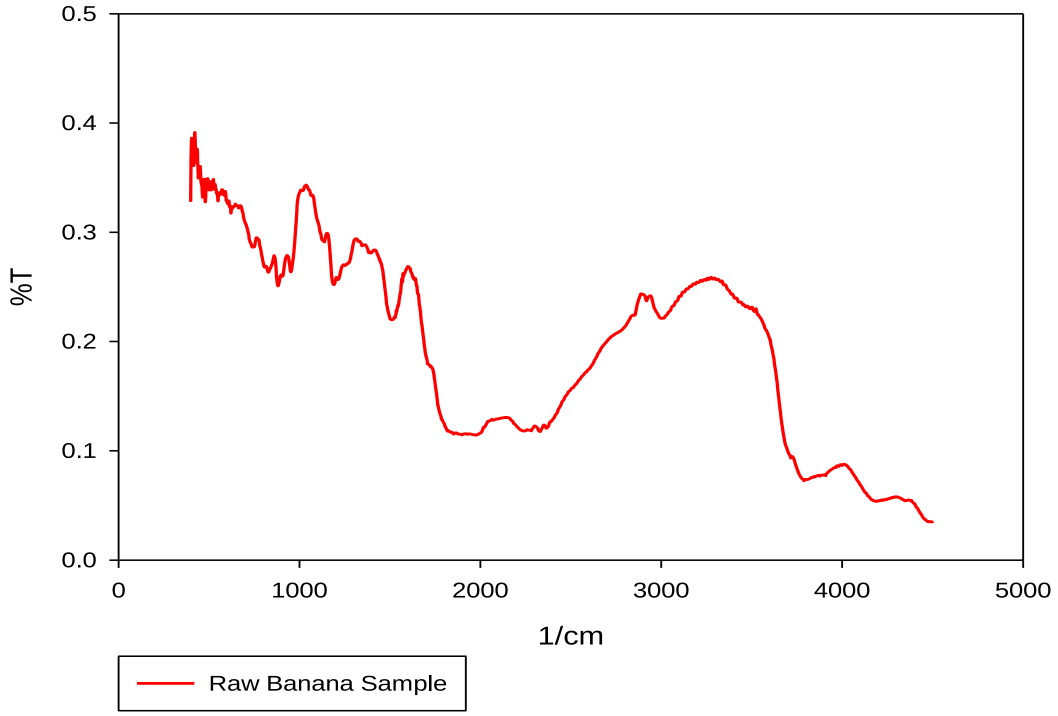


Fig 6.11: FTIR spectrum of the untreated banana stem

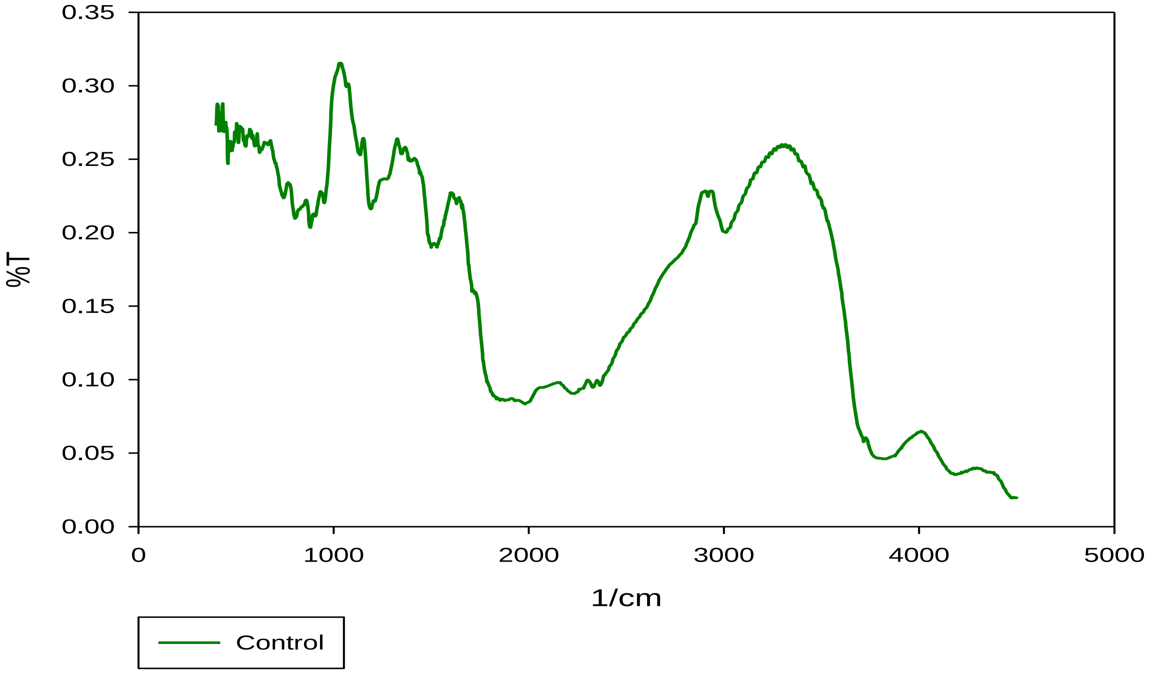


Fig 6.12: FTIR spectrum of control sample

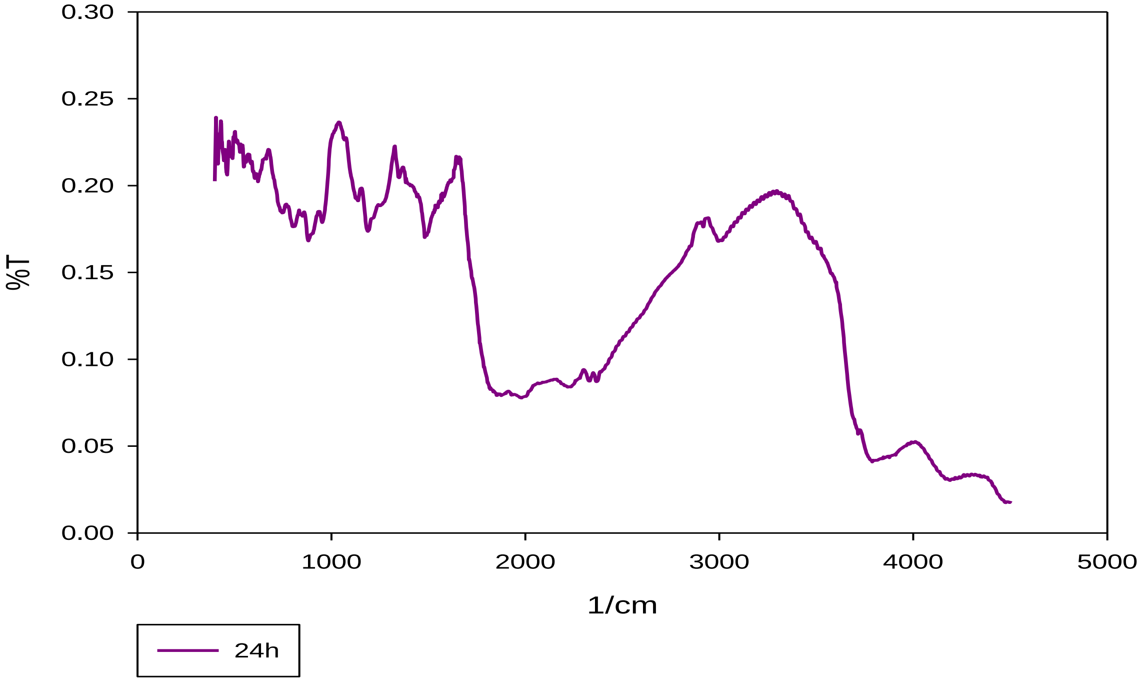


Fig 6.13: FTIR spectrum of yeast treated banana stem with 24h incubation time

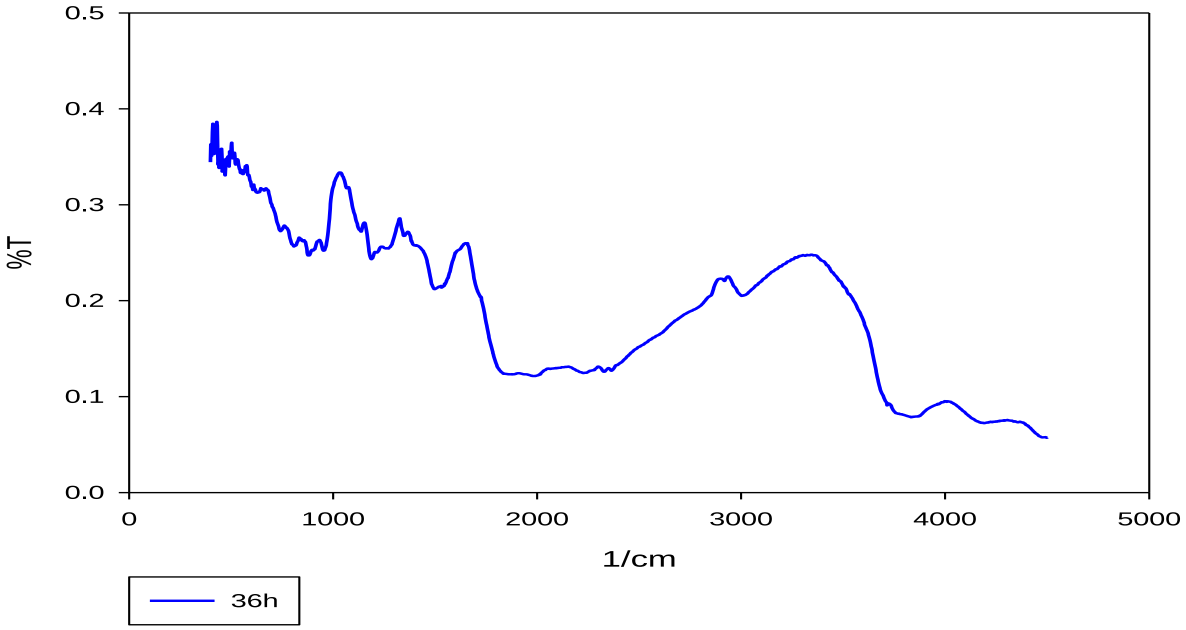


Fig 6.14: FTIR spectrum of yeast treated banana stem with 36h incubation time

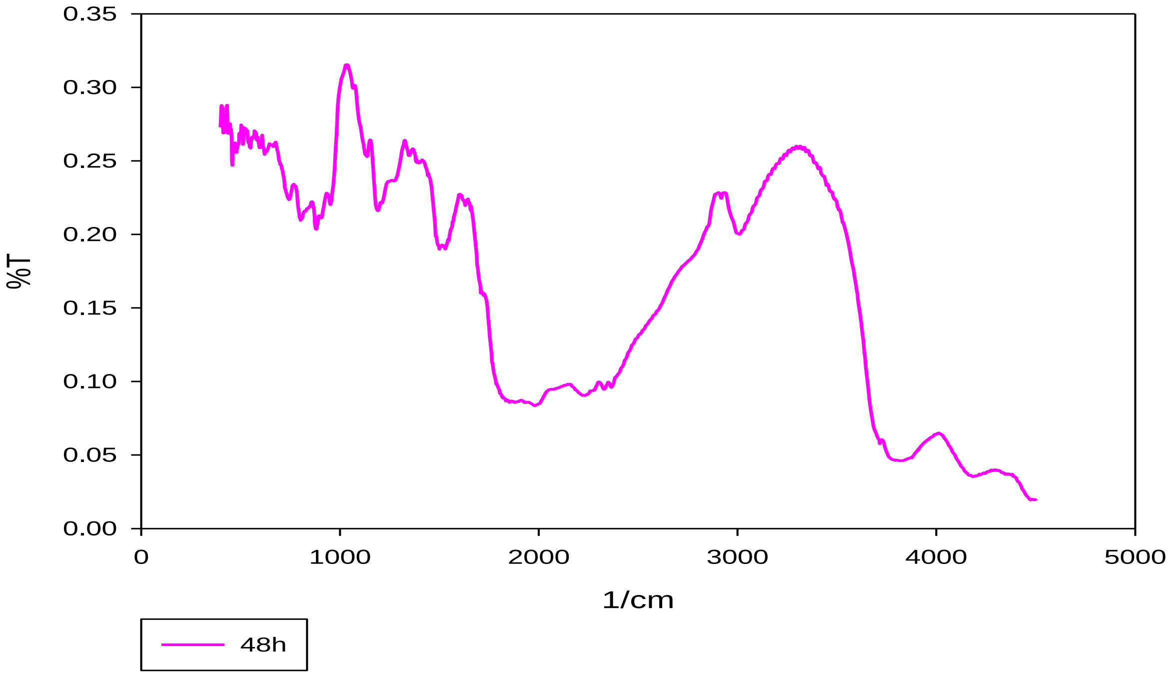


Fig 6.15: FTIR spectrum of yeast treated banana stem with 48h incubation time

The FTIR graphs are plotted with % transmittance (% T) in the y-axis and frequency (cm^{-1}) in the x-axis. From the figures 6.11 to 6.15 the presence of a broad absorbance peak of O – H stretching vibration between 3200 and 3400 cm^{-1} is observed which indicated the presence of water impurities and other polymeric O – H in the samples. The absorbance peak of C – H vibrations between 2850 and 3000 cm^{-1} and C - H vibrations of the several small peaks clustering together between 1325 and 1410 cm^{-1} points out the presence of alkane. The absorption peak of C-O stretching vibration specifies the presence of ether in the samples. The presence of several small and overlapping peaks in the fingerprint region with frequency of 500 to 800 cm^{-1} indicates the presence of several alkyl halides in the treated and untreated feedstock. The presence of a broad trough in the frequency range of 2000 to 3000 cm^{-1} confirms the presence of carboxylic acids in the samples.

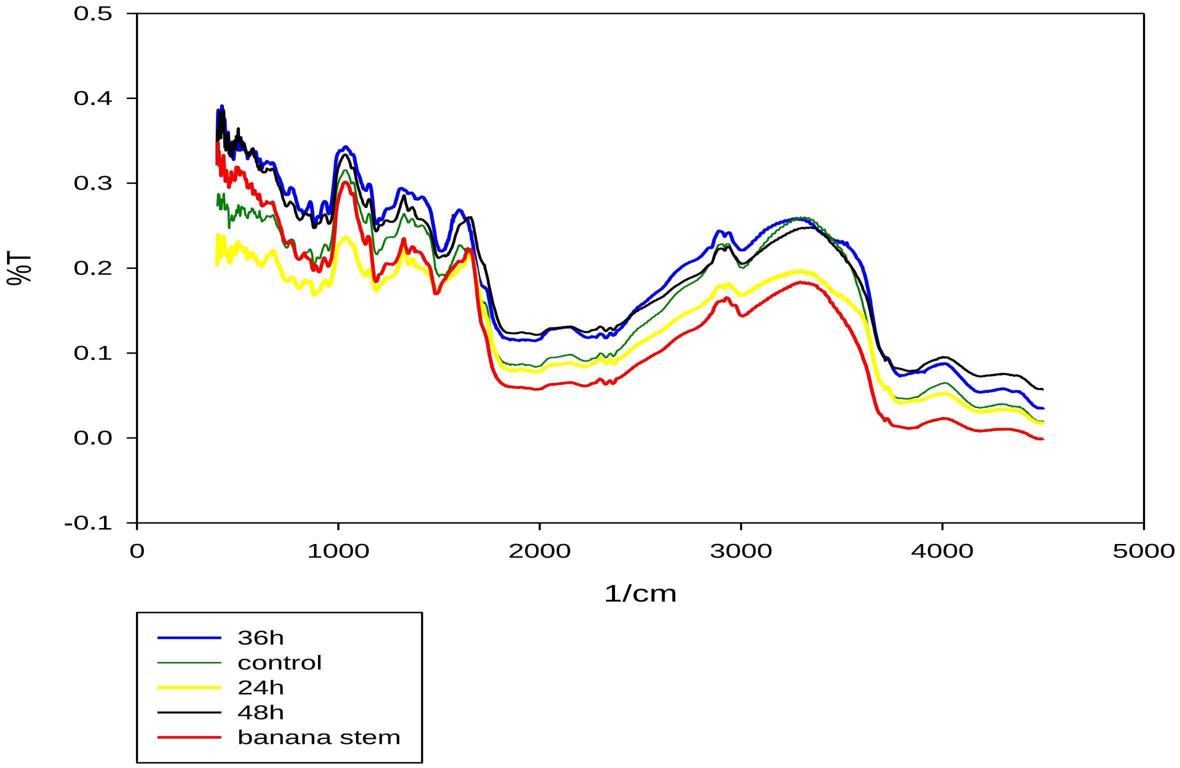


Fig 6.16: Comparative study of the FTIR spectra of the untreated and yeast treated feedstock with varying incubation time (24h, 36h and 48h).

Figure 6.16 shows the comparative study of the untreated banana stem, its control and yeast treated banana stem varying the incubation time (24h, 36h and 48h) at a fixed incubation temperature of 37ºC. It is clearly noticed from the figure 6.16 that the broad trough present in the frequency range of 2000 to 3000 cm^{-1} is due to the presence of carboxylic acid group. The presence of the carbon-oxygen double bond C=O is seen at about 1800 cm^{-1}. A trough just under 3000 cm^{-1} can be ignored because that is probably due to C-H bond which is not much useful in this case. The other useful bond is the O-H bond. The O-H bond in an alcohol gets absorbed at a higher wavelength than that of acid between 3200 and 3550 cm^{-1}.The presence of OH in the acid may be due to the occurrence of the troughs at 2000 to 3000 cm^{-1} because as the decarboxylation time increases the depth of the trough decreases due to the decrease in concentration of carboxylic acid. The greater the depth of the trough, the larger is the concentration of the presence of carboxylic acid in the sample. From the figure 6.16 it is observed that the depth is minimum for yeast treated banana stem with 48h incubation time. Hence 48h incubation time is taken as the optimum time for pre-treatment.

So it is again established that 48h treatment time is the best time for yeast treated banana stem as it gives maximum pyro-oil yield at pyrolysis temperature of 500ºC.

6.7 Pyrolysis kinetics of bio-decarboxylated banana stem:

6.7.1 Weight loss history for feedstock treated with yeast:

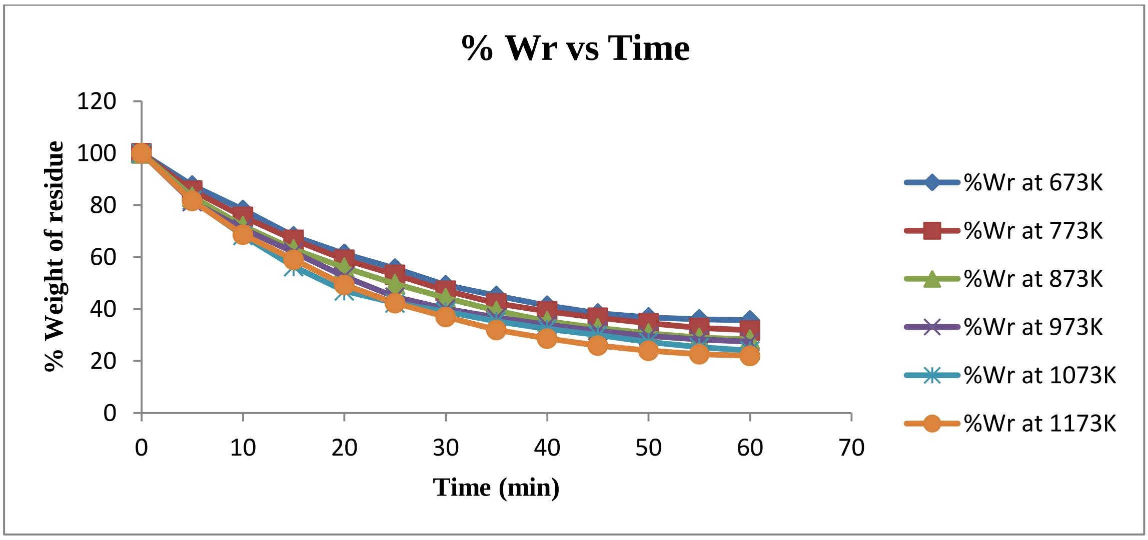


Fig 6.17: Comparative curve of % Wt residue to Time (banana stem treated with yeast)

From figure 6.17 it is observed that there is a gradual weight loss of the yeast treated banana stems as it is pyrolyzed to produce volatiles and char with the increase in temperature over a time period of 1h. At each time the weight loss is increasing with the increase in pyrolysis temperature due to the increase of rate of pyrolysis. Among all the untreated, catalytically treated and yeast treated banana stems, it is observed that the greatest weight loss took place for the banana stem treated with yeast for 48h.

6.7.2 Lumped kinetics for pyrolysis of yeast treated banana stem:

The primary kinetics for yeast treated banana stem 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 and frequency factors reported in Table5. All the rate constants are calculated from the experimental results in the temperature range of 673K to 1173K and are superimposed with the predicted rate constants.

Table6.5: Calculated activation energies and frequency factors as per Arrhenius law for banana stem treated with yeast

Type of Feedstock	Reaction rate constant	Activation Energy (kJ/mol)	Frequency factor (1/min)
banana stem + yeast	k kv kc	3.776219 6.096822 1.948469	0.084992 0.083201 0.018704

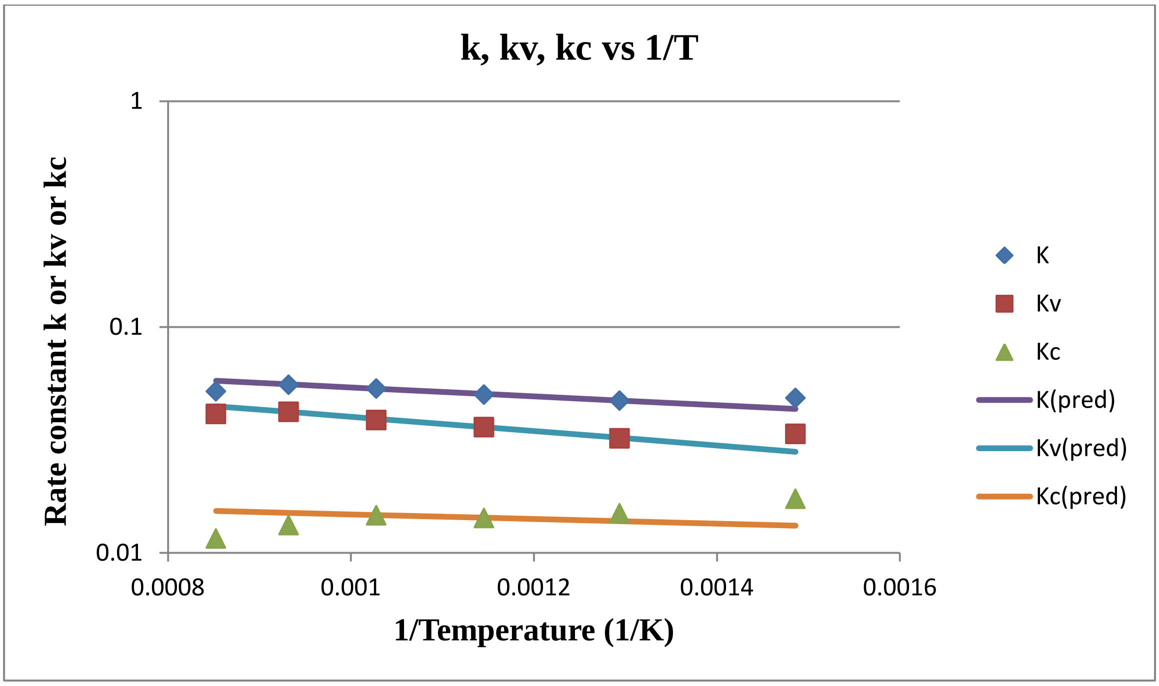


Fig 6.18: k, kv, kc vs. 1/T plot in a semi-logarithmic scale for banana stem treated with yeast

From figure 6.18 it is observed that the plots for the different rate constants for the yeast treated banana stem follow linearity. The experimental results are according to the predicted Arrhenius Law.

6.8 Comparison of weight loss history of untreated and yeast treated banana stem by TGA:

In the thermogravimetric analysis, the samples are exposed to a heating program at two heating rates 10ºC/min and 20ºC/min and the weight loss is simultaneously recorded over the temperature range from room temperature to 900ºC. The samples under analysis are the untreated banana stem and the banana stem pre-treated with yeast at an incubation temperature of 48h at 37ºC. Thermogravimetric analysis (TGA) is performed on a Perkin Elmer make (Singapore) model (Pyris Diamond TG/DTA). Nitrogen atmosphere (150ml/min) is used in this analysis. Platinum crucible is used with alpha alumina powder as reference.

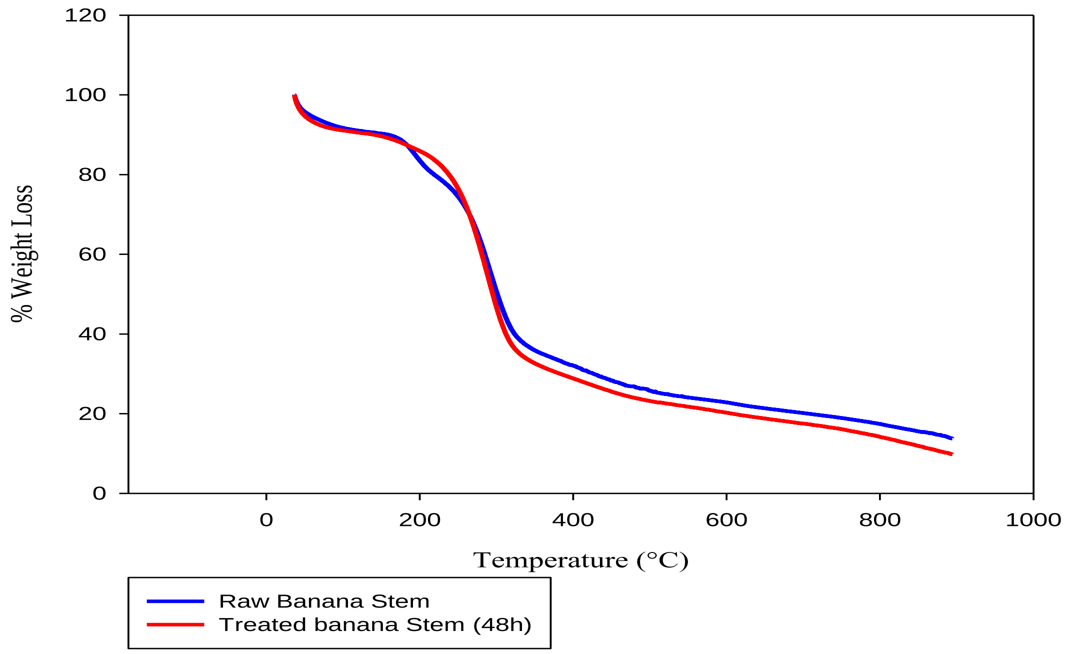


Fig 6.19a: TGA curves of the pyrolysis process of the untreated and yeast treated banana stem at the heating rate of 10°C/min

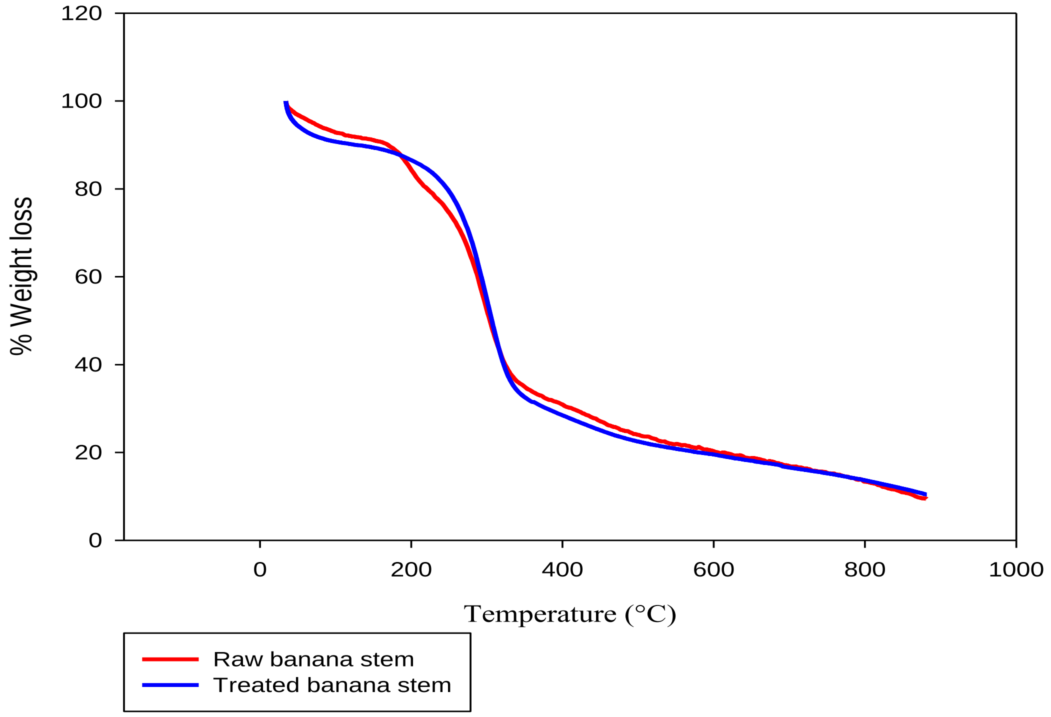


Fig 6.19b: TGA curves of the pyrolysis process of the banana stem and the yeast treated banana stem at the heating rate of 20°C/min

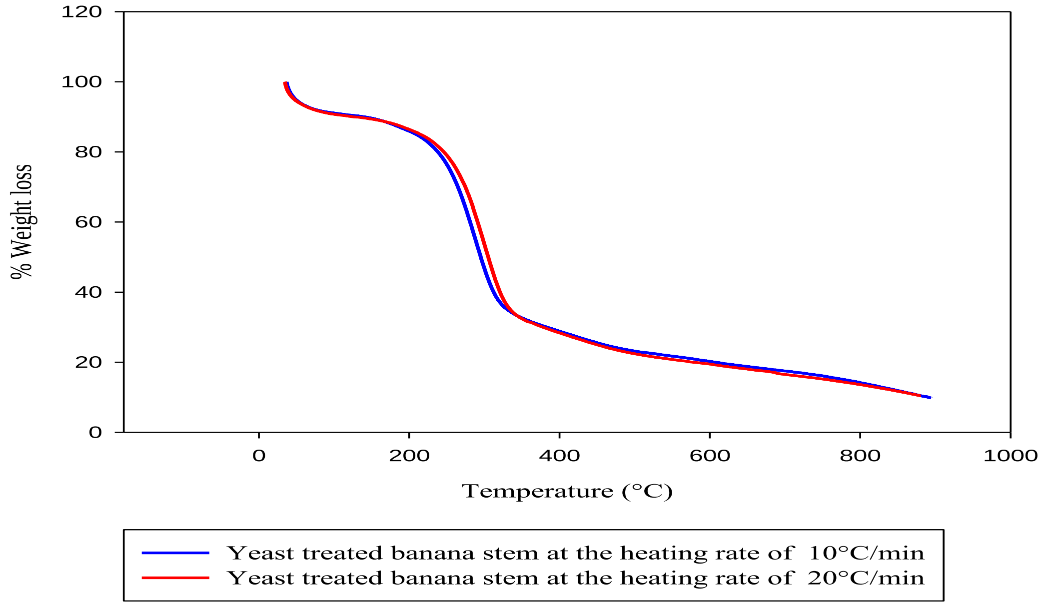


Fig 6.19c: TGA curves of the pyrolysis process of the yeast treated banana stem with 48h incubation time at both the heating rates of 10 and 20°C/min

The figures 6.19a to 6.19c show the TGA profiles for untreated and yeast treated banana stem at both the heating rates of 10 and 20°C/min for the temperature range of 34ºC to 900ºC. The patterns of weight loss profile for the bio-treated banana stem resemble those for untreated ones. For both the heating rates the weight profile is steeper for bio-treated banana stem signifying higher pyrolysis rate with respect to the raw banana stem.

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6.9 Product yields obtained from the pyrolysis of banana stem:

After the completion of pyrolysis of banana stem the condensable fraction of the volatile, pyro-oil is collected from the condensing unit. The solid residual part, pyro-char is also collected from the reactor. Then both the products' yields are calculated by weighing it with a balance. Then finally the pyro-gas yield is calculated by subtracting both the amount of pyro-oil and pyro-char from 100. These variations in yields of the products (char, oil and gases) with the pyrolysis temperature are shown in the figure 6.20.

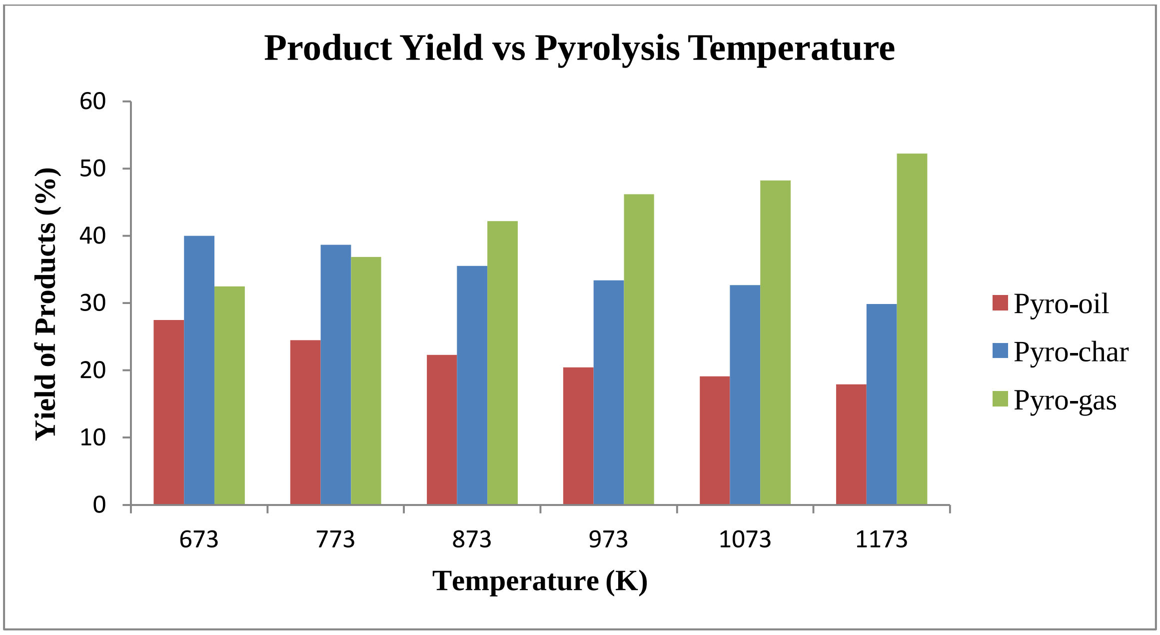

Fig 6.20: Yield of products (%) from pyrolysis of banana stem at different temperatures (K)

From the analysis of figure 6.20 the yield of pyro-oil increases to 27.5 wt% at 673K and then it gradually decreases to 18 wt% at 1173K which means the yield of pyro-oil is maximum at the temperature of 673K.

On the other hand the pyro-char yield decreases with the rise in pyrolysis temperature from 40 wt% at 673K to 30 wt% at 1173K. Under the present experimental conditions, the trends of the products show a distinct influence of temperature on the fractional yields of solid pyro-char and volatiles.

6.10 Product yields from pyrolysis of banana stem using different catalysts (chemical route)

The various product yields (pyro-oil, pyro-char and pyro-gas) from catalytically treated biomass pyrolysis are plotted against varying temperatures from 673K to 1173K. The five different catalysts used for the experiments were Potassium Chloride (KCl), Zinc Oxide (ZnO), Sodium Chloride (NaCl), Alumina (Al_2O_3) and Sodiumaluminosilicate [$NaAl(SiO_3)_2$].

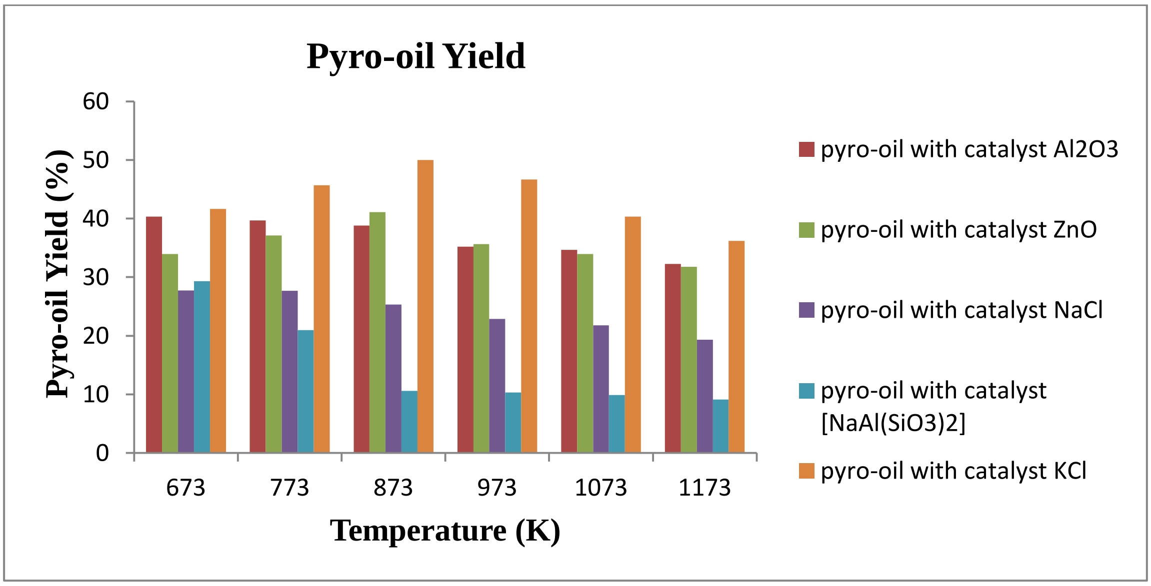

Fig 6.21: Pyro-oil yield (%) from catalytically treated banana stem at different temperatures (K)

From figure 6.21 the trends of pyro-oil yield from pyrolysis of banana stem treated with five different catalysts are compared at different pyrolysis temperature. From the figure it is also observed that the maximum pyro-oil yield is obtained from the pyrolysis of banana stem treated with catalyst Potassium Chloride (KCl), its pyro-oil yield being 50 wt % at 873K .

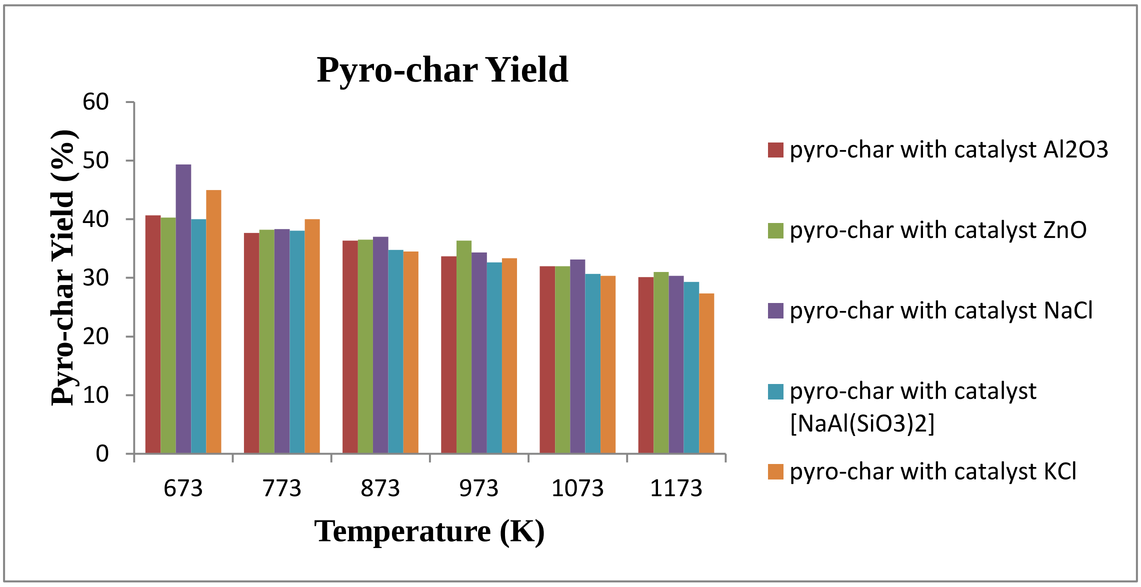

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Fig 6.22: Pyro-char yield (%) from catalytically treated banana stem at different temperatures (K)

From figure 6.22 it is observed that the pyro-char yield from the catalytic pyrolysis of banana stem decreases with the increase in temperature from 673K to 1173K for all the samples under study.

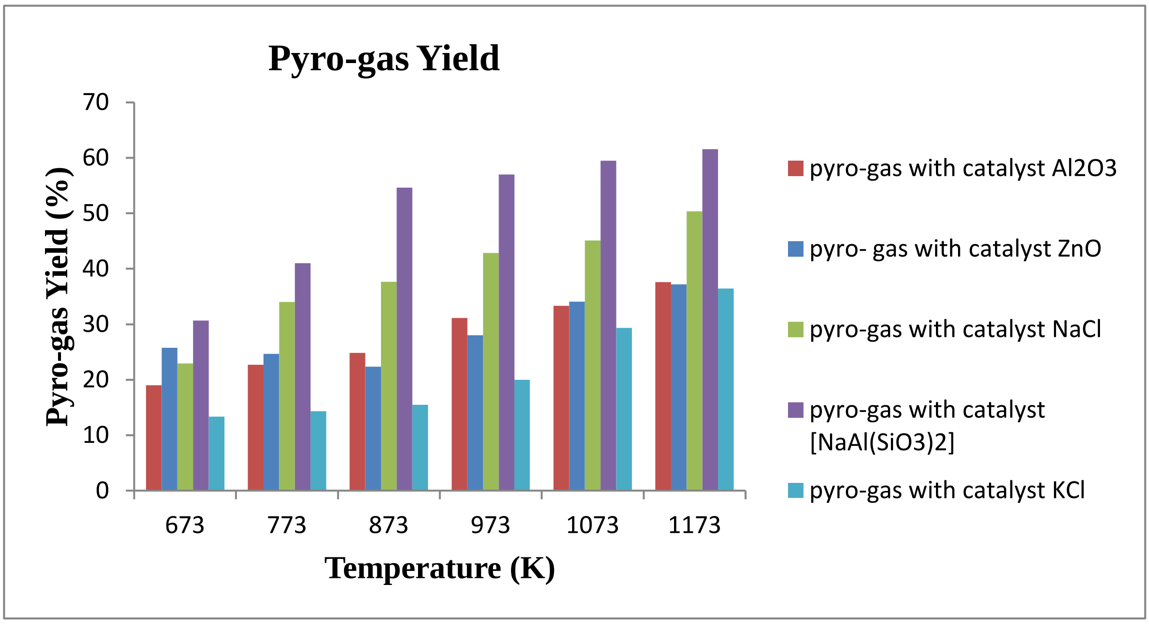


Fig 6.23: Pyro-gas yield (%) from catalytically treated banana stem at different temperatures (K)

From figure 6.23 the trends of pyro-gas yield for the catalytically treated banana stem are observed. The pyro-gas yield increases with the increase in temperature. The maximum pyro-gas yield is obtained from the pyrolysis of banana stem with the catalyst sodiumaluminosilicate and the maximum yield is 61.55 wt % at 1173K, henceforth, concluding that the catalyst sodiumaluminosilicate may be used for the gasification process.

6.11 Product yields from pyrolysis of waste banana stem treated with yeast (bio-route)

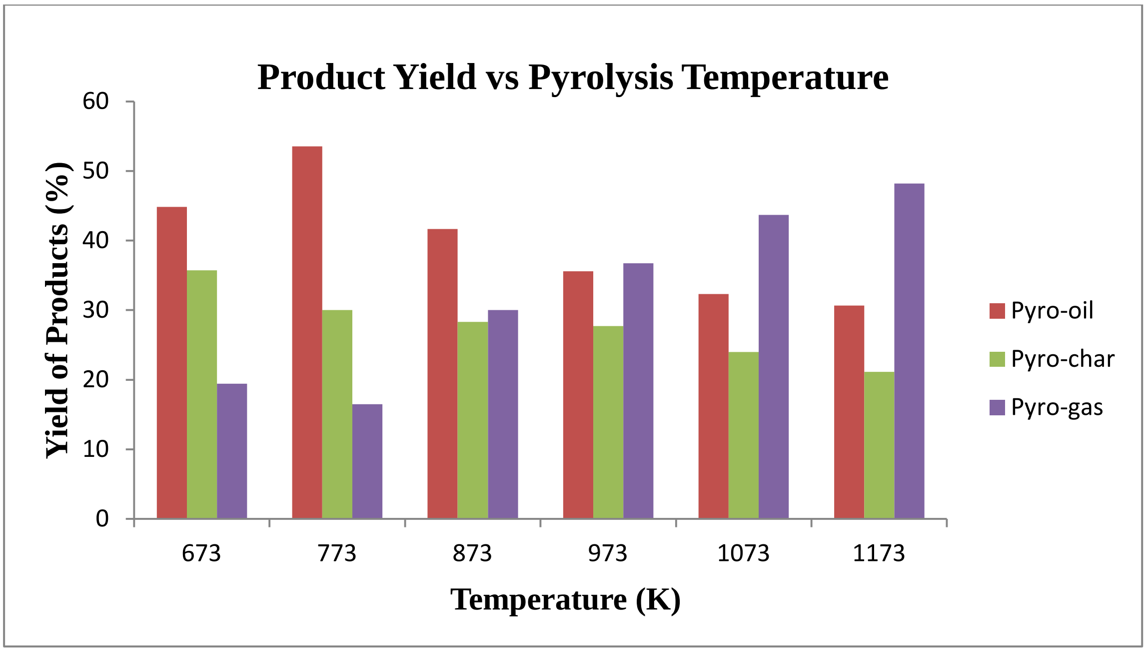


Fig 6.24: Yield of products (%) from bio-treated banana stem at different temperatures (K)

From figure 6.24 it is observed that the pyro-oil obtained from the pyrolysis of yeast treated banana stem gives maximum yield at 773K. The pyro-oil yield is 53.5 wt % at this temperature and the yield gradually decreases with the increase in temperature. The yield of pyro-char gradually decreases with the increase in temperature. The pyro-gas yield decrease from 19.4 wt % at 673K to 16.4 at 773K and then increases with the increase in temperature.

6.12 Comparative study on pyrolysis of untreated, catalytically and bio-treated banana stem:

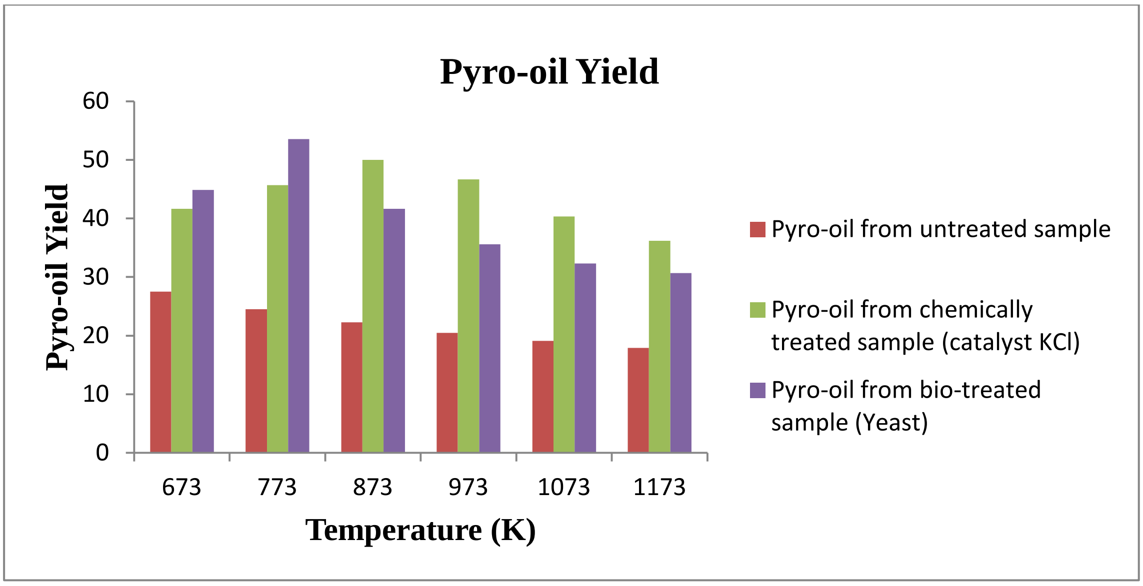


Fig 6.25: Comparison of pyro-oil yield from the pyrolysis of untreated, catalytically and bio-treated banana stem

In the figure 6.25 three different pyrolysis routes are compared. First, the pyro-oil yield from the untreated banana stem, second, the pyro-oil yield from the catalytically treated banana stem. The most effective catalyst namely, potassium chloride (KCl), among the five different catalysts used for the experiments, is considered here. Finally, the pyro-oil yield from the yeast-treated banana stem is also compared here. From the analysis of the figure 6.25 it is observed that the most effective route is the bio-route for the pyrolysis process of banana stem which gives maximum pyro-yield of 53.54 wt % at 773K, whereas, the pyro-oil yield from KCl treated banana stem pyrolysis is 50 wt % at 873K and the pyro-oil yield from that of the untreated banana stem is 27.5 wt % at 673K.

6.13 CHN analysis of pyro-oil from the pyrolysis of untreated, catalytically and yeast treated banana stem:

CHN Analysis is carried out using a CHN Analyser. The following table shows the Carbon, Hydrogen, Nitrogen and Oxygen percent (wt/wt) of the pyro-oil obtained from the pyrolysis of untreated, catalytically (KCl) and bio (yeast) treated banana stem at 500ºC. The high carbon percent indicates the high calorific value of the pyro-oil. Negligible value of sulphur implies that the production of pyro-oil will not produce sulphur oxide in large amounts which is considered harmful to the environment. High oxygen content is not desirable for transportation fuels, hence, both catalytic and bio treatments are performed for the banana stem in order to decrease the oxygen content.

Table 6.6: CHNO results for untreated, catalytically and yeast treated banana stem at 500ºC

Sample No	Sample Type	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)
1	banana stem treated with yeast	37.17	7.14	0.94	54.75
2	banana stem treated with KCl	25.99	6.97	0.41	66.63
3	banana stem treated without catalyst	18.78	6.66	0.46	74.1

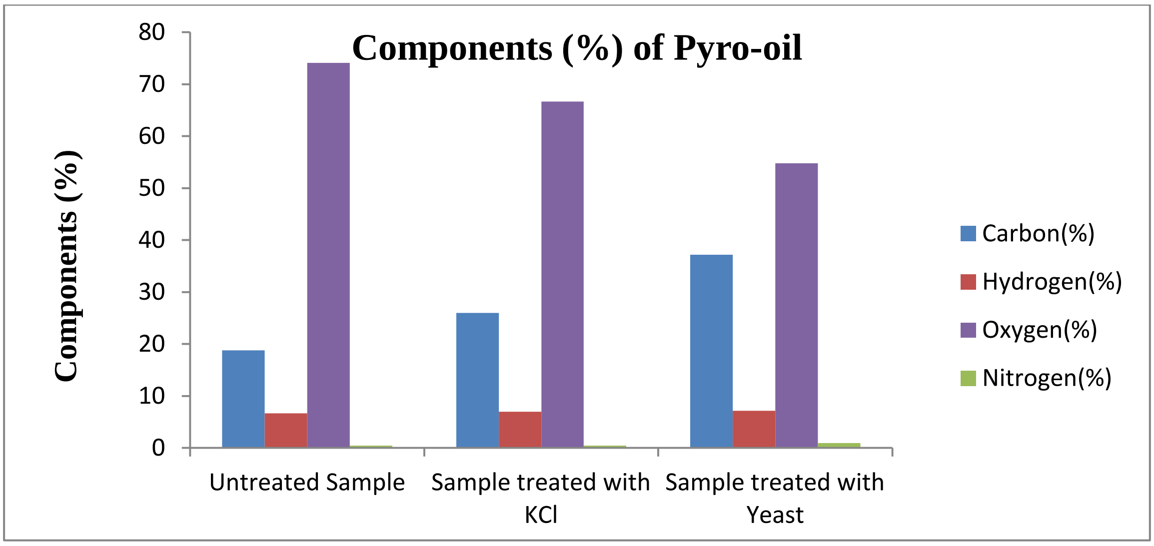


Fig 6.26: Column graph comparing the different components of pyro-oil from the pyrolysis of untreated, KCl and yeast treated banana stem at 500ºC

From the analysis of figure 6.26 it is clearly seen that the oxygen content of the pyro-oil obtained from the pyrolysis of untreated banana stem is 74.1 wt% which is quite high. Hence, in order to decrease the oxygen content of pyro-oil the banana stem are treated both catalytically and with yeast following a bio-route. The oxygen content of the pyro-oil from the KCl treated banana stem is 66.63 wt % and that of the pyro-oil obtained from yeast treated banana stem is 54.57 wt % clearly showing a decrease in its oxygen content thus improving the quality of pyro-oil. On the other hand, the carbon content is also the highest in the pyro-oil generated from biotreated banana stem.

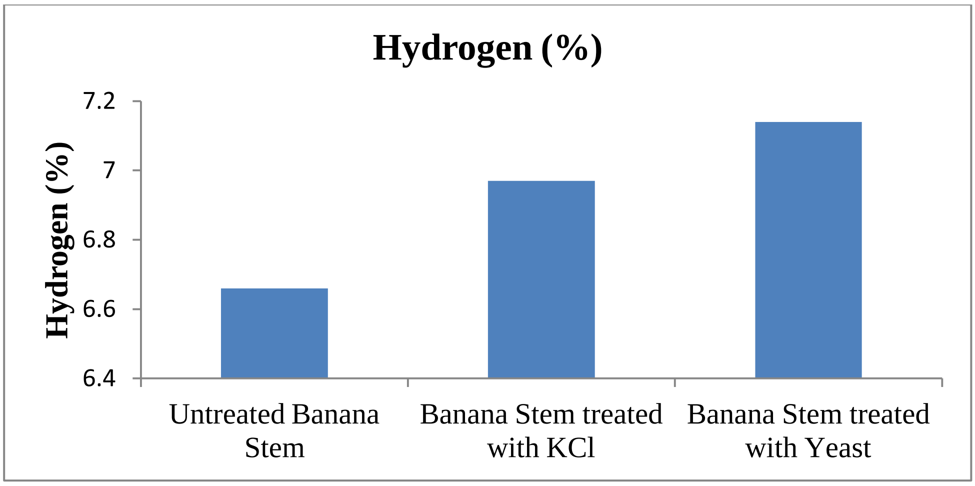


Fig 6.27: Comparative study of the hydrogen content of the pyro-oil from the pyrolysis of untreated, KCl and yeast treated banana stem at 500ºC

From the figure 6.27 it is observed that the change in hydrogen content of the pyro-oil obtained from the pyrolysis of untreated, KCl and yeast treated banana stem at 500ºC is not much pronounced.

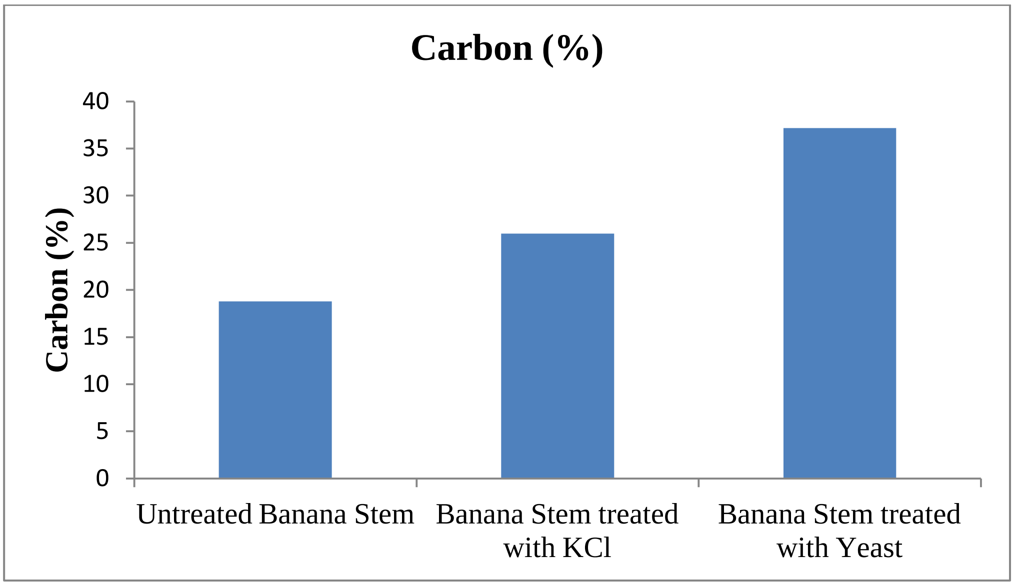


Fig 6.28: Comparative study of the carbon content of the pyro-oil from the pyrolysis of untreated, KCl and yeast treated banana stem at 500ºC

From the figure 6.28 it is observed that the carbon content of the pyro-oil obtained from pyrolysis of yeast treated banana stem (37.17 wt %) is greater than that of pyro-oil obtained from pyrolysis of untreated (18.78 wt %) and KCl treated banana stem (25.99 wt %) at 500ºC, thus improving the calorific value of the pyro-oil.

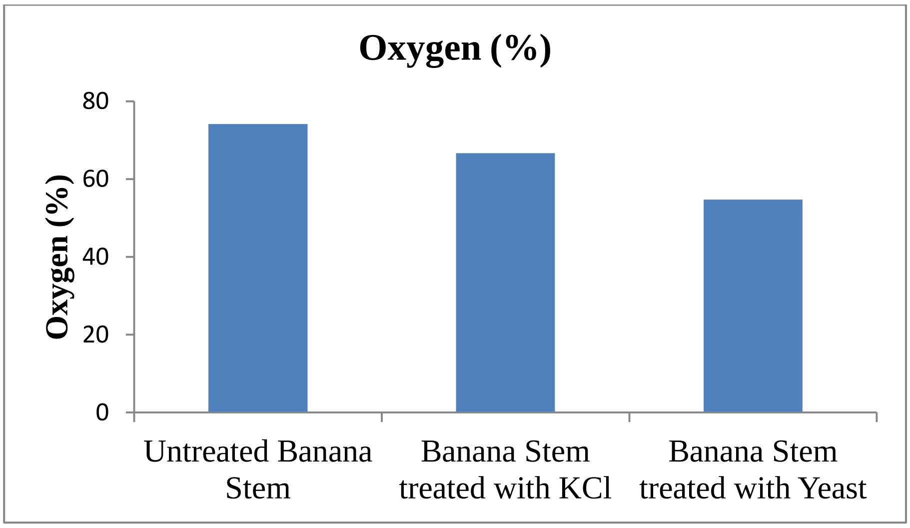


Figure 6.29: Comparative study of the oxygen content of the pyro-oil from the pyrolysis of untreated, KCl and yeast treated banana stem at 500ºC

From the figure 6.29 it is clearly seen that the pyro-oil obtained from pyrolysis of yeast treated banana stem has the least oxygen content ie. 54.57 wt % compared to that of the pyro-oil obtained from untreated and KCl treated banana stem, thus improving the oil quality, the most.

Chapter 7

CONCLUSION AND FUTURE SCOPE

7.1 Conclusions

1. The pyrolysis feedstock (banana stem) was characterized by proximate and ultimate analyses.
2. The pyrolysis reaction for the banana stem was performed in a semi-batch reactor under non-isothermal conditions.
3. The lumped kinetics for the pyrolysis of banana stem was determined in the temperature range of 400-900ºC.From the kinetic study it is concluded that at each time the weight loss increases with the increase in pyrolysis temperature due to the increased rate of pyrolysis.
4. From TGA of untreated banana sample at two heating rates of 10 and 20ºC/min it is concluded that the effect of heating on the weight loss profile for the untreated banana stem is not much pronounced.
5. The kinetics of catalytic pyrolysis of banana stem was determined in the temperature range of 400-900ºC. From the kinetics of untreated and catalytically treated banana stem it is concluded that the plots for the different rate constants follows linearity. The experimental results from the pyrolysis of the treated and untreated banana stem are according to the predictions of Arrhenius law.
6. The prediction of dynamic trends of unreacted banana stem, volatiles and char using lumped kinetics determined under the present study and the multi-component lumped kinetics using kinetic parameters of cellulose, hemicellulose and lignin available in the literature are compared.
7. A suitable microorganism, yeast (*S. cerevisiae*) was selected for decarboxylation of banana stem.
8. The effect of bio-decarboxylation time on the characteristics of chemical bonds in banana stem and on the yield of pyro-oil was studied using FTIR spectroscopy. It is concluded that the variation of incubation time (h) has a very pronounced effect on the product yields of the pyrolysis process. The optimum condition for the maximum pyro-oil yield from the pyrolysis of yeast treated banana stem is 48h incubation time at an incubation temperature of 37ºC. At the optimum condition,

the pyro-oil yield from the pyrolysis of yeast treated banana stem is 53.54 wt %. From the FTIR analysis it is concluded that bio-decarboxylation of banana stem took place after its treatment with Baker's yeast (*S. Cerevisiae*) and the concentration of carboxylic acid decreased with the increase in incubation time of banana stem with yeast.

9. The pyrolysis kinetics of bio-decarboxylated banana stem was determined. From the kinetics of yeast treated banana stem it is concluded that the plots for the different rate constants follows linearity. The experimental results from the pyrolysis of the yeast treated banana stem are according to the predictions of Arrhenius law.
10. The yield and quality of pyro-oil generated through the catalytic and non-catalytic pyrolysis of banana stem with those obtained from pyrolysis of optimally bio-decarboxylated banana stem are compared.
11. Potassium chloride (KCl), among the five different catalysts used for the experiments, gave maximum pyro-oil yield, 50 wt % at 873K. Hence it is concluded that KCl is the best catalyst among all the other catalysts when treated with banana stem.
12. It is also concluded that the most effective route is the bio-route for the pyrolysis process of banana stem which gives maximum pyro-yield of 53.54 wt % at 773K.
13. From CHN analysis it is concluded that the oxygen content of the pyro-oil obtained from pyrolysis of yeast treated banana stem has the least oxygen content ie. 54.57 wt % compared to that of the pyro-oil obtained from untreated and KCl treated banana stem, thus improving the oil quality, the most.

7.2 Future Scope:

1. The future studies can be directed towards investigation on optimization of the pyro-oil obtained from bio-treated banana stem by reducing the oxygen content of the pyro-oil.
2. In future the bio-decarboxylated banana stem can be treated with catalysts and the effects on the kinetics as well as yield may be studied
3. A mathematical model of the bio-decarboxylation reactor may be done further
4. A mathematical model of the catalytic pyrolyzer using banana stem can be done in future.

Appendix

Nomenclature:

E = activation energy (kJ/mol)

A = frequency factor (min^{-1})

k = rate constant (min^{-1})

k_c = rate constant for char formation (min^{-1})

k_v = rate constant for volatile formation (min^{-1})

R = universal gas constant

t = time (min)

T = temperature (K)

$W(t)$ = weight of solid reactant at any time during pyrolysis (g)

$W_c(t)$ = weight of char at any time during pyrolysis (g)

$W_v(t)$ = weight of volatile at any time during pyrolysis (g)

W_R = weight of residue (g)

W_C = weight of cellulose (g)

W_H = weight of hemicellulose (g)

W_L = weight of lignin (g)

W_{AC} = weight of active cellulose (g)

W_{AH} = weight of active hemicellulose (g)

W_{AL} = weight of active lignin (g)

W_T = weight of tar (g)

W_S = weight of syngas (g)

W_{ch} = weight of char (g)

Subscripts:

c = char

v = volatile

R = residue

0 = initial condition

Superscript:

º = Degree of temperature

The calculation for rate constants, activation energy and frequency factor following the Mathematical development:

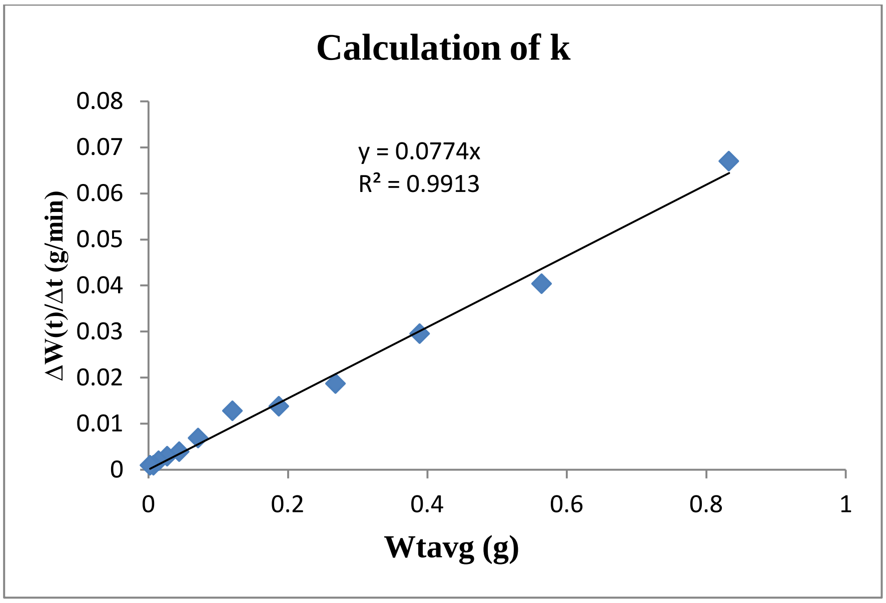
Experimental calculation data sheet of pyrolysis of banana stem treated with KCl at 700ºC

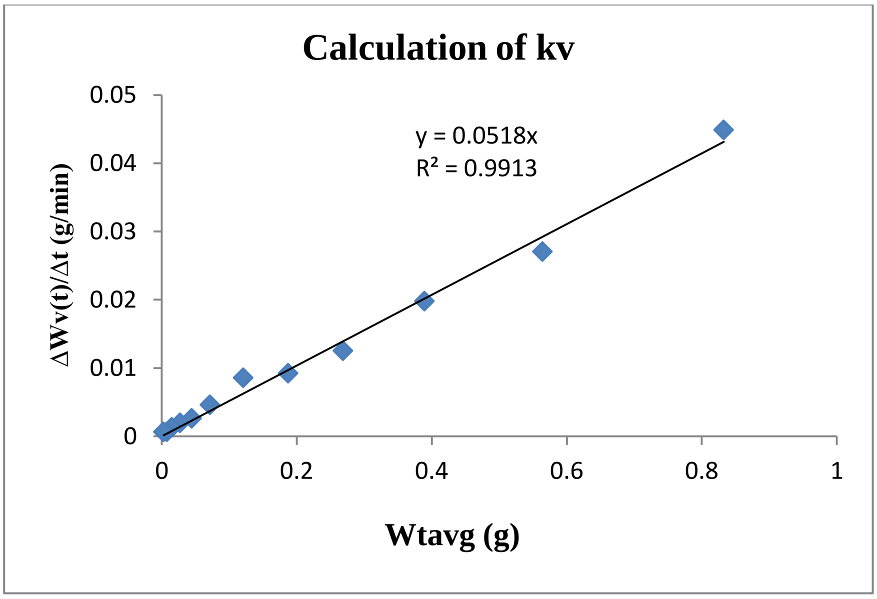
Time	**Sample wt**	**Wt of (Sample + Reactor)**	**% wt loss**	**$W_v(t)$**	**W_R+W_c**	**% wt residue**	**W_0**
0	30.3	1961.1	0	0	0	100	1
5		1954.3	22.44224	0.224422	0.775578	77.55776	1
10		1950.2	35.9736	0.359736	0.640264	64.0264	1
15		1947.2	45.87459	0.458746	0.541254	54.12541	1
20		1945.3	52.14521	0.521452	0.478548	47.85479	1
25		1943.9	56.76568	0.567657	0.432343	43.23432	1
30		1942.6	61.05611	0.610561	0.389439	38.94389	1
35		1941.9	63.36634	0.633663	0.366337	36.63366	1
40		1941.5	64.68647	0.646865	0.353135	35.31353	1
45		1941.2	65.67657	0.656766	0.343234	34.32343	1
50		1941.0	66.33663	0.663366	0.336634	33.66337	1
55		1940.9	66.66667	0.666667	0.333333	33.33333	1
60		1940.8	66.9967	0.669967	0.330033	33.0033	1

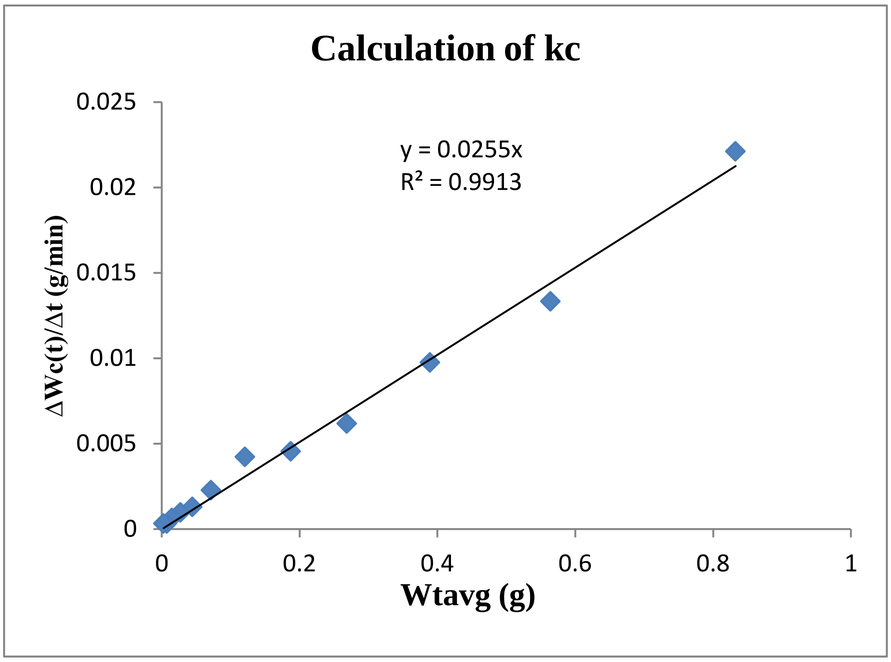
$W_c(t)$	**W(t)**	**$\Delta W(t)/\Delta t$**	**Tavg**	**Wtavg**	**$\Delta W_v(t)/\Delta t$**	**$\Delta W_c(t)/\Delta t$**
0	1	0.066995	2.5	0.832512	0.044884	0.022111
0.110553	0.665025	0.040394	7.5	0.564039	0.027063	0.013331
0.17721	0.463054	0.029557	12.5	0.389163	0.019802	0.009755
0.225983	0.315271	0.018719	17.5	0.268473	0.012541	0.006178
0.256873	0.221675	0.013793	22.5	0.187192	0.009241	0.004552
0.279634	0.152709	0.012808	27.5	0.12069	0.008581	0.004227

0.300769	0.08867	0.006897	32.5	0.071429	0.00462	0.002276
0.312149	0.054187	0.003941	37.5	0.044335	0.00264	0.001301
0.318653	0.034483	0.002956	42.5	0.027094	0.00198	0.000975
0.32353	0.019704	0.00197	47.5	0.014778	0.00132	0.00065
0.326781	0.009852	0.000985	52.5	0.007389	0.00066	0.000325
0.328407	0.004926	0.000985	57.5	0.002463	0.00066	0.000325
0.330033	0	0				

Calculation of k, kv, kc:





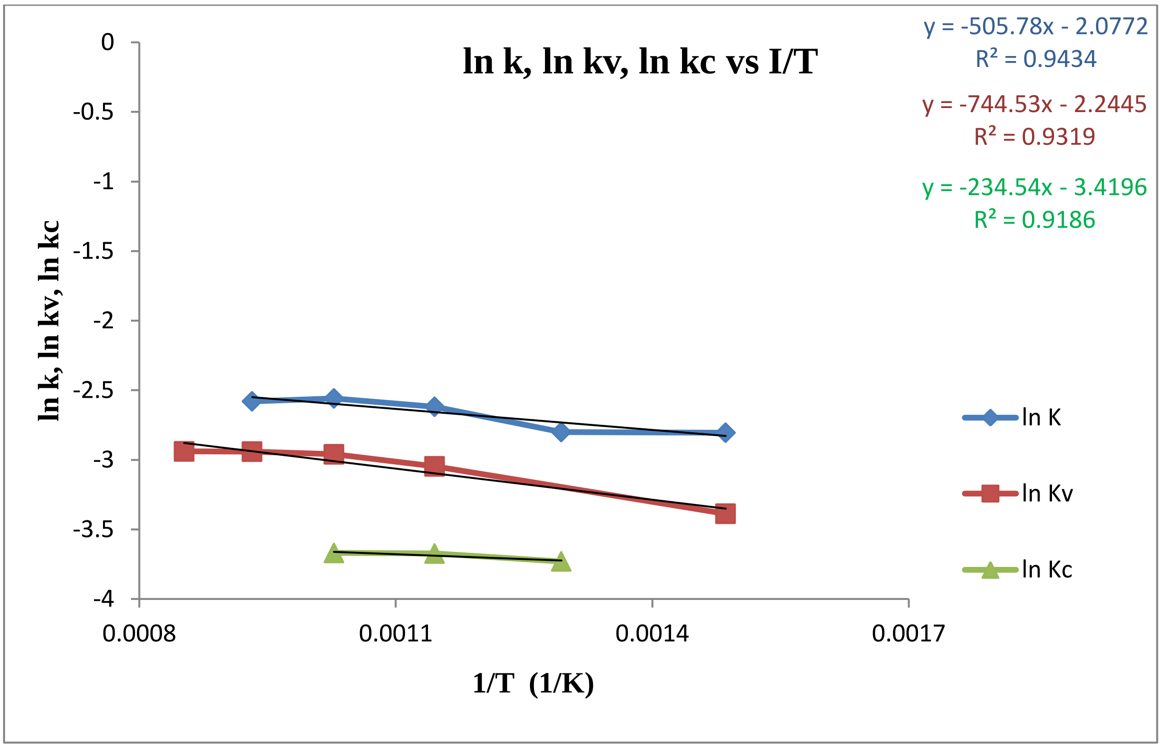


The table below shows the values of k, kv and kc in the pyrolysis temperature range of 673K to 1173K calculated following the same protocol as described above.

T (K)	1/T	k	ln k	kv	ln kv	kc	ln kc	check k
673	0.001486	0.0605	-2.80511	0.0338	-3.38729	0.0267	-3.62309	0.0605
773	0.001294	0.0608	-2.80017	0.0368	-3.30226	0.024	-3.7297	0.0608
873	0.001145	0.0729	-2.61867	0.0475	-3.04703	0.0254	-3.67301	0.0729
973	0.001028	0.0774	-2.55877	0.0518	-2.96037	0.0255	-3.66908	0.0773
1073	0.000932	0.0758	-2.57966	0.0528	-2.94124	0.023	-3.77226	0.0758
1173	0.000853	0.0728	-2.62004	0.0529	-2.93935	0.0199	-3.91704	0.0728

k (pred)	ln k (pred)	kv (pred)	ln kv (pred)	kc (pred)	ln kc (pred)
0.059226	-2.82639	0.035178	-3.34734	0.023121	-3.76701

0.065254	-2.72947	0.040572	-3.20467	0.024184	-3.72207
0.070316	-2.65475	0.045289	-3.09468	0.025036	-3.68742
0.074616	-2.59539	0.049425	-3.0073	0.025735	-3.6599
0.078308	-2.5471	0.053066	-2.93621	0.026318	-3.6375
0.081509	-2.50704	0.05629	-2.87724	0.026811	-3.61893



From this graph, the activation energies and frequency factors are calculated from the slope and intercept respectively.

The activation energies and frequency factors for the pyrolysis of untreated and catalytically and bio- treated banana stem are calculated following the method shown above.

MATLAB Code:

The mass balance equations for the scheme 2 were solved using simultaneous ODE45 method by using MATLAB R2013a software using the following mathematical code.

Function:

```
function dydt = pyroA(t,y)
global kc1 kh1 kl1 kc2 kh2 kl2 kc3 kh3 kl3 k4
dydt = zeros (9,1);
dydt(1) = -kc1 * y(1);
dydt(2) = kc1 * y(1) – kc2 * y(2) – kc3 * y(2);
dydt(3) = -kh1 * y(3);
dydt(4) = kh1 * y(3) – kh2 * y(4) – kh3 * y(4);
dydt(5) = -kl1 * y(5);
dydt(6) = kl1* y(5) – kl2* y(6) – kl3 * y(6);
dydt(7) = kc2 * y(2) + kh2 * y(4) + kl2* y(6) - k4 * y(7);
dydt(8) = 0.65 * kc3 * y(2) + 0.4 * kh3 * y(4) + 0.25 * kl3 * y(6) + k4 * y(7);
dydt(9) = 0.35 * kc3 * y(2) + 0.6 * kh3 * y(4) + 0.75 * kl3 * y(6) ;
if (y <= 0)
y = 0;
end;
```

Mathematical Codes:

```
global kc1 kh1 kl1 kc2 kh2 kl2 kc3 kh3 kl3 k4
kc1 = 4.29;kh1 = 67.77;kl1 = 4.27;kc2 = 0.1836;kh2 = 1.707;kl2 = 0.0103;
kc3 = 0.02707;kh3 = 1.27677;kl3 = 0.0173744;k4 = 0.0177;
Tspan=0:0.5:60;
y0=[0.440;0.0;0.175;0.0;0.373;0.0;0.0;0.0;0.0]
[T Y]=ode45(@(t,y) pyroA(t,y), Tspan,y0);
plot(T,Y);
xlabel('Time (min)');
ylabel('Weight(g)');
[T Y]
```

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