STUDIES ON BIOCONVERSION OF LTLT (LOW TEMPERATURE LONG RESIDENCE TIME) PYROLIQUID GENERATED FROM LIGNOCELLULOSIC AGRO-RESIDUES

Thesis

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Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of her **Master of Chemical Engineering** studies during academic session 2017-2019. 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.

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CERTIFICATE

*This is to certify that the thesis entitled "***Studies On Bioconversion Of Ltlt (Low Temperature Long Residence Time) Pyroliquid Generated From Lignocellulosic Agro-Residues***" has been carried out by Rupak Jana 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.*

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ABSTRACT

The purpose of this study was to find a possible pathway for bioconversion of pyro-liquid. Rice Straw, Jute Stick and Mustard Straw were used as pyrolysis feedstocks. *Shewanella putrefaciens, Clostridium acetobutylicum* and a mixed consortia collected from agricultural lagoon were used as microorganisms for bioconversion. Biomass was pyrolysed between 473K to 673K for 1-2h. Reaction kinetics of pyrolysis was studied to determine the reaction rate constants and activation energy. Vapors produced were condensed in two stages, first one operated at 80°C and the second one was operated at 20°C. The liquid obtained in the first condenser contains the heavy compounds (lignin derived aromatic compounds and anhydro-sugars) and in the second condenser most of the light compounds (including the acids) were collected. The first condenser liquid was extracted with cold water and ethyl acetate, then acid hydrolysis of the extract was done for glucose formation from levoglucosan (main sugar compound in pyrooil). Sugar content of the hydrolysates were measured after neutralization. It was found that pyro-oil from Jute stick (at 350°C) had the maximum sugar content (41.80 g/L). Then detoxification of the hydrolysates were done using Ca(OH)2. Altleast 31.67 g/L Ca(OH)2 concentration were required for detoxification. Hydrolysates both with and without detoxification were fermented using two sets of bacteria culture, *C. acetobutylicum* and mixed consortia. Growth did not occur in case of bio-oil which were not detoxified. Both *C. acetobutylicum* and mixed consortia had given growth on detoxified hydrolysates. pH (5.8) fall was higher in case of mixed consortia, indicated more growth in mixed culture than that of single culture. This suggests possible alcohol and acid production from bio-oil for all the feedstocks. Second condenser liquid was fermented with *S. putrefaciens* and growth kinetics had been studied using Monod's Model. Growth was better when glucose was added to the bio-oil. *S. putrefaciens* degraded acetic acid from bio-oil, which suggests further MFC can be developed from the second condenser liquid to generate bio-electricity. Also various valuable organic acids, phenol, actaldehyde can be produced from the bio-oil. Overall modelling of the pyrolysis-fermentation hybrid process was done using ASPEN ENGINEERING 8.8 for Rice Straw to determine the maximum ethanol yield for diffenrent pyrolysis temperatures. Maximum 2.75 kg ethanol from 100 kg of biomass can be produced, which were pyrolysed at 673K, the yield of ethanol was lower for lower pyrolysis temperatures.

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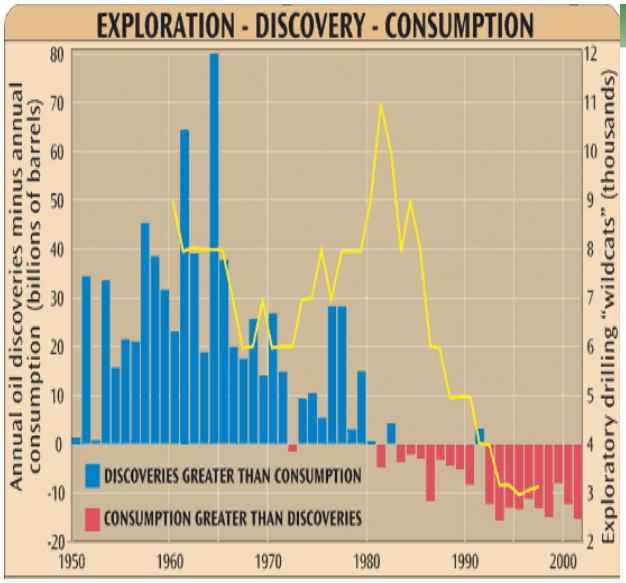
Chapter 1

INTRODUCTION

1.1. Energy Crisis

We are lucky to live on the planet where only life exists (as per our knowledge so far) in this vast cosmic arena, and also lucky enough to be the only species to have developed consciousness since life had evolved from its simplest of forms. We are not only driven by nature but can change it. We learned from nature, used our intuitions and used it in a purposeful manner, and had developed science and technology to an unimaginable level. Especially in last hundred years, science, technology, industries has grown in a rapid pace. But this fast advancement of civilization has also made us face a lot of crisis. One of the major crisis in today's world is the energy crisis. To run our home, to drive our cars, to light our nights, to operate the computers all we need is energy, but we have exploited fossils fuels so much that we are running out of it. Not only that but also excessive consumption of fossil fuels has imbalanced our environment due to emission of greenhouse gases. So, finding a possible alternative is a need of the hour. Nature has given us wonders, and most of it is still unexplored. We have to do more search and be more careful of our mother nature. Thus, shifting from conventional energy sources and trying to make renewable energy more effective and more reliable on a large scale basis is not just a wishful thought but a necessity.

Of the renewable energy sources, bioenergy as sustainable and environmentally friendly alternative to the fossil fuels has stirred substantial research worldwide. Biomass conversion processes have emerged as a rapidly growing field of science and technology endeavoured to fulfil ever-growing energy deficit as well as reduce CO2 emissions by 70–90%.



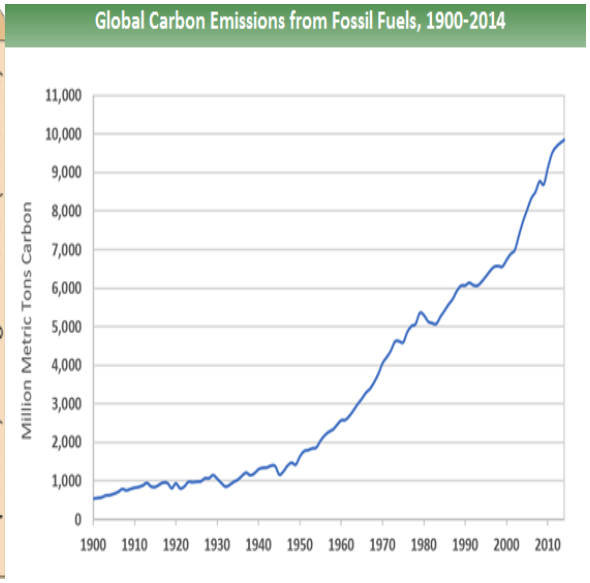


Fig1.1 Annual oil discoveries vs consumption, source: Association for the study of peak oil <www.asponews.org>

Fig1.2 Increment of global carbon emission from 1900-2014, Source: United States Environmental Protection Agency

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) Reduction of extreme reliance on fossil fuels
2) Eventual reduction of greenhouse gases(GHG) emission and
3) Efficient abatement of environmental pollution.

The 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 abundant and renewable material in the world for the production of biofuels. Lignocellulosic biomass refers to plant dry matter, which is mainly composed of cellulose, hemicellulose and lignin, mainly available in agricultural, forest and industrial sectors. Agricultural waste is produced annually worldwide. It can become a suitable option as potential feedstock for both biochemical and thermochemical WTE processes. In developing countries, the large quantities of agricultural residues are currently

utilized either as raw material for paper industry, or as animal feed sources, also used for cooking and heating. But generally since the collection and disposal of these residues are becoming more difficult and expensive, it is left unused as waste material or simply burned in the fields, thereby creating significant environmental problems. By means of thermochemical or biochemical conversion routes, lignocellulosic agro-residues can be converted into energy or energy carriers.

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

1) Biological/bio-chemical:
    a) Fermentation
    b) Anaerobic digestion

2) Thermo-chemical:
    a) Gasification
    b) Liquefaction
    c) Pyrolysis

1.2.1 Biochemical Conversion

Biochemical conversion of biomass involves the use of bacteria, microorganisms or enzymes to breakdown biomass into gaseous or liquid fuels.

1.2.1.1. 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.

1.2.1.2. 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.

1.2.2. Thermochemical conversion

Thermochemical conversion uses heat and chemical processes to produce energy products from biomass, including combustion, pyrolysis, gasification and liquefaction.

1.2.2.1. 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.

1.2.2.2. 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.

1.2.2.3. Pyrolysis

Pyrolysis has been derived from the Greek words: pyro meaning "fire" and lysis meaning "separating". It is used for converting lignocellulosic materials resistant to biotreatment (generally which are having high lignin content) into materials that are highly amenable to biotreatment processes for forming energetic fuels in gaseous and/or liquid states. Pyrolysis is a treatment method in which a substance is changed by subject to heat alone. In conventional pyrolysis, oxygen is substantially excluded and the operating temperatures to achieve destructive distillation are typically about 750° F.-800° F. (399° C.-427° C.). The destructive distillation results in a gas, a liquid and solid matter, i.e. char.

Fig 1.3. Pyro-char

Fig 1.4. Pyro-oil

Fig 1.5. Pyro-gas

1.3. Drawbacks of conventional conversion processes

The main drawbacks of conventional conversion processes are –

a) Although biochemical conversion offers selective processing options which are not available in other processes but it is inherently more complicated and expensive than thermochemical route, and also requires energy intensive pretreatment.

b) Major problems in thermochemical conversion process are generation of Ash during gasification, contamination of syngas with tar and mass transfer limitation. It also consists high energy requirement.

One possible solution to this problems are combining the biochemical path with the thermochemical one.

1.4.LTLT Pyrolysis

A lignocellulosic material is first subjected to pyrolysis at relatively low temperatures (Typically, pyrolysis temperatures between about 175° C. and about 325° C) for an extended time period between about 0.1 hour and about 2.0 hours (*U.S. Patent No. 9,416,374*), depending upon the particle size of the lignocellulosic feed material and the particular operating

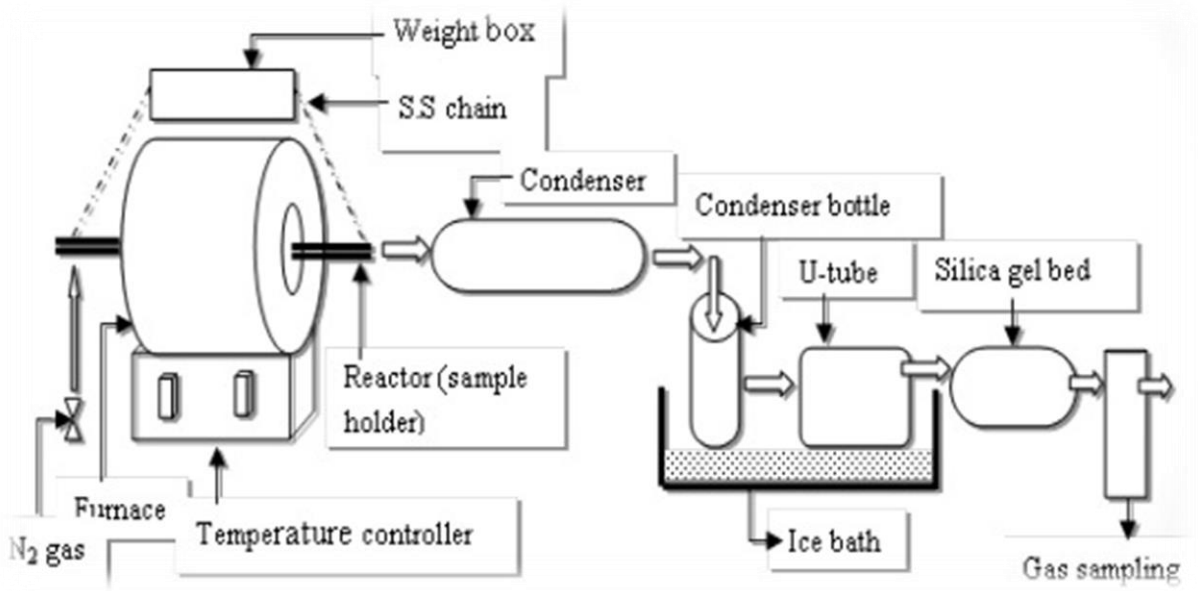


Fig 1.6: lab-scale pyrolysis set-up (Source: A. Sarkar and R. Chowdhury, 2014)

temperature, resulting in conversion of volatile materials to (a) an aqueous "pyroligneous acid" containing organic acids (such as acetic acid), alcohols (principally methanol), and other organic compounds, and a gas stream (pyrogas) containing methane, carbon dioxide, hydrogen, water, and lesser quantities of other volatile organic substances. A residual solid phase primarily comprises char (fixed carbon) and ash. It requires less energy than conventional pyrolysis process.

1.5. Combining Pyrolysis with bioconversion

Fermentable sugar obtained from lignocellulosic material exhibits great potential as a cheap and renewable feedstock for the production of bio-ethanol and other products. But

Lignocellulosic biomass is hard to be treated by micro-organisms directly due to complex lignin content in it. Pyrolysis can be used to break lignocellulose. Pyrolysis fractionate biomass into three process streams (solid, liquid and gas), each containing value-added components. Following separation of the solid phase from the gas and liquid phases, the liquid phase is subjected to biological treatment by anaerobic methanogenic organisms to produce a mixed gaseous stream of methane and carbon dioxide, useful as an energetic fuel gas or the pyroligneous acid from the extended pyrolysis step is biotreated by yeast or yeast-like organisms to produce a liquid fuel such as ethanol. If necessary, toxic materials (typically phenolic materials) may be removed from the "pyroligneous acid" before introduction into the biotreatment step.

Pyrogas formed in the pyrolysis step may be combined with fuel gases formed in the biotreatment step, or may be used separately, or may be introduced into the biotreatment step itself and pass therethrough, increasing the generation of methane gas. Known methods for removing carbon dioxide from the energetic fuel content of the pyrogas and/or biogas may be used to concentrate the fuel gases and reduce carbon dioxide emissions.

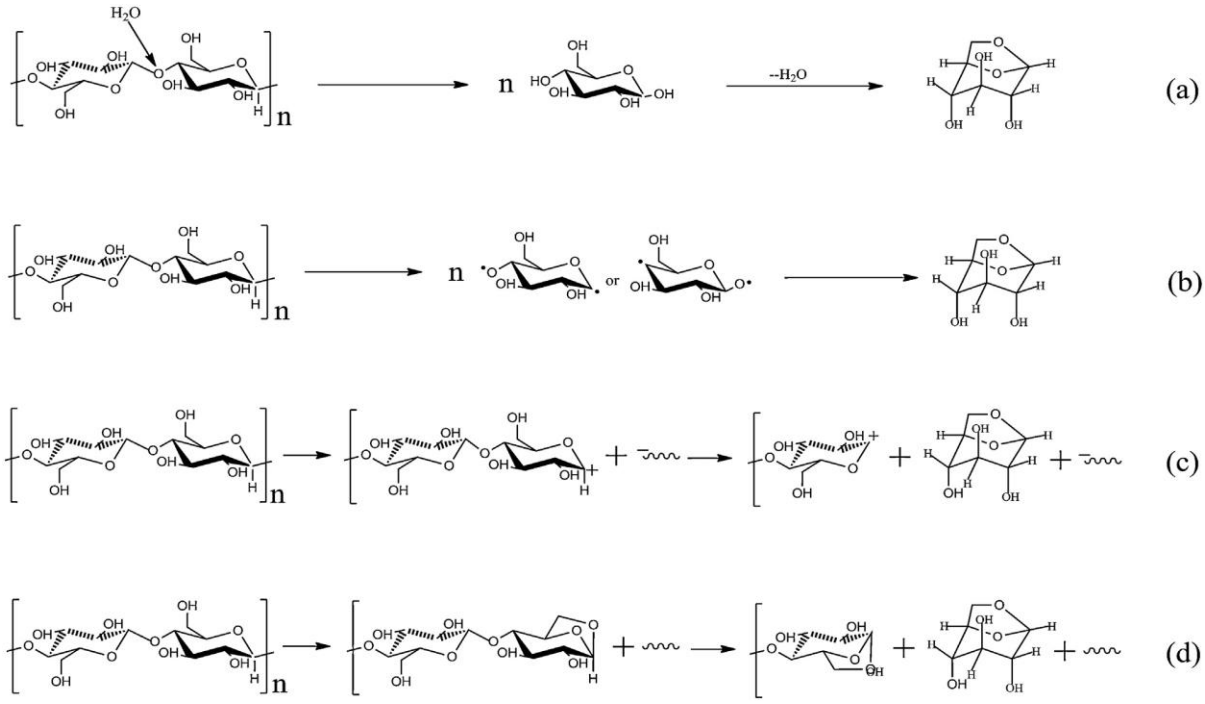


Fig. 1.6. Main mechanisms for the formation of levoglucosan from cellulose pyrolysis (Source: Zhang et al., 2013).

In this process, the extended pyrolysis step converts lignin-containing materials which are resistant to biotreatment into liquid materials which are readily bioconverted into fuels. Thus, the result is an enhanced yield of fuel.

1.5.1. Pre-treatment of Pyro-liquid before Fermentation

Integrating pyrolysis oil into traditional petrochemical refineries or direct biotreatmemt of pyrooil can be challenging and has not been realized at commercial scale, largely due to its complex and variable composition and, especially, its high oxygen and water concentrations. Firstly pyrolysis vapours are fractioned in two stage to separate heavier (sugar, aromatics) parts from lighter (acetic acid, water) parts (Oudenhoven et al., 2013). Then in order to reduce complexity of pyrolysis oil, it is extracted with water. The aqueous extract is subsequently separated to recover polar compounds (Garcia-perez et al., 2008), whereas organic residue is further treated to isolate phenolic compounds (Lian et al., 2010). Acid treatment of pyrooil increase levoglucosan yield (main sugar product of pyrolysis). Anhydrosugars can be converted to glucose through hydrolysis that can be directly used for fermentation (Bennett et al., 2009). But some of pyrolysis oil compounds substantially inhibit the microoganisms. So, detoxification of hydrolysate is needed, which can be achieved through simple overliming (Chi, Zhanyou, et al, 2013).

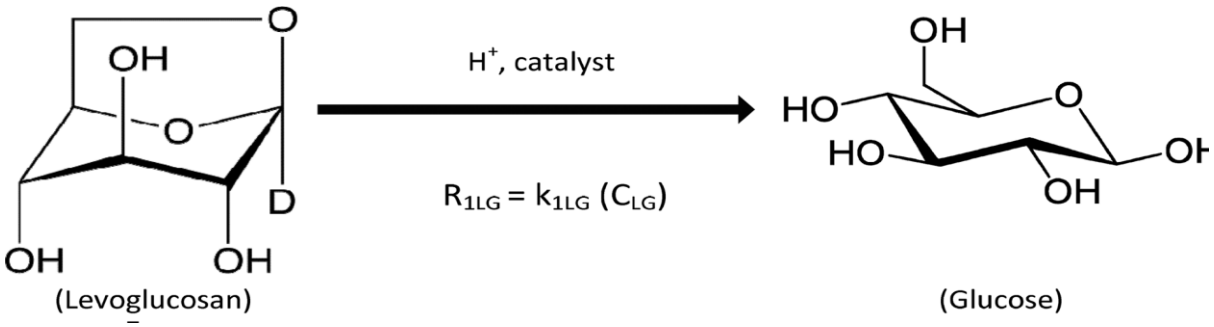


Fig 1.7 production of glucose from levoglucosan via acid hydrolysis (Source: Abdilla et al., 2018)

1.6. Selection of feedstocks

Due to its geographical situation from tropical to temperate climate region and variation of soil properties, India produces diverse cultures of agricultural-biomass, of which rice is being the major production. A large amount of residual argo-waste are derived from them annually which remains unused or simply wasted. These lignocellulosic wastes are rich in carbon content and can be utilized as an alternative energy source through different conversion routes. Since there is no commercial use for these bio-wastes they are available in the market at minimal price. Depending upon the availability and energy content rice straw, mustard straw and jute stick has been selected as the raw materials for pyrolysis.

Table 1 Major types of Indian crops and the post-harvesting and post-processing residues derived from them

Indian crops	Post-harvesting residue	Post-processing residue
Rice	Straw/stalk, leaves, stubble,	Husk/hull
Wheat	Straw/stalk, leaves, stubble	Pod/panicle
Sugarcane	Top, leaves	Bagasse
Maize	Stalks	Cobs
Banana	Leaves, pseudo-stem, fruit branch	Pith, fruit peels
Mustard	Stalks	Husk, press cakes
Sesame	Stalks	Press cakes
Castor	Stalks	Husk, press cakes
Soybean	Stalks	N.A.
Coconut	Fruit brunch, fronds	Husk/coir, pith, shell
Areca nut	Fruit brunch, fronds	Husk
Groundnut	Stalks	Shell
Bajra	Stalks	Husk, cobs
Jowar	Stalks	Husk, cobs
Ragi	Stalks	N.A.
Pulses*	Stalks	Husk

Source: Chowdhury et al. (2018)

Table 2: Annual availability of agro-wastes of major agricultural crop varieties of India

Indian crops (corresponding agro-wastes)	Annual availability (Kt/year)
Rice waste	161893.00
Rice straw	141120.00
Rice husk	20773.00
Wheat (straw)	122991.00
Sugarcane wastes	114761.00
Sugarcane bagasse	73775.00
Sugarcane tops and leaves	40986.00
Maize waste	33720.00
Maize straw	28396.00
Maize cobs	5324.00
Banana waste	67776.00
Banana fruit peels	393.00
Banana pseudo-stem	67383.00
Mustard waste	16877.00
Mustard press cake	2681.00
Mustard seedpod	1355.00
Mustard stalks	12841.00
Sesame (stalks)	1207.70
Soybean husk	671.00
Coconut waste	9060.00
Coconut fronds	7769.00
Coconut shell	726.00
Coconut coir pith	565.00
Areca nut (fronds, husk)	1000.80
Groundnut (shells)	1385.00
Bajra(stalks, cobs, husk)	15831.80
Jowar (cobs, stalks, husk)	24207.80
Ragi (straw)	2630.20
Cotton waste	38281.00
Cotton stalks	35397.00
Cotton hull	2884.00
Pulses* (stalks, husk)	13462.90

Source: Chowdhury et al. (2018)

Chapter 2

LITERATURE RIVIEW

Sl No.	Name of author and year of publication	Description of the Study
1.	J. Cai et al. (2017)	Different physiochemical properties of lignocellulosic biomass were reviewed in this paper, which are key to understand prior to any thermochemical or biochemical processing method. They presented the characterization techniques and their recent development for the properties, including particle size, grindability, density, flowability, moisture sorption, thermal properties, proximate analysis properties, elemental composition, energy content and chemical composition.
2.	Sohni et al. (2017)	They used oil palm frond (OPF), oil palm trunk (OPT), empty fruit bunches (EFB), palm kernel shell (PKS), rice husk (RH), rice straw (RS) and kenaf biomass (K) as feedstocks for characterization based on proximate composition, CHNS/O analysis, calorific value and lignocellulosic content determination, and various analytical techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry (TG) and X-ray fluorescence spectroscopy (XRF) were used to study various microscopic properties of biomass residues such as functional groups, crystallographic structure, thermal degradation and mineralogical composition. They found that PKS can be an interesting candidate for conversion technologies based on combustion and gasification processes because of maximum FC and lignin content. OPF, OPT and K possessing high polysaccharide quantity along with lower lignin content are recommended as valuable feedstock for biochemical conversion. Excellent yields would be obtained in case of EFB,

		K and OPT via fast pyrolysis due to high VM content. Lowest VM content and highest amount of ash of non-catalytic nature make RH suitable for combustion.
3.	Biswas et al. (2017)	They presented slow pyrolysis studies on four different biomass residues such as corn cob (CC), wheat straw (WS), rice straw (RS) and rice husk (RH), carried out in fixed bed reactor at different temperatures 300, 350, 400 and 450 °C. The gross calorific value and the elemental composition of C, H, N, S and O of the biomass were measured. The kinetics of the samples was studied by Thermogravimetric Analysis (TGA). The optimum temperatures for these residues were 450, 400, 400 and 450 °C for CC, WS, RS and RH respectively. The maximum bio-oil yield in case of corn cob, wheat straw, rice straw and rice husk were 47.3, 36.7, 28.4 and 38.1 wt% respectively. Maximum organic carbon conversion (56.62%) calculated from TOC measurement was observed for rice husk. From FT-IR and H NMR spectra showed a high percentage of aliphatic functional groups for all bio-oils and distribution of products is different due to differences in the composition of agricultural biomass. The analysis of four bio-char derived from pyrolysis by XRD and FT-IR, which indicating that biomass components units were broken down in pyrolysis and converted into products.
4.	Saleh Al Arni (2017)	They compared two pyrolysis methods; namely, fast pyrolysis and slow or conventional pyrolysis of sugarcane, based on the thermal decomposition of biomass into fuel and on the product yields. The conversion was carried out experimentally in a batch pyrolysis reactor. The heating rate of conventional pyrolysis was about 45-50 oC/min while it was 120-127 oC/min for fast pyrolysis, and the residence times were about one hour and twenty minutes, respectively and were conducted at three fixed temperature values of 753, 853 and 953 K. The

		conventional pyrolysis produce more syngas yield with the increases of temperature. In the case of fast pyrolysis, it was observed that losses and solid yield increase with temperature increase. The highest losses in both cases are less than 15% and that it was higher in conventional pyrolysis. Gases released during the thermal decomposition of biomass were identified as H2, CO, CO2, CH4 and some light molecular weight of hydrocarbons, such as C2H4 and C2H6. The hydrogen yield increases with the rise of temperature for both processes; the maximum value was obtained at 953K (about 45 Vol%) by fast pyrolysis. The maximum value of methane was obtained at 853K (about 30 Vol%) by conventional pyrolysis. The low temperature was favored for the production of methane other than hydrogen for both processes, while high temperature was favored for the production of hydrogen.
5.	Park et al. (2011)	They investigated effects of operation conditions on the fast pyrolysis method of two different agricultural residues, red pepper stem and garlic stem. Thermogravimetric analysis (TGA) was used to determine the temperature range for pyrolysis. Proximate and ultimate analyses were carried out for both raw biomass and biooil. GC-MS was used to identify the species contained in the bio-oil. Water content was measured by Karl Fischer titrator. The ash content was obtained by igniting the bio-oil in a muffle furnace. The gaseous pyrolysis product was analyzed using a GC and CO, CO2, H2 and CH4 were measured by a TCD. Pyrolysis Temperature turned out to be an important parameter determining the product yields. The gas yield increased and the char yield decreased with increasing pyrolysis temperature. The optimum temperature was determined to be 500 °C for garlic stem and 480 °C for pepper stem at which the bio-oil yield was 39.6 wt.% and 45.8 wt.%, respectively. The bio-oil yield increased and the char yield decreased with increasing sample particle size.

6.	Bradbury et al. (1979)	They investigated the kinetic data for pyrolysis of cellulose within the temperature range of 260-340°C where the production of volatiles predominates. Cellulose macromolecules are not directly converted to low molecular weight volatile products, gases and char, but undergo intermediate physical and chemical changes such as a glass transition and depolymerisation. These changes may be responsible for the activation of the macromolecules before they undergo rapid thermal degradation. In this model, They assumed that an "initiation reaction" leads to formation of an "active cellulose" which subsequently decomposes by two competitive first-order reactions, one yielding volatiles and the other char and a gaseous fraction. The rate constants of these reactions, *k;* (for cellulose to "active cellulose"), *k,* (for "active cellulose" to "volatiles"), and *k,* (for "active cellulose" to char + the gaseous fraction) were also determined.
7.	Bandyopadhyay et al. (1999)	They presented kinetics of pyrolysis of coconut shell sample in the temperature range of 523 K to I023 K in an inert atmosphere by captive sample technique. A kinetic scheme had been proposed where two parallel reactions are given for the production of volatiles and char. The reaction rate constants are found to decrease with high temperatures above 673 K due to chemical and physical changes of the reactant during devolatilisation reaction.
8.	Chowdhury et al. (2018)	They presented a categorical classification of Indian agro-wastes based on their appearance in the supply chain. The adaptability of Indian agro wastes towards 2ng generation (2G) biorefinery has been assessed using their availability, thermochemical properties and composition of a few specific feedstocks, namely, rice straw, rice husk, wheat straw, oil seed press cakes, sugarcane bagasse, coconut shell, banana peels and stems. An assessment on the abundance of Indian agro-residues and their overall energy potential were made. Based

		on the lignin content, the residues were classified as high lignin, medium lignin and low lignin ones. The analytic hierarchy process (AHP) had been used to decide on the strategy of application of stand-alone biochemical or thermochemical processes and their hybrids for the conversion of different candidate feedstocks in the 2G biorefineries with respect to sustainability parameters.
9.	Shen et al. (2015)	They presented a comprehensive review of two thermochemical-biochemical hybrid processes (pyrolysis-fermentation, gasification-fermentation) including their features, challenges and mitigating strategies. The current challenges of these two biomass conversion pathways include toxicity of the crude pyrolytic substrates, the inhibition of raw syngas contaminants, and the mass-transfer limitations in syngas fermentation. Possible approaches for mitigating substrate toxicities were discussed. The review also provides a summary of the current efforts to commercialize hybrid processing.
10.	Luque et al. (2014)	They presented a combination of thermochemical and biochemical conversion process for pinewood. Fast pyrolysis (at 480°C) of lignocellulosic biomasss with fractional condensation of the products was used as the thermochemical process to obtain a pyrolysis-oil rich in anhydro-sugars (levoglucosan). Then oil was cold water extracted to remove water insoluble parts. After that hydrolysis of these anhydro-sugars were performed to obtain glucose, which was successfully fermented with S. cerevisiae, after detoxification, to obtain bioethanol. Ethanol yields comparable to traditional biochemical processing were achieved (41.3% of theoretical yield based on cellulose fraction). Sugar content were quantified by liquid chromatography, Karl Fischer titration was used to determine the water content of the oils. oils were analysed using GC–MS. Additional benefits of the proposed

		biorefinery concept comprise valuable by-products of the thermochemical conversion like bio-char, mono-phenols (production of BTX) and pyrolytic lignin as a source of aromatic rich fuel additive.
11.	Westerhof et al. (2011)	They presented fractional condensation of pyroliquid as a promising cheap downstream approach to concentrate compounds (classes) and, thus, to control the quality of pyrolysis oils, making it more suitable for further upgrading and/or direct applications. Pine wood was pyrolyzed in a 1 kg/h fluidized-bed pyrolysis reactor operated at 330 or 480°C. The pyrolysis vapors produced were condensed using a condenser train of two countercurrent spray columns arranged in series. The temperature of the first condenser was varied between 20 and 115 °C, while the second condenser temperature was kept at 20 °C. The composition of the oil were measured by several analytical techniques (Gas Chromatography/Flame Ionization Detector (GC/FID), KF Titration, GC/MS). They observed that pyrolysis at 330 °C gives a light oil with a low amount of mid-boilers [normal boiling point of 150-300 °C] and heavy compounds (water insolubles and mono- and oligosugars). Sugars, mid-boilers, and water-insoluble ligninderived oligomers are more present in the oil obtained at 480 °C, while the yields of light organics are approximately the same for 330 and 480 °C. Operating the first condenser around 70-90 °C gives an aqueous liquid in the second condenser containing 40 wt % light organics, which are interesting for extraction (e.g., 10 wt % acetic acid) and supercritical water gasification to produce hydrogen. Under these conditions, the oils from the first condenser have a high content of sugars (20 wt %) and lignin-derived oligomers (40 wt %), which are attractive fractions for fermentation/sugar chemistry and gasoline production via fluidized catalytic cracking (FCC)/hydrotreatment, respectively.

12.	Oudenhoven et al. (2012)	They performed pyrolysis (at 530°C) of Pine wood in a fluidized bed fast pyrolysis reactor in which the produced vapors were condensed in two stages, first one operated at 80°C and the second one was operated at -5°C. The liquid obtained in the first condenser contains the heavy compounds (lignin derived aromatic compounds and anhydro-sugars) and in the second condenser most of the light compounds (including the acids) are collected. Pine wood was washed with this second condenser liquid at 90 ◦C for 2 h to remove the (alkali) minerals to increase the selectivity towards levoglucosan during pyrolysis. Rinsing of the biomass after acid washing is required for maximal levoglucosan production, to remove the washing liquid containing the dissolved minerals. The water content of the pyrolysis oil was measured by KF titration, amount of water insoluble fraction was determined by the cold water precipitation method, identification and quantification of biooil was done using GCMS analysis. The ash composition was determined with X-ray fluorescence (XRF) spectroscopy. The biomass before and after acid washing was characterized by FTIR spectroscopy to study the effects of washing on the biomass structure. This whole process resulted in an increase in organic oil yield and is accompanied with a decrease in water and char yield. The levoglucosan production increased up to 18 wt% on biomass intake, and was concentrated, by staged condensation, in a single fraction up to a concentration of 37 wt% in the first condenser oil.
13.	Bennett et al. (2009)	They investigated the extraction of levoglucosan from pyrolysis oil via phase separation, the acid-hydrolysis of the levoglucosan into glucose, and the subsequent fermentation of this hydrolysate into ethanol. The pyrolysis oil was prepared from Scots Pine feedstock. Saccharomyces cerevisiae was used for fermentation. Sugars and Ethanol were analyzed using

		GC. Optimal extraction conditions (41 wt% water, 34 °C) produced an aqueous extract with a concentration of up to 88 g/L LG. Optimal conditions for hydrolysis of the LG were 125 °C, 44 min, 0.5 M H2SO4 resulted in a maximum glucose yield of 216% (when based on original levoglucosan). The aqueous phase contained solutes which inhibited fermentation, however, up to 20% hydrolysate solutions were efficiently fermented (yield = 0.46 g EtOH/g glucose; productivity = 0.55 g/L h) using high yeast inoculums (1 g/L in flask) and micro-aerophilic conditions.
14.	Jiang et al. (2015)	They presented the effects of glycerol pretreatment on subsequent glycerol fermentation and biomass fast pyrolysis. Sugarcane bagasse was used as feedstock. The liquid fraction from the pretreatment process was evaluated to be feasible for fermentation by Paenibacillus polymyxa. The pretreated biomass was further utilized to obtain levoglucosan by fast pyrolysis. The pretreated sugarcane bagasse exhibited significantly higher levoglucosan yield (47.70%) than that of un-pretreated sample (11.25%). The sugars in the neutralized filtrate were analysed by liquid chromatography. Carbon (C), hydrogen (H) and nitrogen (N) contents were measured with an Organic Elemental Analyzer. The contents of potassium (K), sodium (Na), calcium (Ca) and magnesium (Mg) were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES).
15.	Lian et al. (2010)	They described new scheme to convert anhydrosugars found in pyrolysis oils into ethanol and lipids. Bio-oil was derived from the fast pyrolysis of acid washed poplar. Pyrolytic sugars were separated from phenols by solvent extraction and were hydrolyzed into glucose using sulfuric acid as a catalyst. Toxicological studies showed that phenols and acids were the main species inhibiting growth of the yeast Saccharomyces cerevisiae. The sulfuric acids, and carboxylic acids from the

		bio-oils, were neutralized with Ba(OH)2. The phase rich in sugar was further detoxified with activated carbon. The resulting aqueous phase rich in glucose was fermented with three different yeasts: S. cerevisiae to produce ethanol, and Cryptococcus curvatus and Rhodotorula glutinis to produce lipids. Pyrolytic sugar fermentation to produce ethanolis (max yield 0.473 g ethanol/g glucose) were found to be more efficient than for lipid production (max yield 0.167g lipids/g sugar which is equivalent to 0.266 g ethanol/ g sugar). Bio-oil was analysed by KF titration and GC/MS. The content of sugars in the bio-oil was quantified by ion exchange chromatography.
16.	Chi et al. (2013)	They tested overliming as a simple detoxification method, using the Escherichia coli KO11+ lgk to directly convert levoglucosan into ethanol. Red oak was used as feedstock, and the pyrolysis was conducted in a fluidized bed pyrolyzer operated at 450–500 °C. After treatment with at least 14.8 g/L of Ca(OH)2, fermentation with 2% (w/v) pyrolytic sugar syrup was observed with no inhibition of ethanol production (pH found to be 9.8). 8–16 h of treatment at 20 °C, and 1–4 h of treatment at 60 °C are necessary to obtain consistent ethanol production. A pH close to 10.0 is also necessary to remove toxic compounds from pyrolytic sugar. Overliming treatment removed about 80% of phenolic compounds from pyrolytic sugar, and the total phenolic content was reduced from 25.6 to 5.1 g/L. GC–MS was used for analysis.The overliming treatment of pyrolytic sugar did not cause significant loss of sugar. Levoglucosan from detoxified pyrolytic sugars was successfully metabolized into ethanol with E. coli.
17.	Zhang et al. (2013)	They studied three available mechanisms for levoglucosan formation from cellulose (free-radical mechanism; glucose intermediate mechanism; and levoglucosan chain-end mechanism). Thermal properties including activation energy,

		Gibbs free energy, and enthalpy for every pathway were also calculated. In cellulose chain, C1-O bond is slightly weaker than the bond O-C4´, with an energy difference of 4 kJ/mol. But this trend can be enlarged during the hydrolysis process, the water molecule reacts at C1-O position gives much lower activation energy than that at O-C4´ position, the activation energy difference is about 78 kJ/mol. The rate-determining step for all these three mechanisms is the one with breaking of C1-O bond. It was concluded that free radical mechanism has the highest energy barrier because of the difficulty of breaking C1-O bond directly. Glucose intermediate mechanism has lower energy barrier than free-radical mechanism, and levoglucosan chain-end mechanism is the most reasonable pathway because of the lowest energy barrier.
18.	Abdilla et al. (2018)	They reported a kinetic study on the conversion of levoglucosan (LG) to glucose (GLC) in water using sulphuric and acetic acid as the catalysts under a wide range of conditions in a batch setup. The effects of the initial LG loading (0.1−1 M), sulfuric and acetic acid concentrations (0.05−0.5 M and 0.5−1 M, respectively), and reaction temperatures (80−200 °C) were determined. The composition of the reaction mixture was determined by HPLC. Highest GLC yields were obtained using sulfuric acid (98 mol %), whereas the yields were lower for acetic acid (maximum 90 mol %) due to the formation of byproducts such as insoluble polymers (humins). GLC yield is at the highest when the reaction temperature is between 100 and 120 °C (with sulfuric acid) and between 140 and 160 °C (with acetic acid). The experimental data were modeled using MATLAB software, and kinetic parameters were determined. The reaction was first order with respect to LG. The activation energies were 123.4 kJ mol−1 and 120.9 kJ mol−1 for sulfuric and acetic acid, respectively.

Chapter 3

AIMS AND OBJECTIVES

1. To determine and compare kinetics for the pyrolysis of different feedstocks in the temperature range of 200-400ºC.
2. To study and compare the yields of bio-char, bio-oil, bio-gas for different feedstocks.
3. To perform suitable pretreatment of pyroliquid for upgrading pyrolysis sugar-syrup prior to bioconversion.
4. To select a suitable microorganism for fermentation of pyroliquid.
5. To study the growth kinetics of different microorganisms suitable for production of carboxylic acid, bio-alcohol and bio-electricity generation using bio-oils or derivatives as C- substrates.
6. Process simulation of large scale pyrolysis set-up using ASPEN Engineering 8.8 and sensitivity analysis.

Chapter 4

MATERIALS AND METHODS

4.1 Materials

4.1.1 Feedstocks Used

Jute stick (JS), Rice Straw (RS), Mustard Stalk (MS) from agricultural fields in West Bengal are used for pyrolysis feedstocks.

Fig 4.1 Jute stick

Fig 4.2 Rice straw

Fig 4.3 Mustard straw

4.1.2 Micro-organisms used for bioconversion:

a. *Clostridium acetobutylicum:* The strain *Clostridium acetobutylicum* was purchased from the MTCC (microbial type culture collection). The strain is gram-positive, obligate anaerobe, mesophilic (10-65ºC) and saccharolytic in nature.

b. *Mixed culture:* A bacterial mixed culture was isolated from the soil sample collected from agricultural field of hoogly district and used in this study. The consortium was enriched using Reinforced Clostridial Medium (RCM) and glucose as primary carbon source and was identified as an acidogenic consortium based on the fall of pH over time indicating production of acidic products.

c. *Shewanella putrefaciens* MTCC 8104: This was purchased from MTCC, India and was revived as prescribed in Nutrient Broth Media having Beef Extract 1 g/L, Yeast Extract 2 g/L, Peptone 5 g/L, Sodium Chloride or NaCl 5 g/L, Distilled Water 1L (pH 7) and sub-

cultured on Nutrient Agar Media (with same composition and Agar 15 g/L) plates and slants (with 10-15% glycerol suspension over it) for preservation. Since, *S. putrefaciens* is a facultative anaerobe, the broth media, after inoculation, was made anaerobic by flushing with nitrogen gas for 15 min, tightly sealed and incubated at 37^{o}C for 24 h. The agar plates were covered with light paraffin to avoid contact of oxygen with the bacterium.

4.1.2.1 Growth medium for *C. acetobutylicum* (Reinforced Clostridial Agar medium)

Peptone(Merck)- 10 gm/l, Beef Extract(Merck)- 10 gm/l, Yeast Extract(Merck)-3 gm/l, Dextrose(Merck)-5 gm/l, NaCl(Merck)-5 gm/l, L-cysteine HCl(Merck)-0.5 g/l, Sodium acetate(Merck) – 3 gm/l, Distilled water- 1000 mL.

4.1.2.2. Growth Medium for mixed culture bacteria:

Same RCM media was used.

4.1.2.3. Growth Medium for *S. putrefaciens* (modified Minimal Salt Media or M9 (1 X strength))

Disodium Hydrogen Phosphate or Na_2HPO_4 7.5 g/L, Potassium Dihydrogen Phosphate or KH_2PO_4 3 g/L, Sodium Chloride or NaCl 5 g/L, Ammonium Chloride or NH_4Cl 5 g/L, 1M Magnesium Sulfate or $MgSO_4$ 2.46 g/L, 1 M Calcium Chloride or $CaCl_2$ 1.47 g/L, Vitamin solutions (Biotin 1g/L, Thiamin 1g/L) 100 L, 10X Trace element solution (EDTA 0.5 g/L, Ferric Chloride or $FeCl_3$ 83 mg/L, Zinc Chloride or $ZnCl_2$ 8.4 mg/L, Copper Chloride or $CuCl_2$ 1.3 mg/L, Cobalt Chloride or $CoCl_2$ 1 mg/L, Boric Acid or H_3BO_3 1 mg/L, Manganese Chloride or $MnCl_2$ 0.1 mg/L) 1 mL, Potassium Chloride or KCl 50 mg/L, Distilled Water 1 L; pH 6.8

4.2 Experimental Setup for Pyrolysis

The different components for the experimental set-up are:

a. PID temperature controller

   PID temperature controller was used to maintain the isothermal condition for the pyrolyzer.

Fig 4.5: PID Temperature Controller

b. Furnace

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

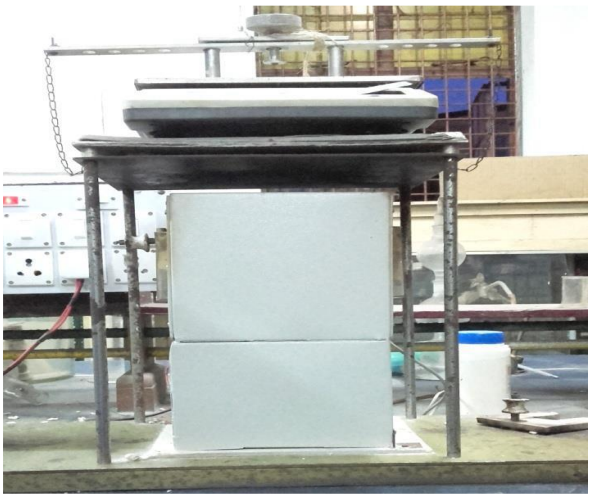


Fig 4.5: Furnace with the weighing machine on the top

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 was connected to the condenser. The cooling circulating water inside the condenser was maintained at 20ºC by the water bath.

e. Pyrolyzer reactor

The semi-batch pyrolyzer (sample holder) was 50 mm in diameter and 640 mm long cylindrical and made up of stainless steel. It operated isothermally.

4.3 Experimental Procedure

4.3.1 LTLT Pyrolysis

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

a) The operating temperature of the furnace was varied from 473K to 673K. The isothermal condition for the pyrolyzer was maintained by using the PID temperature controller.

b) Once the furnace attained its pre-set temperature the pyrolyzer was inserted into the furnace in a horizontal manner.

c) The duration of experimental run was 1-2 h at all temperatures.

d) Nitrogen was supplied to the pyrolyser throughout the experiment to maintain inert atmosphere.

e) The outlet of the pyrolyzer was connected to two condensers. Condenser 1 is operated at 80°C and condenser 2 was operated at 20°C, which in turn was connected to an ice-bath system.

f) The volatile product stream was passed through the water jacketed condensers.

g) The condensable volatiles were collected from the condensing units and non-condensable gaseous products were driven out.

h) 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.

i) The solid pyro-char and the liquid pyro-oil from both the condensers were collected carefully after the experimental run was completed.

4.3.2 Studying Growth curve of *S. putrefaciens on* pyroliquid (20°C condensate)

Growth kinetics of s. putrefaciens on 20°C condensate of rice straw and mustard straw were studied to check the possibility of developing microbial fuel cell (MFC) by following steps:

a) 20°C condensate from RS and MS were first diluted to 80 to 0.0395 vol% and taken as samples.
b) 500 µL of M9 minimal media is taken and added with 150µL of samples and inoculated with s. putrefaciens which was sub-cultured in nutrient agar media in 50 ml flasks.
c) After inoculation, the head space volume of the test tubes were sparged with argon gas for 2-3 min to make the system anaerobic. It was immediately followed by air tight sealing of tubes with cotton plug and paraffin film strips.
d) All the inoculated flasks were kept in incubator at 37°C
e) OD of all the sets were measured after 48 hrs to determine the MIC value of the substrates.
f) Two sets of RS bio-oil and two sets of MS bio-oil which have given better growth were taken for further growth study.
g) The growth pattern of *S. putrefaciens* was studied, over a week's time, by initially inoculating 100 µL of *S. putrefaciens* suspension in M9 broth media with varying substrate concentrations. Other growth conditions were followed after optimization, as above. These were incubated under previously stated conditions. Absorbance of each such concentration checked at 600 nm at regular intervals of time starting from 0^{th} hr of incubation. Initially, bio-oil was used as sole carbon source, in absence of glucose. Later, to enhance overall growth, glucose (20g/L) was also added in the media. Growth kinetics was accordingly studied in each case.

4.3.3 Bioconversion of pyroliquid from condenser 1

4.3.3.1 Upgradation of pyroliquid

Pretreatment of pyroliquid from the condenser 1 was done according to the following protocol.

a) *Cold water extraction:* Cold water extraction of pyrolysis oil was carried out for all samples using chilled water kept at 4°c to remove insoluble lignin. Pyrolysis oil were added dropwise to chilled water at 1:10 W/V and mixed in a vortex for 5-10 minutes for proper homogenization.

Water insoluble part of the pyroliquid solution was separated by filtration using 0.22 µm pore size micro-filter membrane and stored at 4°C.

b) *Ethyl Acetate (EA) extraction:* After cold water extraction the filtrate was further extracted with ethyl acetate to remove organic compounds, known to be inhibitory for microorganisms, leaving an aqueous phase rich in anhydrous carbohydrates. A 1:2 wt% filtrate to EA solution was prepared and mixed for 12 h in a shaker at 100-150 rpm and 37°c. After mixing the samples were left standing in test tubes for phase separation. The organic layer was separated using separating funnel. Remaining EA was removed by evaporation at 50°C for 24h in an oven.

c) *Acid Hydrolysis:* Glucose was produced from levoglucosan as a result of acid hydrolysis. Samples were diluted to 10times adding distilled water, followed by addition of H2SO4 (final concentration of 0.5 M) and hydrolysis at 120°C for 20 min in an autoclave.

d) *Neutralization:* 5 ml of hydrolyzate were neutralized using 5M NaOH for the purpose of determination of the sugar content using DNS method.

e) *Detoxification:* Various amount of Ca(OH)2 powder, from 0.000 g/L to 31.67 g/L were added to other remaining hydrolysate to obtain a pH over 10.0. Treatment time was 4h and was conducted at 60°C in a water bath and mixed with magnetic stirrer.

After the treatment, samples were centrifuged at 10000rpm for 15 min. The supernatant was treated with 50% (W/V) sulphuric acid and adjusted to pH 7.0. The samples were then centrifuged again at 10000 rpm for 20 min to remove precipitates and was filtered through 0.22 µm membrane filter, and stored at 4°C until use.

4.3.3.2 Analysis of sugar

Sugar content in the pyro-syrup, both before and after the detoxification were analysed by DNS test. All the samples were diluted ten times adding distilled water, and then added to 3, 5-

dinitrosalicylic acid (DNS) solution (1:1 V/V) in test-tubes at 90-100°C for 5-10 min; water bath was used for controlling the temperature. Then, the optical density (OD) value of the samples were measured using spectrometry and subsequent values of TRS concentration was determined using the calibration plot correlating OD and sugar concentration.

4.3.3.3 Fermentation

a) Both sets of hydrolysate before and after detoxification were used as carbon source in the fermentation experiments performed in two sets using two different inoculum, c. acetobutylicum and mixed consortia.

b) 20 ml test tubes were taken and autoclaved at 120°C for 15 min for sterilization.

c) Hydrolysates were added to RCM media (1ml hydrolysate to 10ml media) in test tubes and inoculated with both sets of bacteria with the help of a micropipette and sterile microtip. Inoculum was taken for previously prepared seed culture.

d) In one test tubes only 10ml media was inoculated without hydrolysate and taken as control.

e) After inoculation, the head space volume of the test tubes were sparged with argon gas for 2-3 min to make the system anaerobic. It was immediately followed by air tight sealing of tubes with cotton plug and paraffin film strips.

f) All the inoculated test tubes were kept in incubator at 37°C and the growth was monitored for 48h.

4.3.4: Modelling of overall process using ASPEN:

Modelling for the overall thermochemical- biochemical hybridization was done by ASPEN ENGINEERING 8.8.

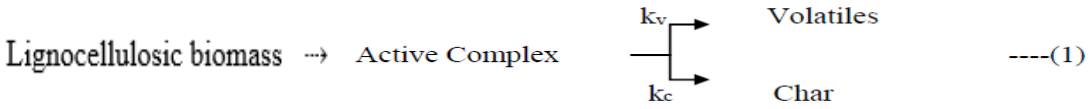
Chapter 5

THEORETICAL ANALYSIS

5.1 Kinetics of pyrolysis

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)

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:



----(1)

$$-\frac{dW}{dt} = (k_v + k_C)W \quad ---(2)$$

Let, $k_v + k_C = k$

Therefore,

$$-\frac{dWv}{dt} = kW \quad ---(3)$$

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

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

$$= k_v W_0 \cdot \exp(-kt) \quad ---(4)$$

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

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

$$= k_c W_0 \cdot \exp(-kt) \quad ---(5)$$

Similarly,

$$\frac{dWoil}{dt} = k_{oil}W$$

$$= k_{oil}W_0 \cdot \exp(-kt) \quad ---(6)$$

And,

$$\frac{dWg}{dt} = k_gW$$

$$= k_gW_0 \cdot \exp(-kt) \quad ---(7)$$

Equation (3), (4), (5), (6) and (7) have been solved analytically with the following initial conditions:

$$W(t \to 0) = W_0, W_v(t \to 0) = W_{v0} = 0, W_c(t \to 0) = W_{c0} = 0,$$
$$W_{oil}(t \to 0) = W_{oil0} = 0, \quad W_g(t \to 0) = W_{g0} = 0 \quad ---(8)$$

The solutions under isothermal conditions are as follows:

$$W(t) = W_0 \exp(-kt) \quad ---(9)$$

$$W_v(t) = \left(\frac{k_v}{k}\right) W_0[1 - \exp(-kt)] \quad ---(10)$$

$$W_c(t) = \left(\frac{k_c}{k}\right) W_0[1 - \exp(-kt)] \quad ---(11)$$

$$W_{oil}(t) = \left(\frac{k_{oil}}{k}\right) W_0[1 - \exp(-kt)] \quad ---(12)$$

$$W_g(t) = \left(\frac{k_g}{k}\right) W_0[1 - \exp(-kt)] \quad ---(13)$$

Under isothermal condition:

$$\frac{W_c(t) - W_{c_0}}{W_v(t) - W_{v_0}} = \frac{k_cW}{k_vW}$$

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

$$= \frac{W_C(t \to \alpha) - W_{C_0}}{W_v(t \to \alpha) - W_{vo}} \quad ---(14)$$

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

$W_C(t \to \alpha) = W_R(t \to \alpha)$

And, $W_v(t \to \alpha) = Wo - W_R(t \to \alpha) \; ---(15)$

Therefore:

$$\frac{W_c(t)}{W_v(t)} = \frac{W_R(t \to \alpha)}{W_o - W_R(t \to \alpha)} = \frac{W_C(t \to \alpha)}{W_v(t \to \alpha)} = \frac{k_c}{k_v}$$

Or, $W_c(t) = \frac{k_c}{k_v} * W_v(t) \; ---(16)$

Similarly, Woil and Wg at any time t are given by:

$$W_{oil}(t) = \frac{k_{oil}}{k_v} * W_v(t) \; ---(17)$$

And, $W_g(t) = \frac{k_g}{k_v} * W_v(t) \; ---(18)$

Regression analysis of equations (9), (10), (11), (12) and (13) gives the values of the rate constants k, kv, kc, koil and kg respectively, at different temperatures.
Kinetic parameters have been determined for the pyrolysis of all the feedstocks.

5.2 Evaluation of the Growth Kinetic Parameters

From the experimental data obtained by performing batch studies on both of the bacteria, the growth kinetic parameters for both were calculated. The growth of a bacteria growing in a batch reactor is given by,

$$\mu = \frac{1}{X}\frac{dX}{dt} \; ---(1)$$

Integration of the above equation with biomass concentration from X0 to X and time from 0 to t, the equation is converted to the form,

$$ln\frac{X}{X_0} = \mu t \; ---(2)$$

Equation 2 is in the form y = mx, where m is the slope of the straight line which is equal to μ. So, if ln(X/X0) values of one bacteria are plotted against corresponding time values then the value of the slope of the curve will be equal to the value of specific growth rate (μ) of that bacteria.

Following this method four different μ values for four different substrate concentrations (0.5%, 1%, 1.5% and 2%) was calculated. Using these four μ values the growth kinetic parameters μm and KS of the bacteria was evaluated. Linearized form of Monod**'s equation** was used to calculate μ m and KS.

Linearized form of Monod's equation is given by,

$$\frac{1}{\mu} = \frac{k_s}{\mu_m} * \frac{1}{s} + \frac{1}{\mu_m} \quad ---(3)$$

This equation is in the form y = mx + c, where the slope m of the curve gives the value of KS/μ m and the value of the intercept c is equal to 1/μm. From the value of the intercept μ m is calculated and using this value KS is calculated.

This procedure of batch study was performed for *Shewanella putrefaciens MTCC 8104* in modified Minimal Salt Media or M9 medium formulated and μ m and KS values for both of the cases, using pyrooil as sole carbon source and adding glucose with pyrooil for support.

Chapter 6

RESULTS AND DISCUSSION

6.1 Determination of the kinetics for the pyrolysis of biomass

6.1.1 Weight loss history for different feedstocks:

The weight loss history for rice straw (RS), jute stick (JS), mustard straw (MS) has been studied in pyrolysis process. The fraction of weight residue had been plotted against time in the temperature range of 200-400°C.

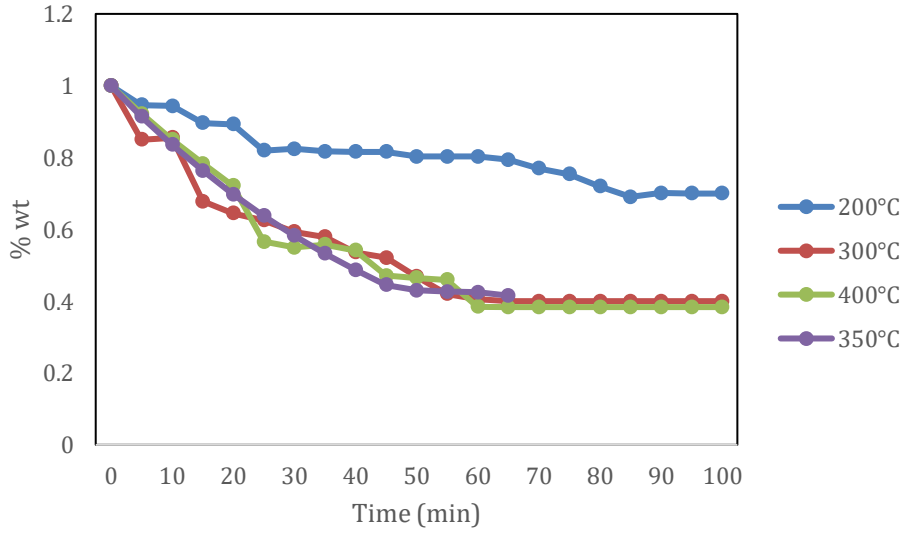


Fig6.1: Comparative curve of % Wt residue to Time (Rice Straw)

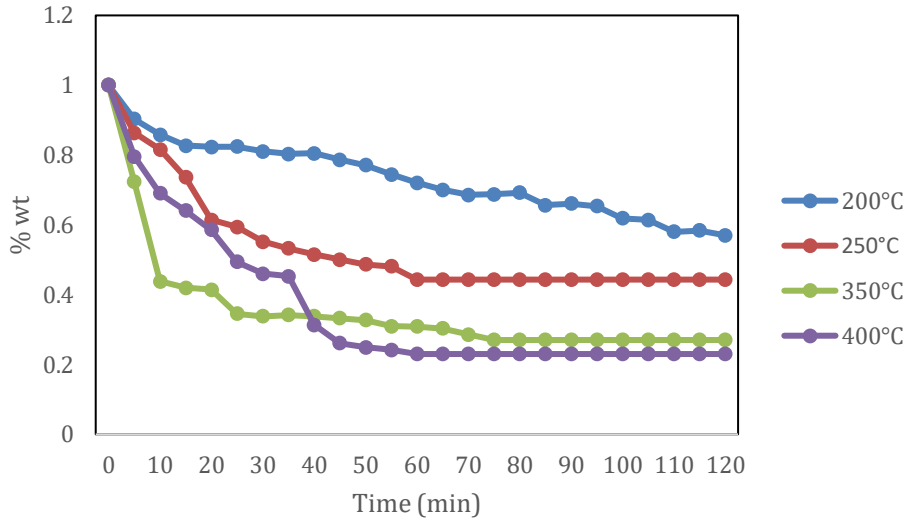


Fig 6.2: Comparative curve of % Wt residue to Time (Jute Stick)

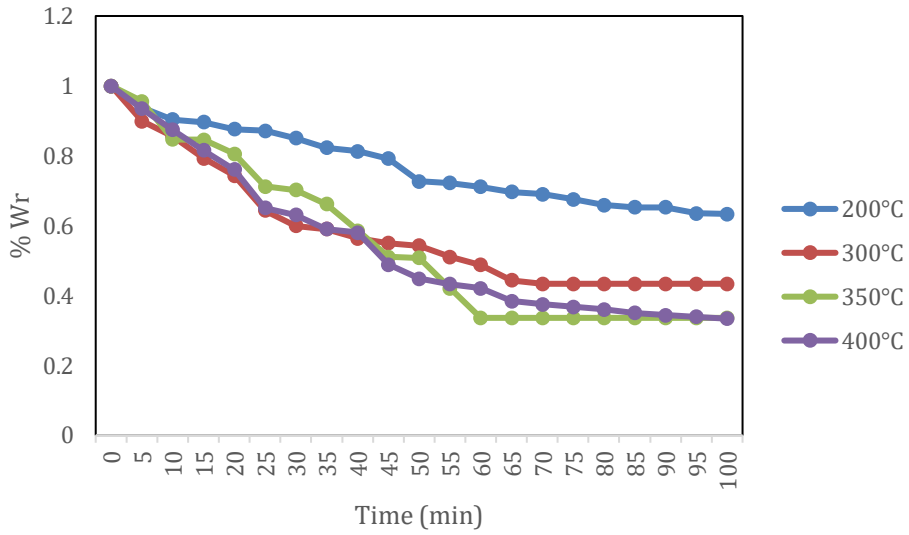


Fig 6.3: Comparative curve of % Wt residue to Time (mustard straw)

From the figures (fig 6.1, fig 6.2, fig 6.3 and fig 6.4) it is observed that there is a gradual weight loss of the biomass as it is pyrolyzed to produce volatiles and char with the increase in temperature over a time period of 1h-2h. At each time the weight loss is increasing with the increase in pyrolysis temperature due to the increase of rate of pyrolysis.

6.1.2. Comparative study on Yield of char, tar and gas:

The % yield of char, pyro-liquid and pyro-gas for RS, JS, MS for all pyrolysis temperature had been plotted.

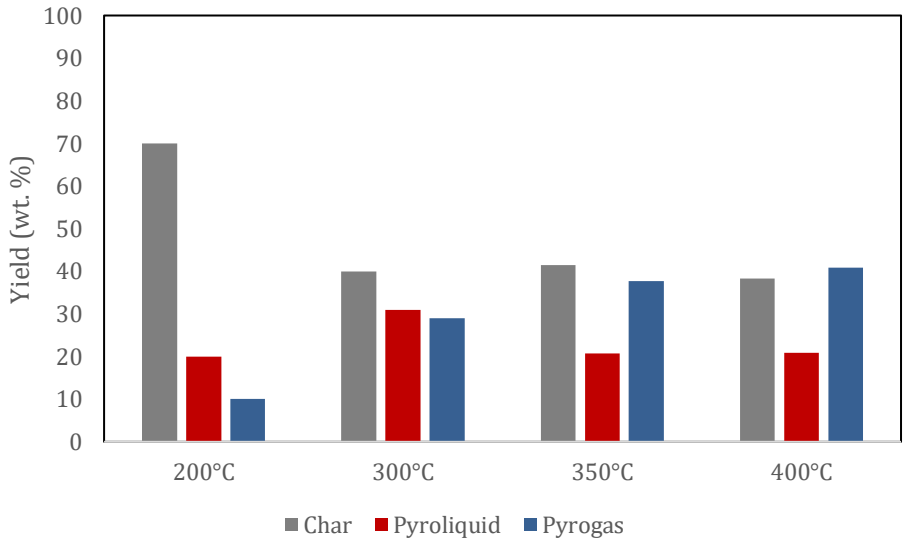


Fig 6.4: % yield of char, pyro-liquid, pyro-gas at different pyrolysis temperature (RS)

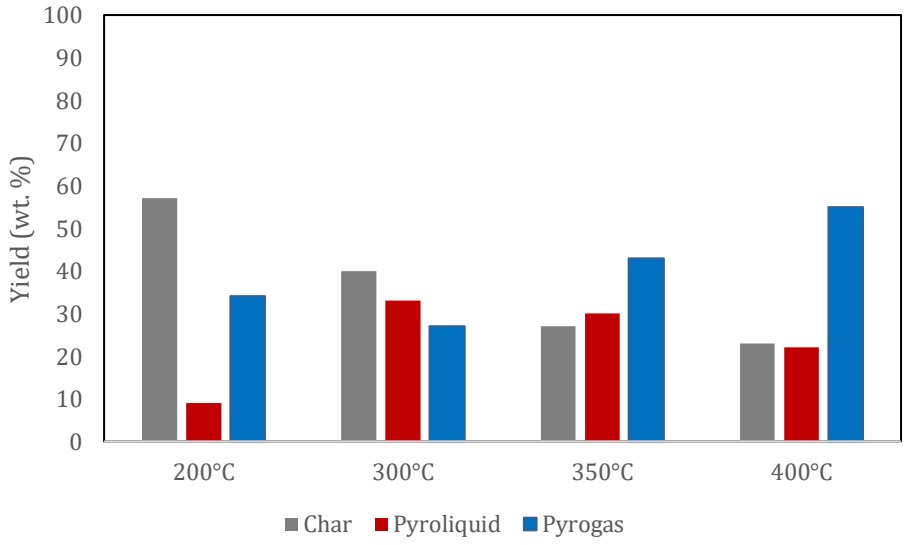


Fig 6.5: % yield of char, pyro-liquid, pyro-gas at different pyrolysis temperature (JS)

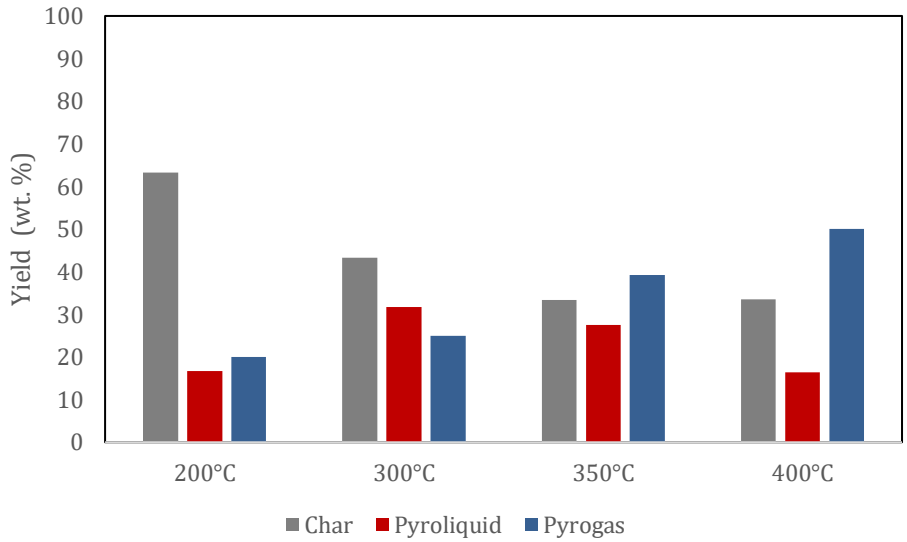


Fig 6.6: % yield of char, pyro-liquid, pyro-gas at different pyrolysis temperature (JS)

It is observed that the char yield decreases with increase in pyrolysis temperature and gas yield gradually increases with temperature. Maximum yield of pyro-liquid was found at 300°C which is 31%, 30%, 31.6% for Rice Straw, Jute Stick and Mustard Straw respectively. Maximum yield of char was at 200°C, 70%, 57% and 63.3% for rice straw, jute stick and mustard straw respectively. Maximum pyro-oil yield was 40.83%, 55% and 50% for Rice Straw (at 400°C), Jute Stick (at 400°C) and Mustard Straw (at 350°C) respectively.

6.1.3. Volatile, char, oil, gas generation:

From the are experiment we gave got the values for weight of residue and any time [WR(t)], Wv at any time was calculated. Wc, Woil, Wg were calculated from Wv using equation no. (16), (17) and (18).weight fraction of volatile, char, oil and gas were determined by dividing the values of Wv, Wc, Woil and Wg by the initial value of feed (Wo), and had been plotted with respect to time for all the feedstocks (RS, JS, MS) at each pyrolysis temperature.

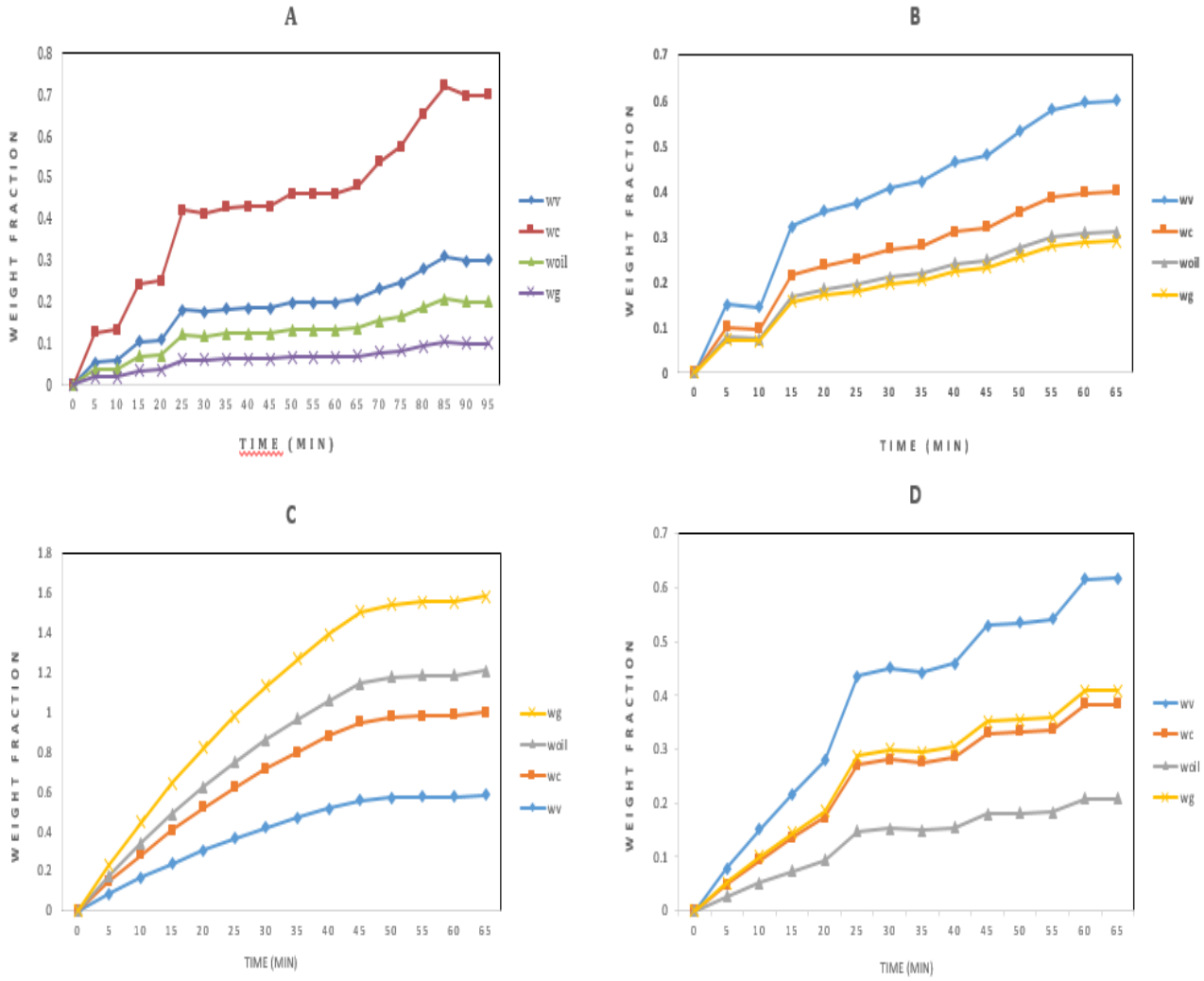


Fig 6.7: weight fraction of volatile matter, char, pyro-oil, gas vs Time (min) plot at different pyrolysis temperatures for Rice Straw, fig A, fig B, fig C and fig D are at 473K, 573K, 623 K and 673K respectively.

For rice straw, at 200°C char generation was highest, at 300°C volatile generation was highest, and oil generation was higher than gas generated. At 350°C gas generation was highest. And at 400°C volatiles generation was highest, where gas generated is higher than that of oil. (from Fig 6.7)

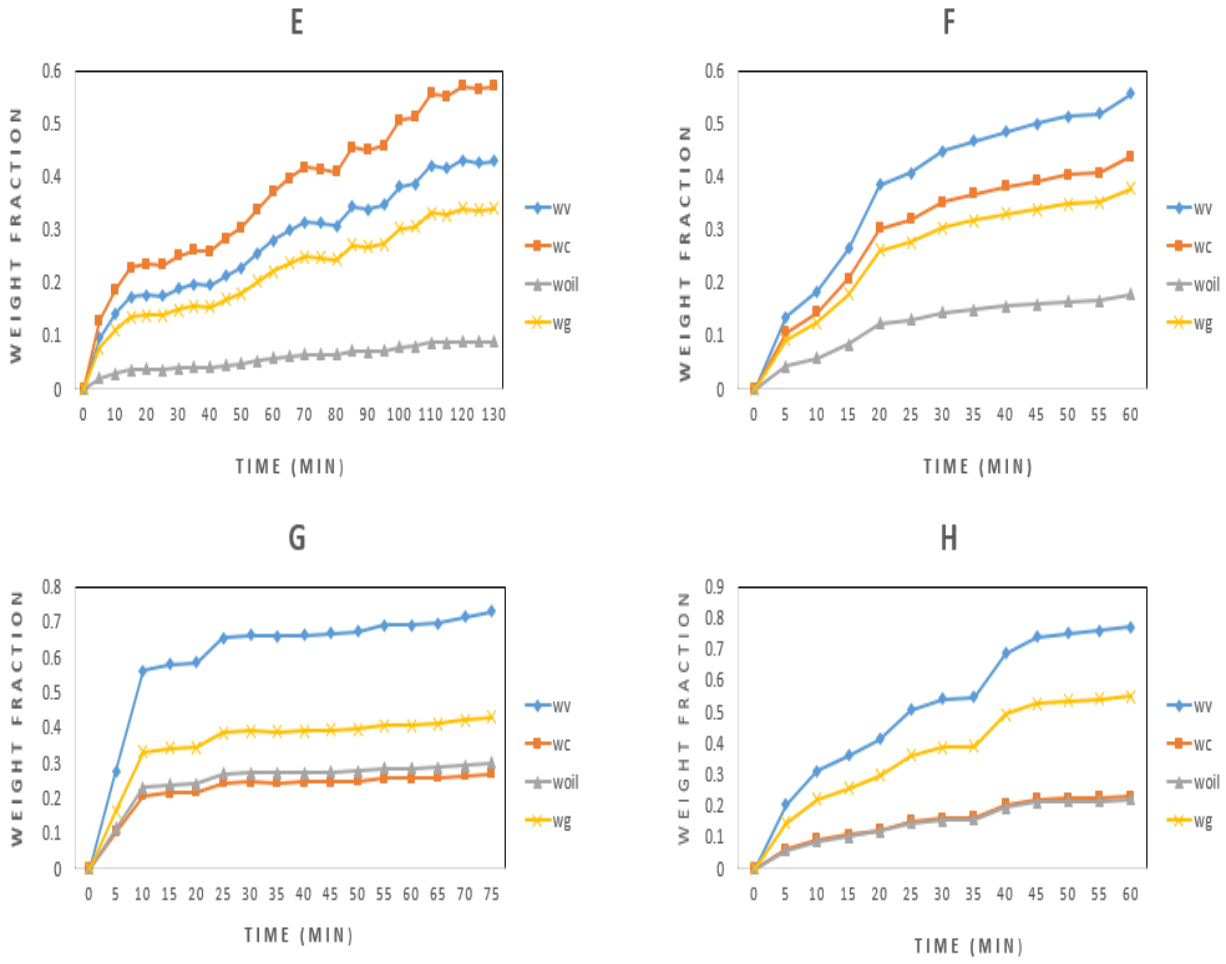


Fig 6.8: weight fraction of volatile matter, char, pyro-oil, gas vs Time (min) plot at different pyrolysis temperatures for Jute Stick. Fig E, fig F, fig G and fig H are at 473K, 573K, 623 K and 673K respectively.

For jute stick, at 200°C char generation was highest, at 300°C volatile generation was highest, and oil generation was lower than gas generated. At 350°C volatile generation was highest. And at 400°C volatiles generation was highest, where gas generated is higher than that of oil. (from Fig 6.8)

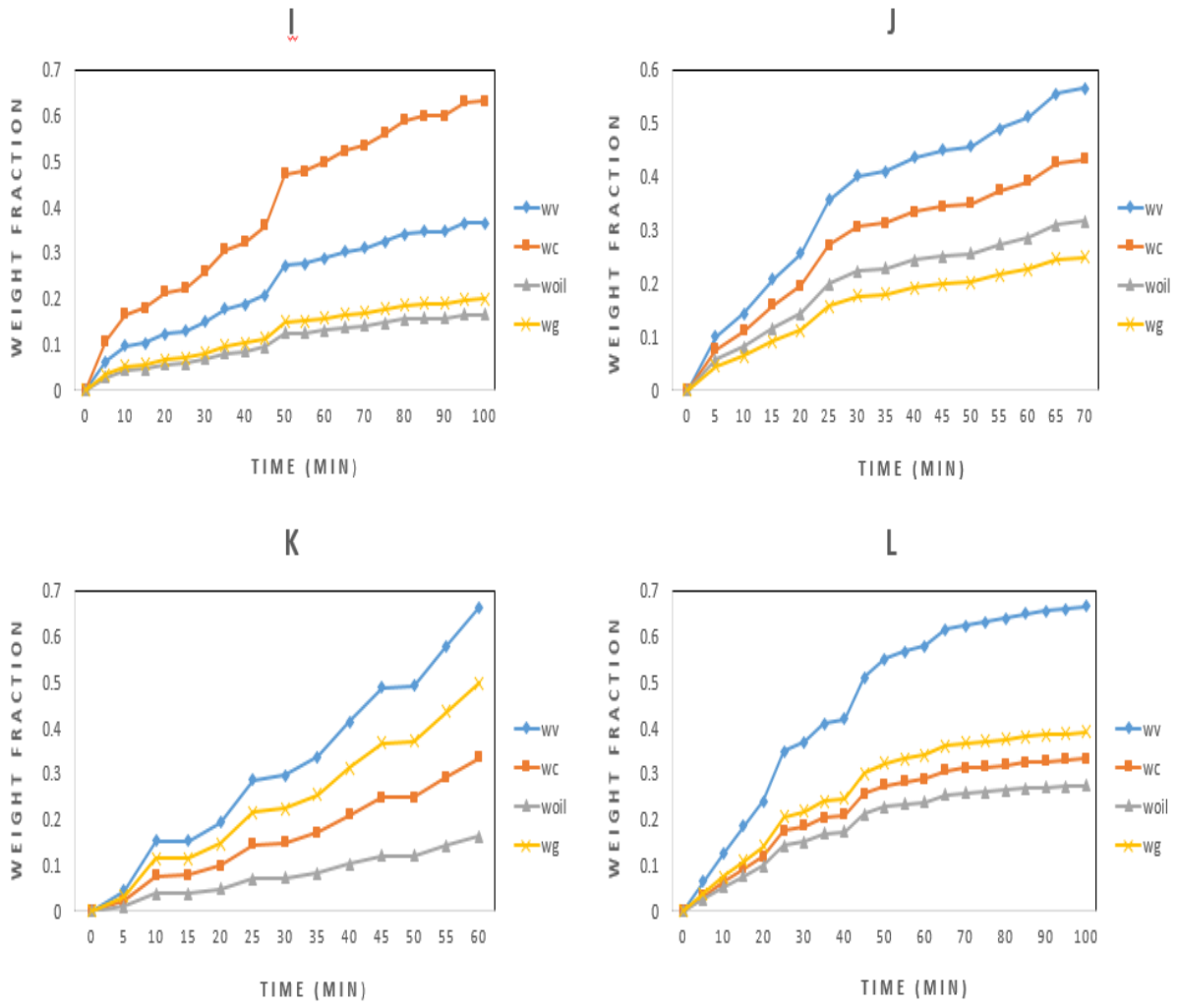


Fig 6.9: weight fraction of volatile matter, char, pyro-oil, gas vs Time (min) plot at different pyrolysis temperatures for Mustard Straw. Fig I, fig J, fig K and fig L are at 473K, 573K, 623 K and 673K respectively.

For mustard straw, at 200°C char generation was highest, at 300°C volatile generation was highest, and oil generation was higher than gas generated. At 350°C volatile generation was highest. And at 400°C volatiles generation was highest, where gas generated is higher than generation of oil. (from Fig 6.9)

6.1.4. Determination of reaction rate constants (k, kv, kc, koil, kg):

Reaction rate constants were determined using the equations (9), (10), (11), (12) and (13) and provided in the Table 1.

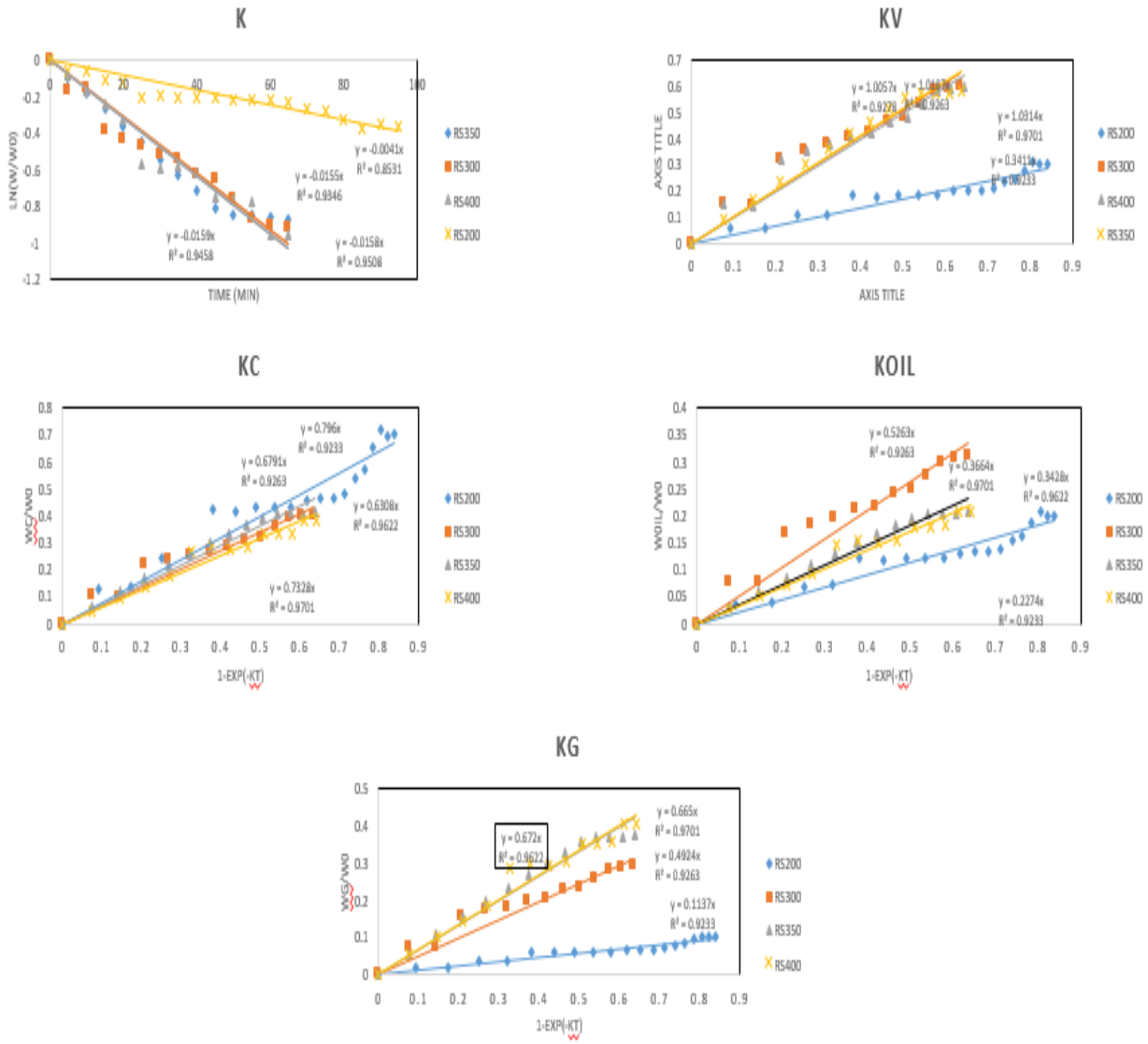


Fig 6.10: Determination of reaction rate constants for Rice Straw. ln(W/W0) vs. Time was plotted for determination of k. Wv/Wo, Wc/Wo, Woil/Wo and Wg/Wo at different temperature had been plotted against [1-exp(-kt)] to determine the kv, kc, koil and kg values respectively.

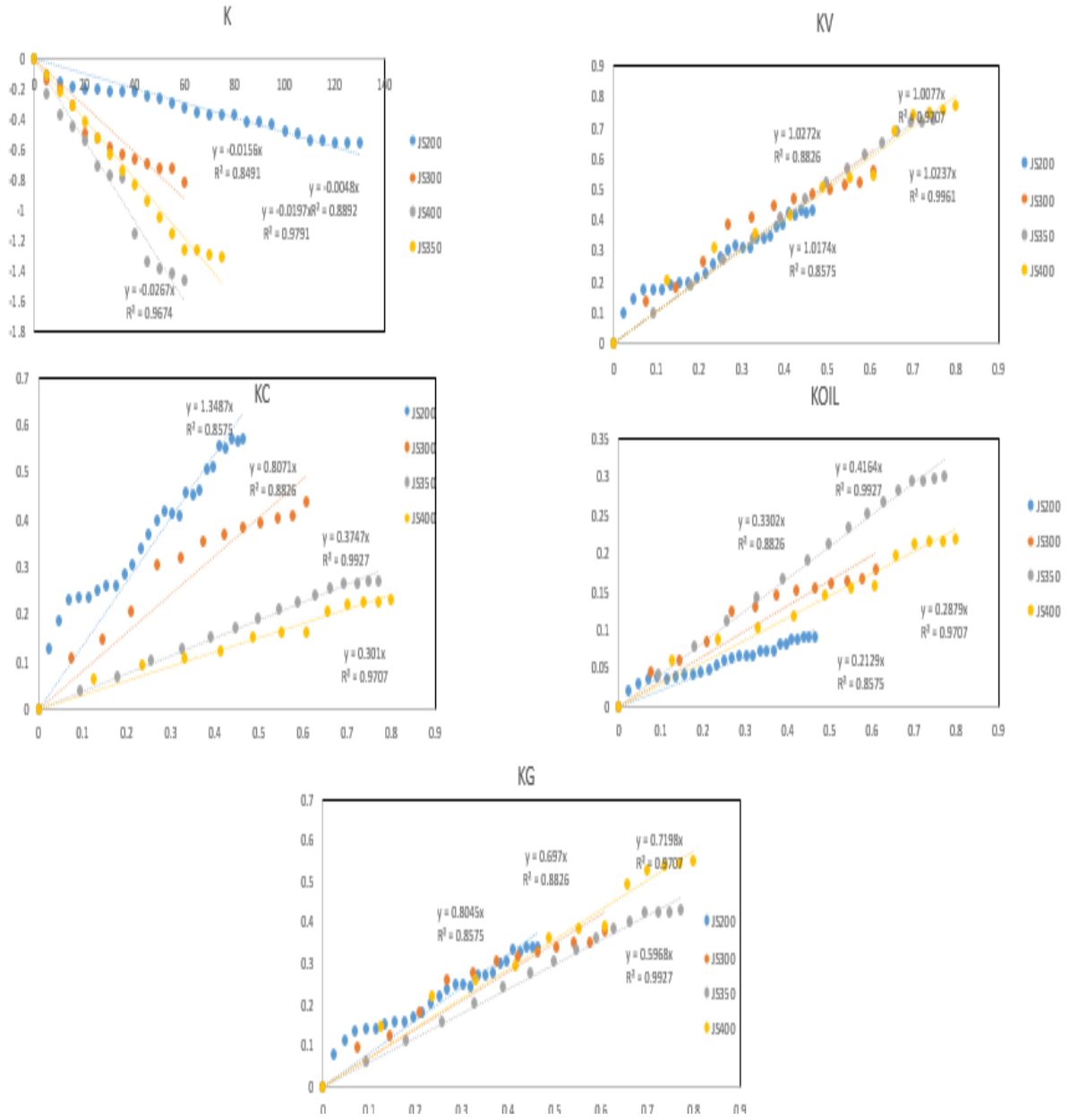


Fig 6.11: Determination of reaction rate constants for Jute Stick. ln(W/W0) vs. Time was plotted for determination of k. Wv/Wo, Wc/Wo, Woil/Wo and Wg/Wo at different temperature had been plotted against [1-exp(-kt)] to determine the kv, kc, koil and kg values respectively.

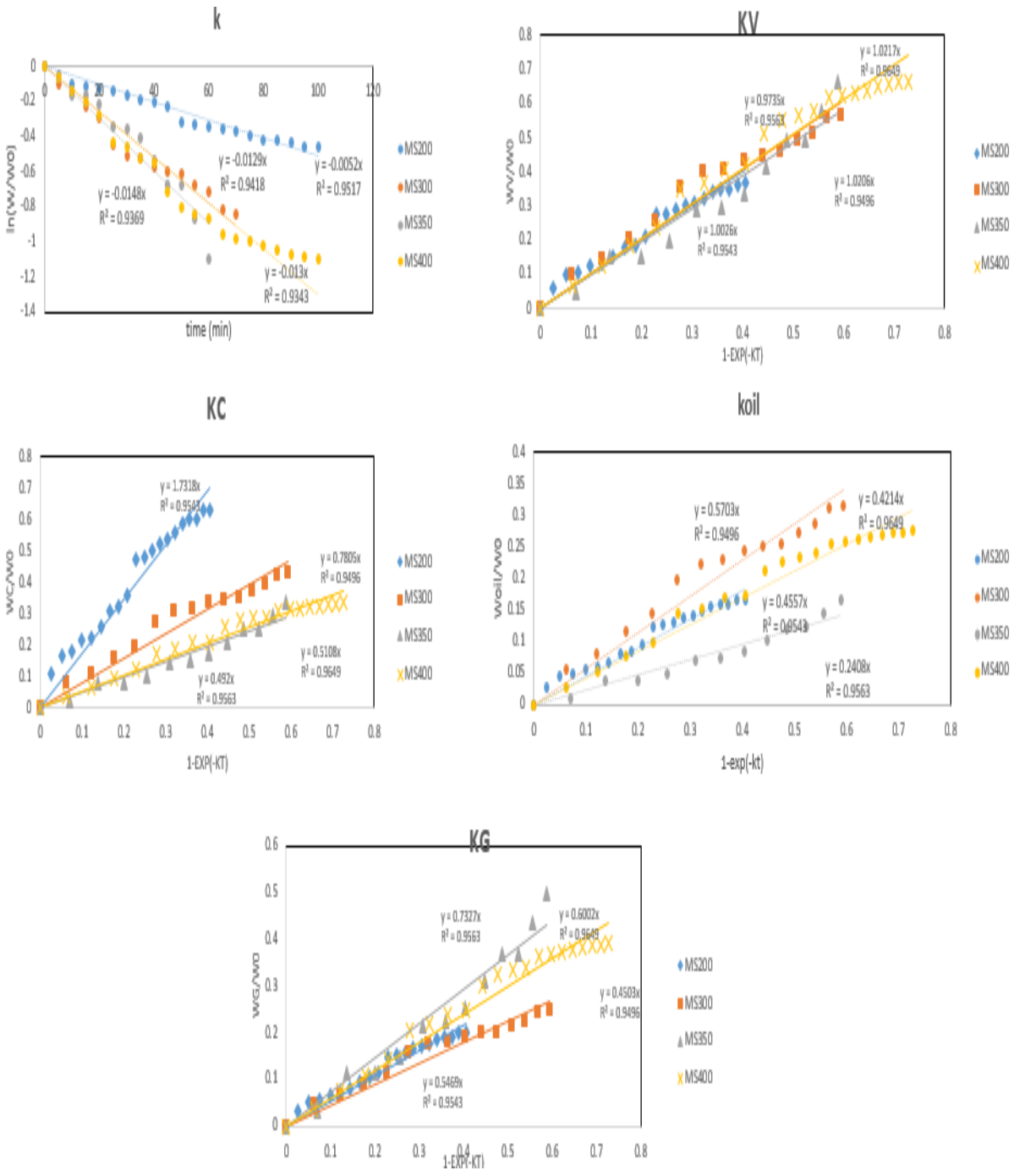


Fig 6.12: Determination of reaction rate constants for Mustard Straw. ln(W/W0) vs. Time was plotted for determination of k. Wv/Wo, Wc/Wo, Woil/Wo and Wg/Wo at different temperature had been plotted against [1-exp(-kt)] to determine the kv, kc, koil and kg values respectively.

Table 6.1: Reaction rate constants at different temperatures for RS, JS and MS

Material	Temp	Rate constants (min^{-1})				
		k	kv	kc	Koil	Kg
Rice straw	200°C	0.0041	0.0013	0.0033	0.0009	0.0004
	300°C	0.0155	0.0158	0.0105	0.0082	0.0076
	350°C	0.0156	0.0161	0.0114	0.0057	0.0104
	400°C	0.0158	0.0160	0.0099	0.0054	0.0106
Jute stick	200°C	0.0048	0.0049	0.0065	0.0010	0.0039
	300°C	0.0156	0.0161	0.0126	0.0052	0.0109
	350°C	0.0197	0.0200	0.0074	0.0082	0.0118
	400°C	0.0267	0.0269	0.0080	0.0077	0.0192
Mustard straw	200°C	0.0052	0.0052	0.0090	0.0024	0.0028
	300°C	0.0129	0.0142	0.0101	0.0084	0.0058
	350°C	0.0148	0.0144	0.0073	0.0036	0.0108
	400°C	0.0130	0.0133	0.0066	0.0055	0.0078

6.1.5. Calculation of Activation Energies as per Arrhenius Law:

The primary kinetics RS, JS and Ms 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 reported in Table3. All the rate constants are calculated from the experimental results in the temperature range of 473K to 673K and are superimposed with the predicted rate constants.

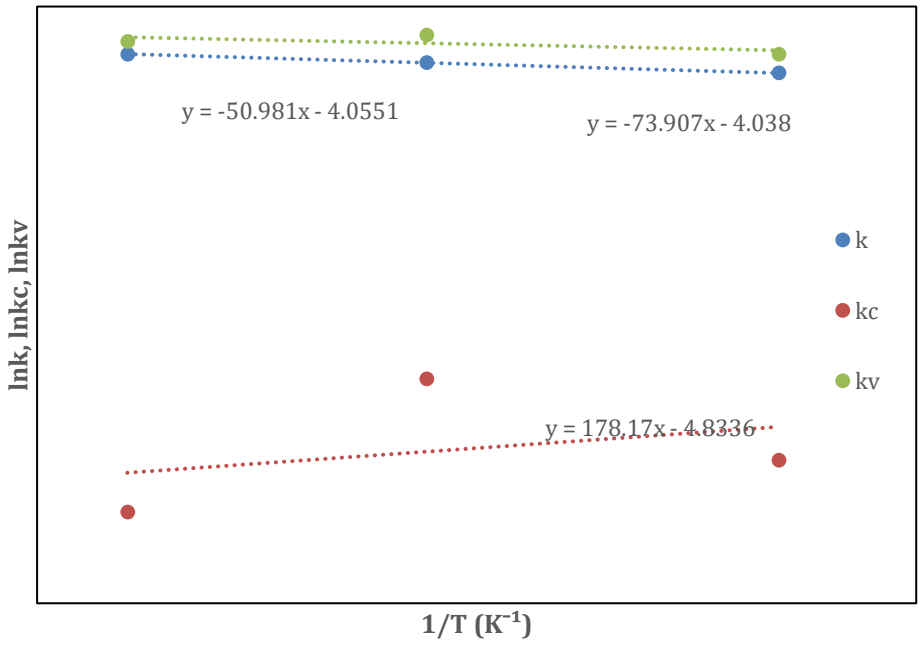


Fig 6.13: lnk, lnkv, lnkc vs. 1/T plot for Rice Straw

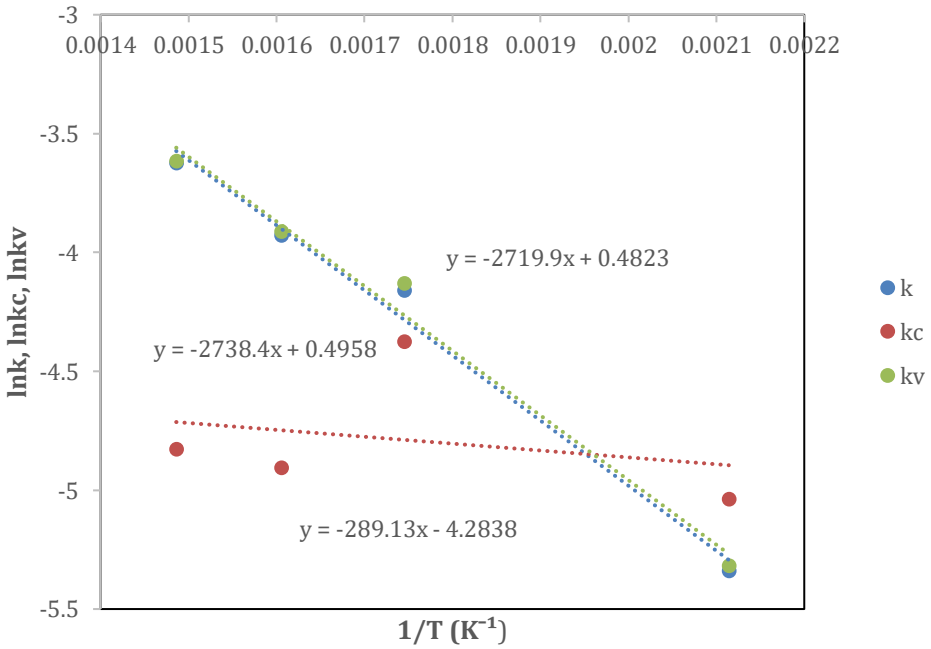


Fig 6.14: lnk, lnkv, lnkc vs. 1/T plot for Jute Stick

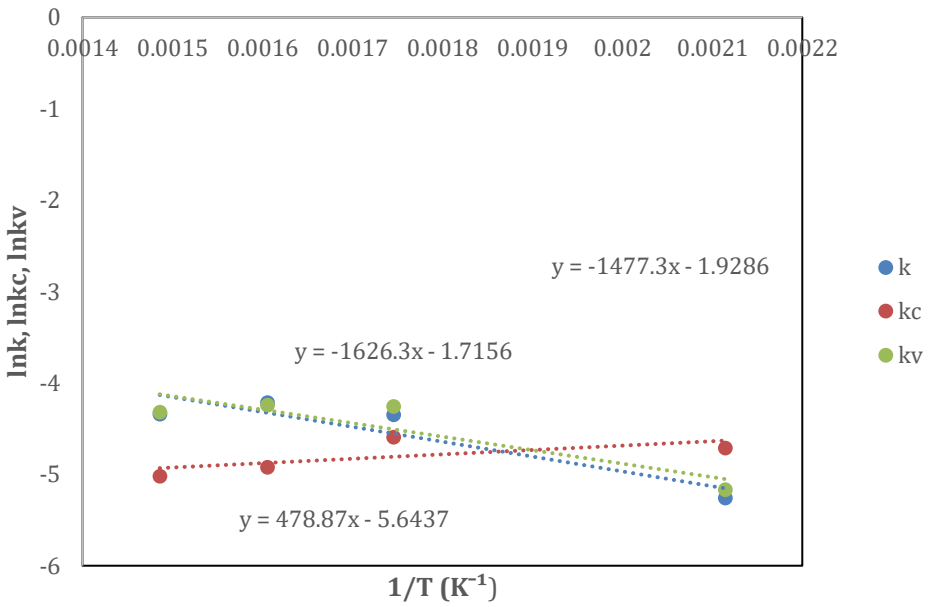


Fig 6.15: lnk, lnkv, lnkc vs. 1/T plot for Mustard Straw

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 are provided in the Table 2.

Table6.2: Calculated activation energies and frequency factors as per Arrhenius law

Types of feedstock	Reaction rate constants	Activation Energy (KJ/mol)
Rice Straw	k	0.60777
	kv	0.4239
	kc	1.4813

Jute Stick	k kv kc	22.7671 22.6133 2.4038
Mustard Straw	k kv kc	13.5211 12.2823 3.9813

6.2. Growth Study of *S. putrefaciens* on pyro-oil from 20°C condenser:

6.2.1. Determination of Minimum Inhibition Concentration (MIC):

The bio-oils are diluted with distilled water to concentrations from 40 to 0.039 vol% subsequent growth were measured using their OD values to find their minimum inhibition concentrations for the bio-oils (RS and MS).

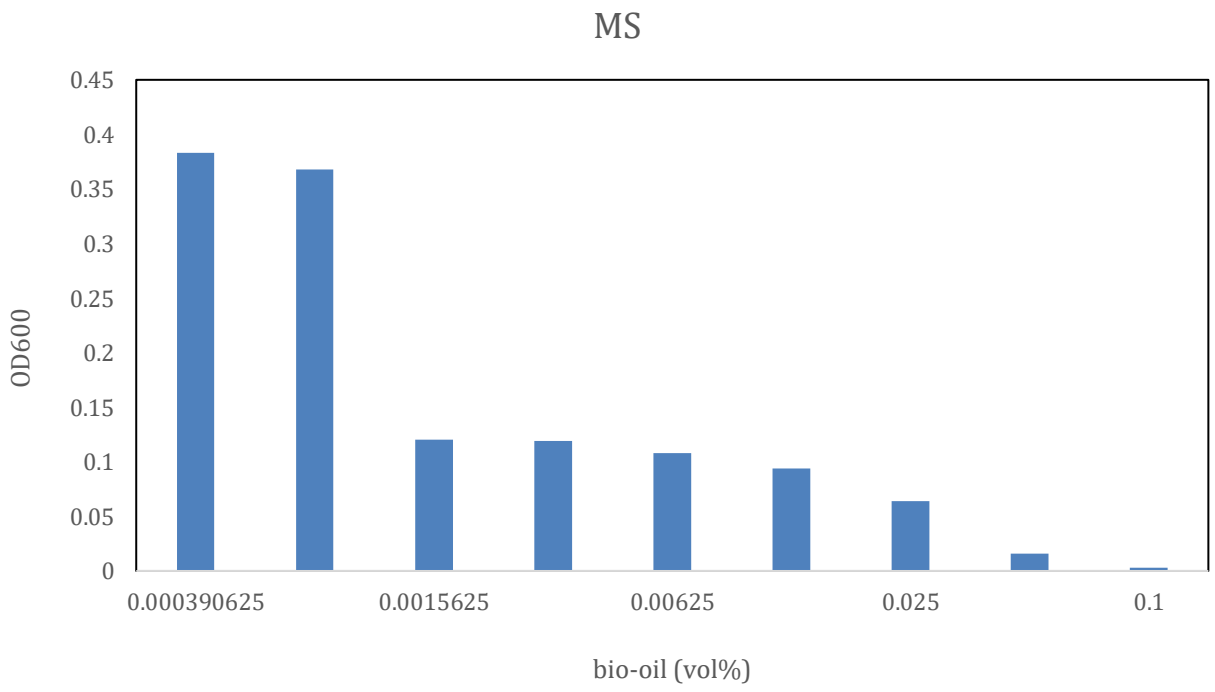


Fig 6.16: OD vs. bio-oil concentration (vol%) for Mustard Straw

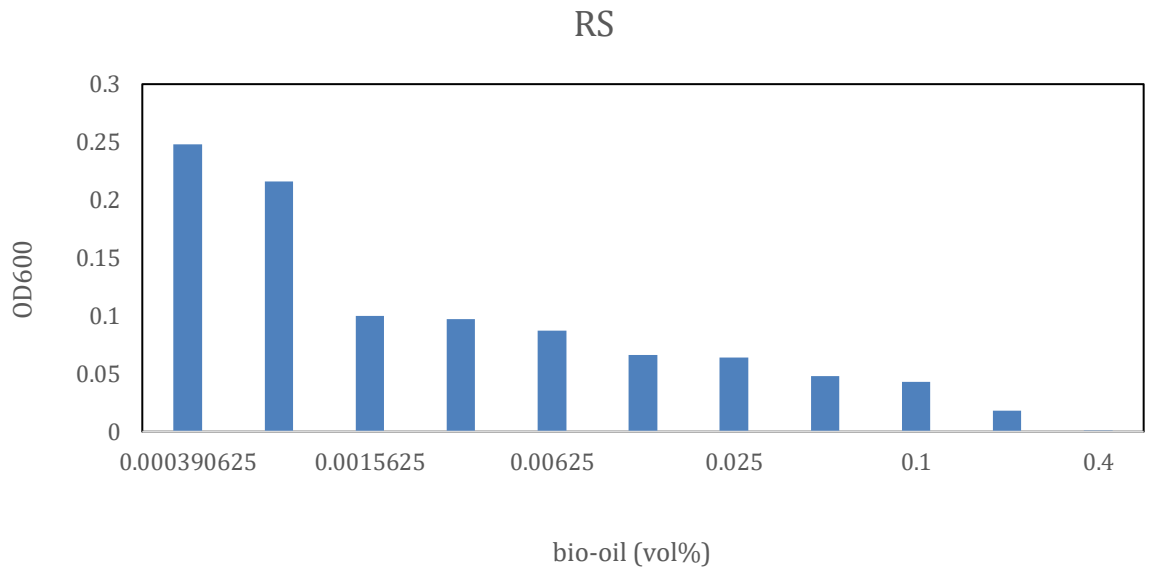


Fig 6.17: OD vs. bio-oil concentration (vol%) for Rice Straw

From the figures 6.16 and 6.17 it was found that the MIC of Rice Straw and Mustard Straw were 10 and 40 vol% respectively. The subsequent acetic acid concentrations was 17ppm and 44 ppm.

6.2.2. Growth curve kinetic study of *S. putrefaciens* with varying substrate concentration:

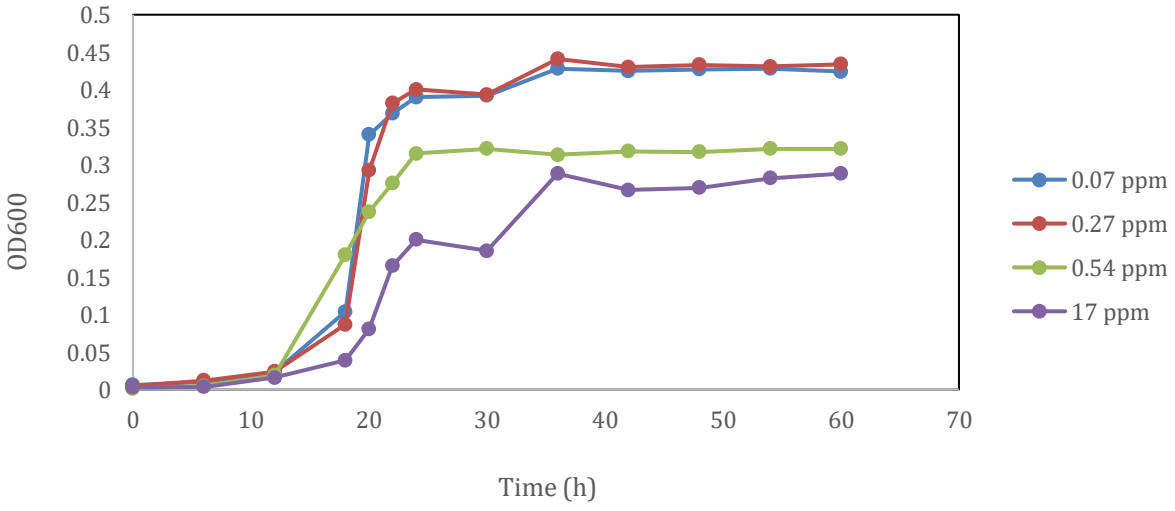


Fig 6.18: OD vs Time plot for different concentrations of bio-oil from RS (without glucose)

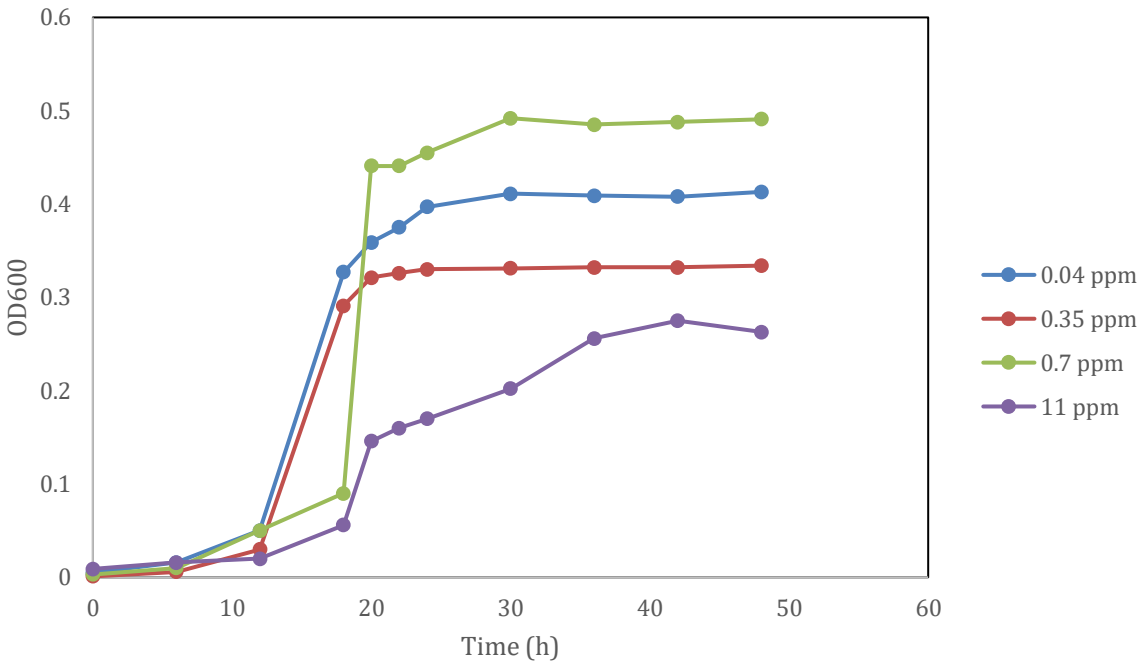


Fig 6.19: OD vs Time plot for different concentrations of bio-oil from RS (without glucose)

As it is evident from the figure above, *S. putrefaciens* showed increase in biomass concentration in case of media having bio-oil as substrate as compared to the medium having no bio-oil. This could possibly be due to the fact that the culture used acetic acid from the bio-oil as substrate, because no other carbon source was used in this study. Growth profile of. *S. putrefaciens* displays a typical sigmoidal curve. Growth curve figure shows Lag phase starts from 0 to 6 hours, exponential phase ranges from 6 to 36 hours, in case of both the substrates. Stationary phase starts 36 after hours. After 36 hours biomass concentration remains constant, growth stabilizes and stationary phase occurs. As the biooil concentration increases lag phase elongates, may be due to the fact that more time was needed for adaption for the culture on oil with higher concentration.

However, to enhance overall growth, glucose (20 g/L) was also added in the media, already having bio-oil.

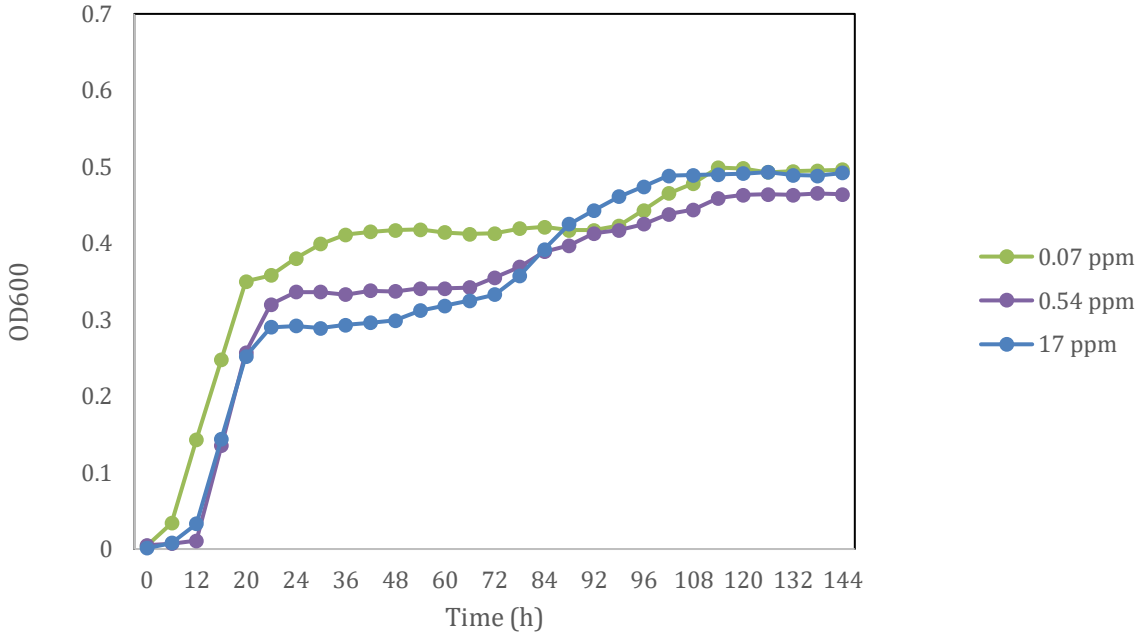


Fig 6.20: OD vs Time plot for different concentrations of bio-oil from RS (with glucose)

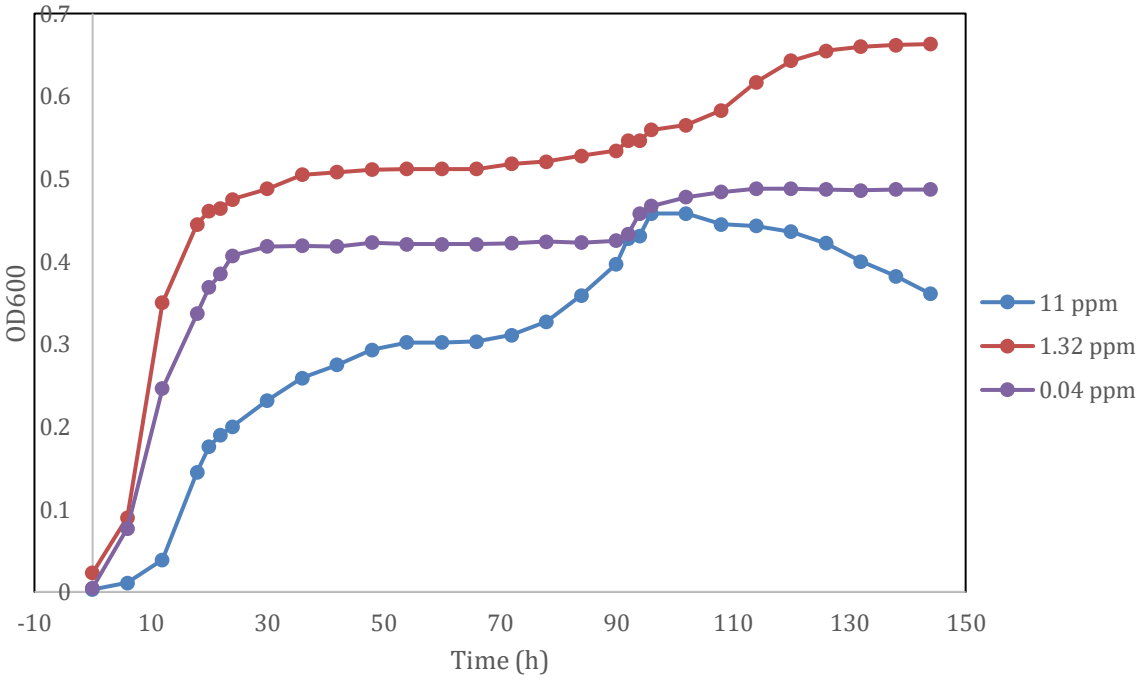


Fig 6.21: OD vs Time plot for different concentrations of bio-oil from MS (with glucose)

The media having both bio-oil and glucose (0.6mM), as carbon-sources, showed better biomass growth than the one having single carbon source. *S. putrefaciens,* in 'Bio-oil + glucose'-medium, showed a shorter primary lag phase (0-5h), followed by primary log phase from 6-30h, and primary stationary phase varied for different concentrations of bio-oil, higher as the concentration decreases. Secondary lag phase merged with primary stationary phase. It then entered a secondary log phase (shorter for lower concentrations), followed by secondary 'stationary-cum-death' phase (120-150h), after which growth ceased. This is a typical case of diauxic growth, where glucose is used as the first carbon-source, thereby performing primary lag/log/stationary phases and the intermediate transition phases in between. After depletion of glucose, *S. putrefaciens* uses the bio-oil (mainly the acetic acid component) as the secondary carbon-source for performing secondary log and staionary phases. The growth of biomass was almost similar for both the bio-oils (MS and RS).

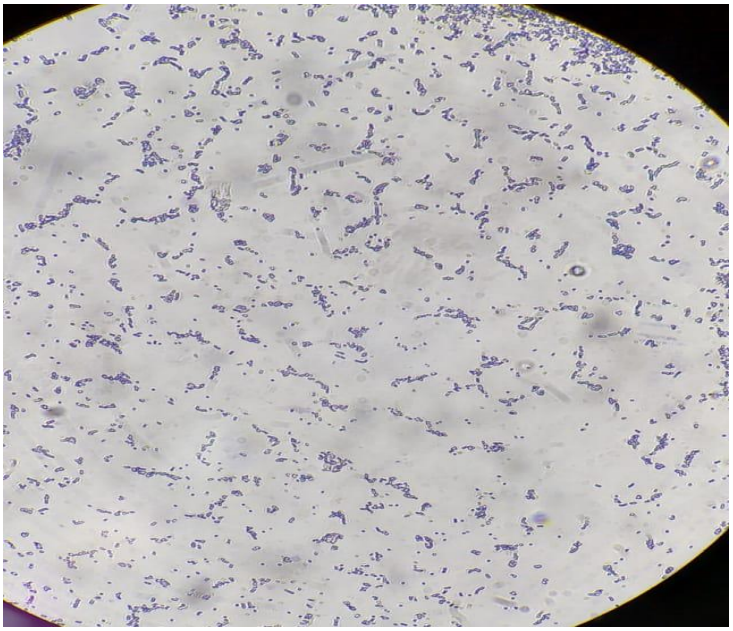


Fig 6.22: Microscopic observation of *Shewanella putrefaciens*

6.2.3. Determination of μm and ks:

S. putrefaciens take acetic acid as substrate, acetic acid percentage in RS and MS is 5.73 and 3.5 respectively (). The acetic acid concentration in the bio-oil which were taken for batch study was 0.07 ppm, 0.27 ppm, 0.54 ppm. 17 ppm for RS, and 0.04, 0.67, 1.32 and 11 ppm for MS. ln(X/Xo) vs. time had been plotted for all the concentrations.

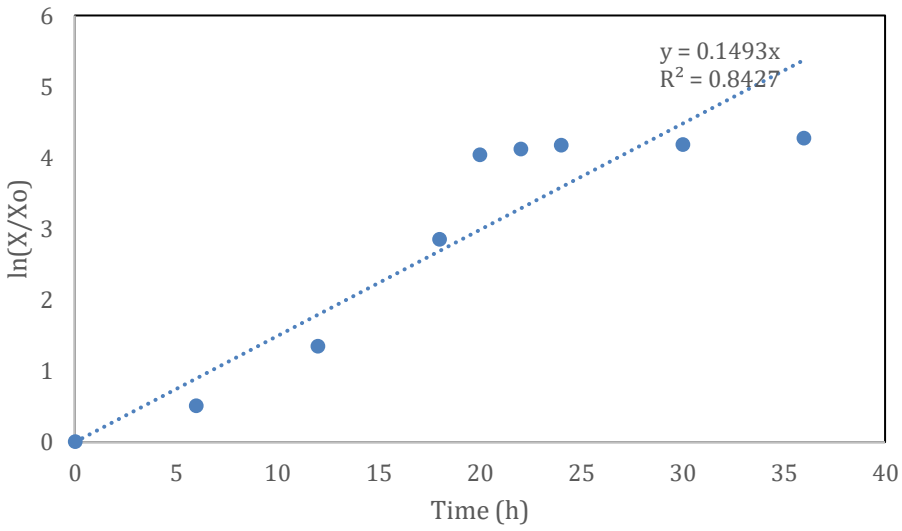


Fig 6.23: Showing the plot of ln(X/X0) vs. time for 0. 07ppm acetic acid from RS bio-oil

The slope of this curve gives the value of specific growth rate (μ) of *S. putrefaciens* for 0.07ppm acetic acid (bio-oil generated from RS) and the numeric value of μ is 0.1493 h-1.

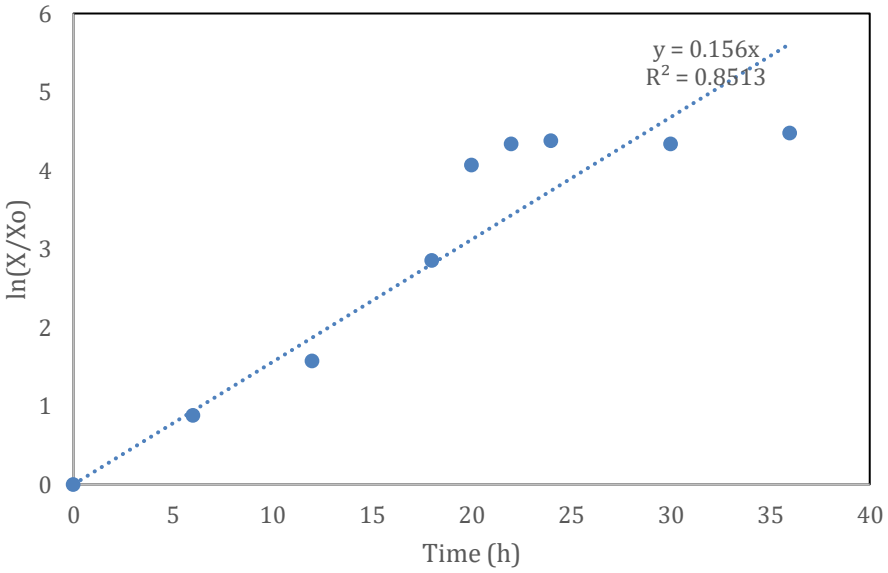


Fig 6.24: Showing the plot of ln(X/X0) vs. time for 0.27ppm acetic acid concentration from RS bio-oil

The slope of this curve gives the value of specific growth rate (μ) of *S. putrefaciens* 0.27 acetic acid concentration (bio-oil generated from RS) and the numeric value of μ is 0.156 h-1.

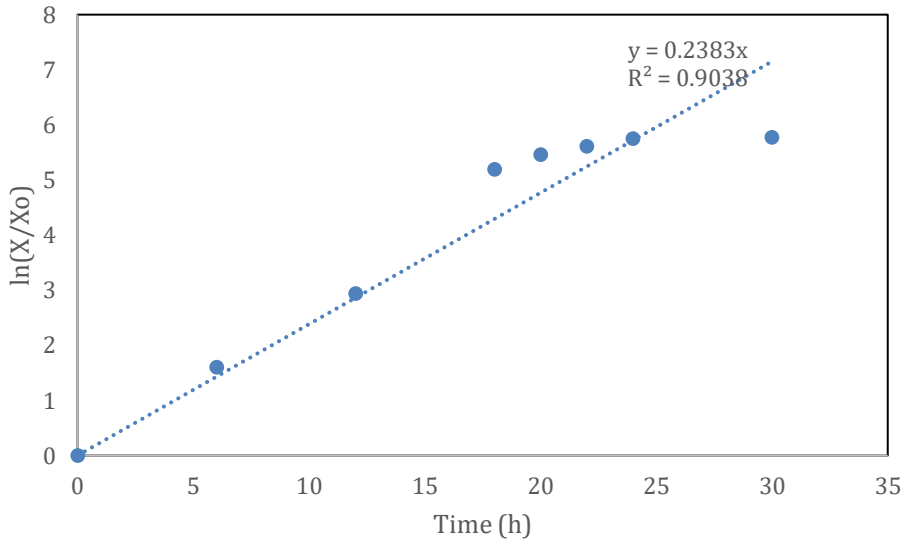


Fig 6.25: Showing the plot of ln(X/X0) vs. time for 0.54ppm acetic acid concentration from RS bio-oil.

The slope of this curve gives the μ of *S. putrefaciens* for 0.54ppm acetic acid concentration (bio-oil generated from RS) and the numeric value of μ is 0.2383 h-1

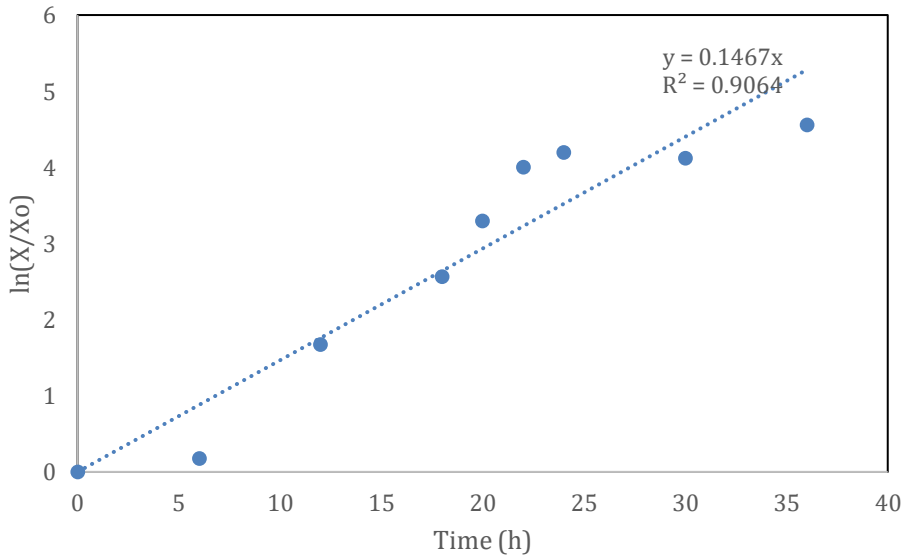


Fig 6.26: Showing the plot of ln(X/X0) vs. time for 17ppm acetic acid concentration from RS bio-oil.

The slope of this curve gives the value of specific growth rate (μ) of *S. putrefaciens* for 17ppm acetic acid concentration (bio-oil generated from RS) and the numeric value of μ is 0.1467h¯1.

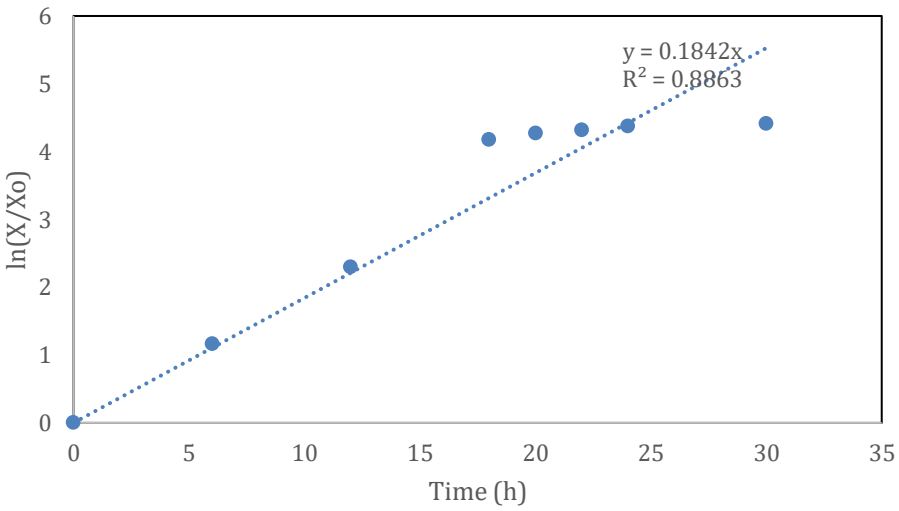


Fig 6.27: Showing the plot of ln(X/X0) vs. time for 0.04ppm acetic acid concentration from MS bio-oil.

The slope of this curve gives the value of μ of *S. putrefaciens* for 0.04 acetic acid concentration (bio-oil generated from MS) and the numeric value of μ is 0.1842 h-1.

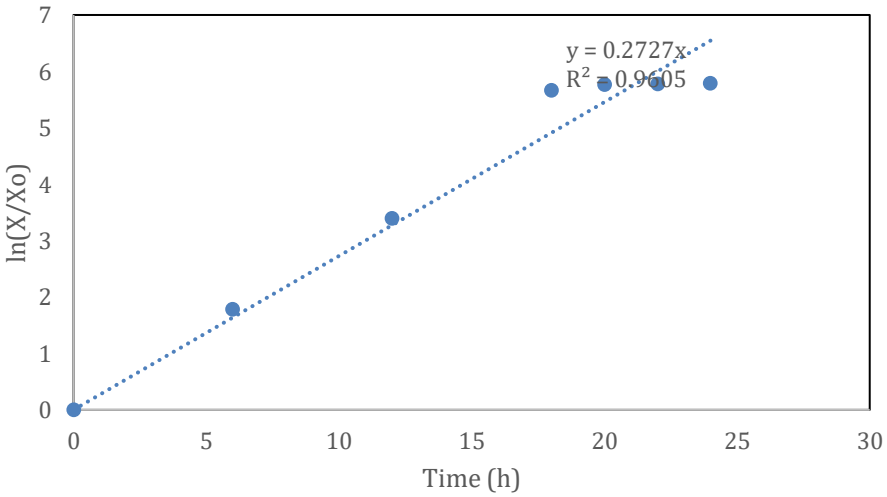


Fig 6.28: Showing the plot of ln(X/X0) vs. time for 0.67ppm acetic acid concentration from MS bio-oil.

The slope of this curve gives the value of μ of *S. putrefaciens* for 0.04 acetic acid concentration (bio-oil generated from MS) and the numeric value of μ is 0.2727 h-1.

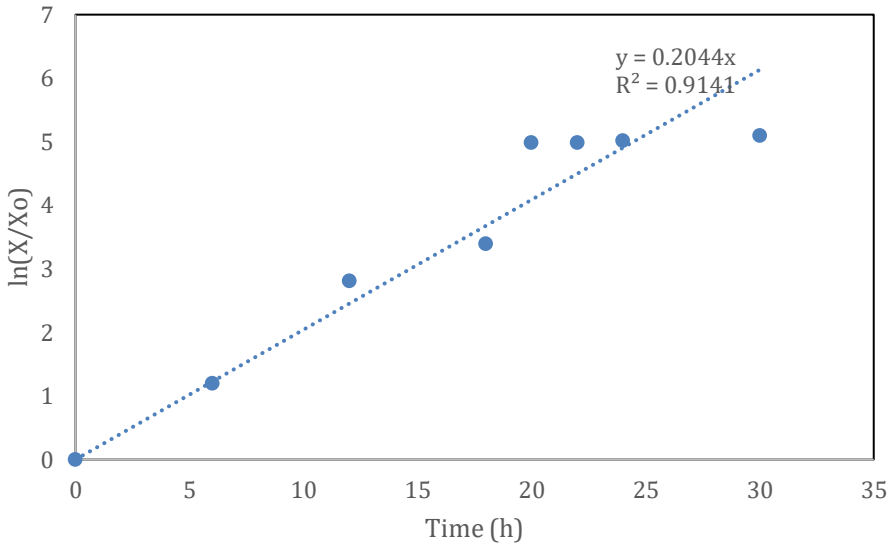


Fig 6.29: Showing the plot of ln(X/X0) vs. time for 1.32ppm acetic acid concentration from MS bio-oil.

The slope of this curve gives the value of specific growth rate (μ) of *S. putrefaciens* for 0.04 acetic acid concentration (bio-oil generated from MS) and the numeric value of μ is 0.2044 h-1.

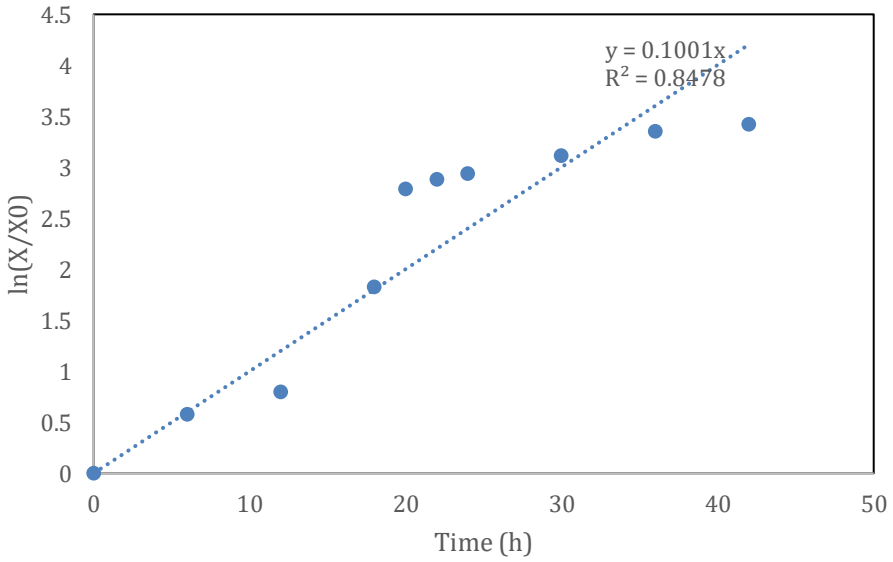


Fig 6.30: Showing the plot of ln(X/X0) vs. time for 11ppm acetic acid concentration from MS bio-oil.

The slope of this curve gives the value of μ of *S. putrefaciens* for 11 acetic acid concentration (bio-oil generated from MS) and the numeric value of μ is 0.1001h-¹.

1/μ vs 1/S for both the substrates had been plotted. For Mustard straw the slop was negative, which indicated that there were inhibition. For Rice straw μm and Ks was calculated to be 0.207 h^{-1} and 0.029 g/L respectively using the plot.

6.3. Bio-conversion of pyro-liquid from condenser 1 (80°C):

6.3.1. Upgradation of pyroliquid (80°C condensate) prior to fermentation:

The 80°C condensate from Rice Straw at 300°C (S1) and 350°C (S2), and Jute Stick at 350°C (S3), and one condensate from conventional pyrolysis process generated from Rice Straw at 300°C (S4) were taken as samples for bioconversion. All the samples were subjected to cold water extraction to remove water insoluble lignin oligomers, and was further extracted with EA.

Fig6.31: Pyro-oils after CW extraction and EA Extraction

Above figure suggested a clear separation between the organic phase (upper part) and aqueous phase (the phase below). The aqueous extract were taken out and all four extracts were subjected to acid hydrolysis and neutralization under the conditions previously described. Ethyl acetate extraction favors the hydrolysis reaction. After neutralization step samples were drawn to analyze sugar. Sugar contents of the hydrolysate were reported in Table 3.

Table 6.3: Concentration of sugar in hydrolysates

Set no	Sugar concentration (g/L)
S1	0.53
S2	39.15
S3	41.80
S4	0.54

Almost no sugar was found in the hydrolysates which were pyrolyzed at 300°C. Only the sets which have higher sugar concentrations (S2 and S3) were further treated. Detoxification steps were performed prior to acid hydrolysis is due to the well-known generation of additional inhibitory compounds during this high temperature/low pH process (Sun and Cheng, 2002). The pH of 10% pyrolytic sugar solution prior to addition of Ca(OH)2 was measured as 1-1.5; A pH close to 10.0 is also necessary to remove toxic compounds from pyrolytic sugar. It has been reported that overliming treatment of biomass hydrolyzed with 0.65% sulfuric acid requires about 31.67 g/L Ca(OH)2 to obtain a pH over 10.0. Addition of increasing amounts of Ca(OH)2 increased the pH. Ca(OH)2 concentrations at 18.5 g/L or higher led to a pH greater than 7.0, 25.9 g/L raised the pH to 9.8, and 31.67 g/L raised the pH to 10.9.

6.3.2. Fermentation:

S2 and S3 both before detoxification and after detoxification were subjected to fermentation, inoculated with two sets of bacteria, namely *clostridium acetobutylicum* and mixed consortia.

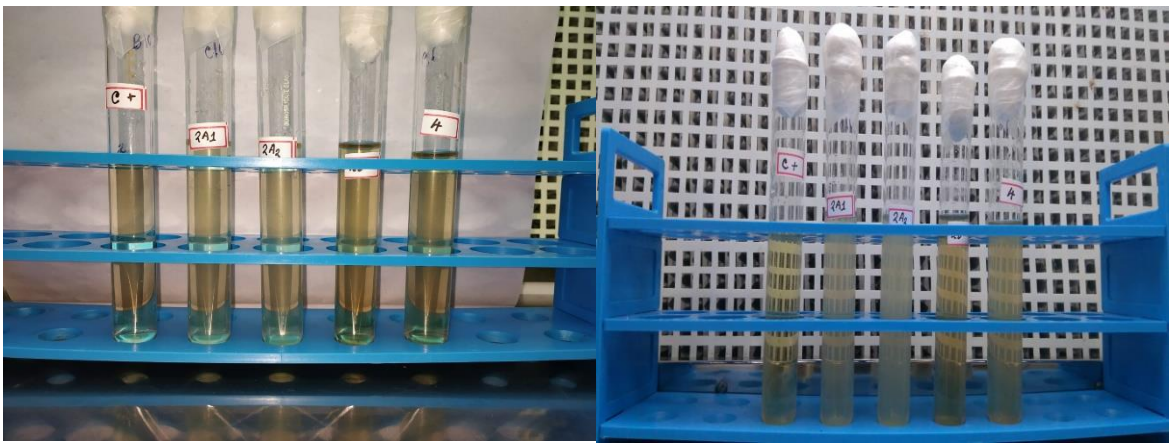


Fig 6.32: Inoculated hydrolysates after 0 hour and after 48 hours.

Above figure showed two sets with better growth compare to the other two sets, and the one is control. Almost no growth was observed in case of hydrolysates without detoxification. Growth of both the cultures were observed in the bio-oils which were detoxified prior to fermentation, and subsequent fall of pH had been observed. For the mixed consortia pH fall was measured as 5.8, and in case of *c. acetobutylicum* pH had fallen to 6.0, which indicates acid generation during fermentation. The kinetic study and analysis of product had not been evaluated.

Gram staining technique was used to stain a slide such as a fecal smear to observe the bacterial microflora present based on their gram stain reaction.

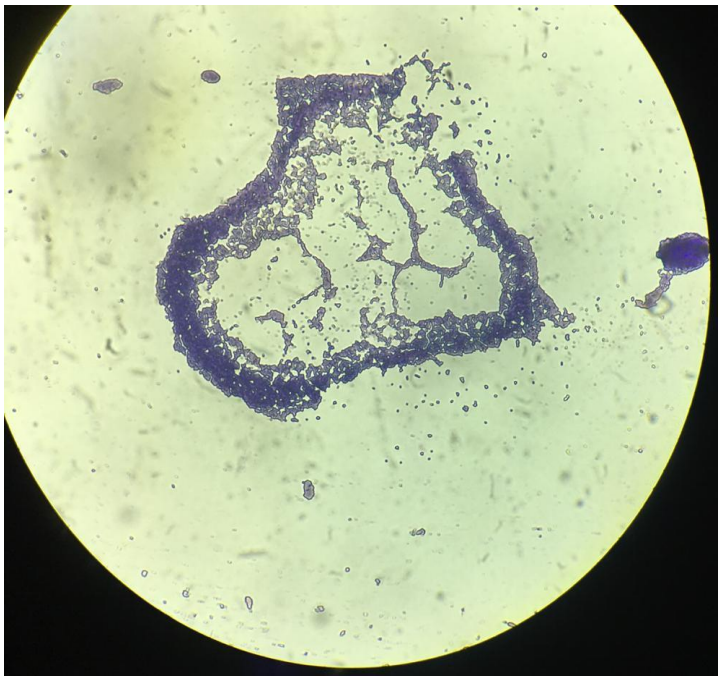


Fig6.33: Microscopic observation of the clostridium acetobutylicum sp. After gram staining procedure

As visible from the figure, rod shaped bacteria species are strained purple after gram staining procedure which indicates that the species is Gram positive as it retains the colour of primary strain crystal violet.

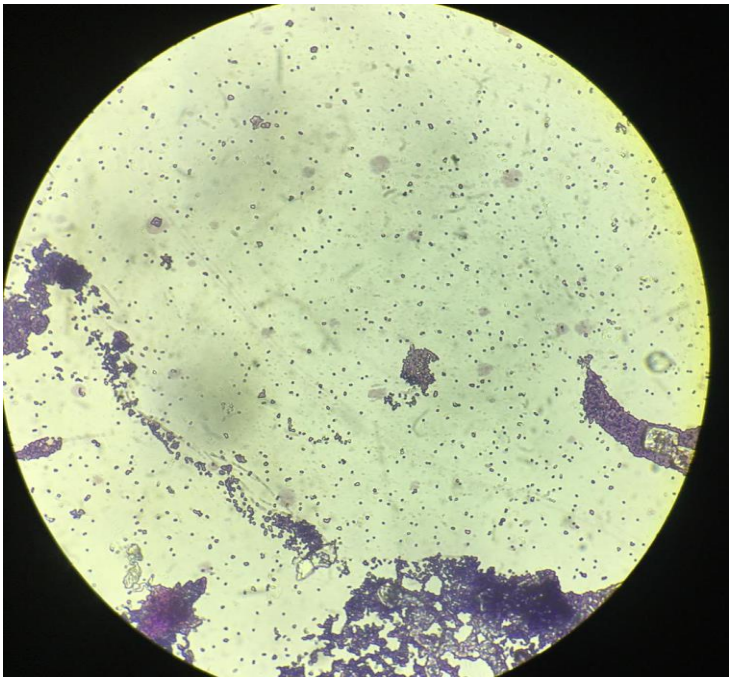


Fig 6.34: Microscopic observation of the mixed consortia after gram staining procedure

As visible from the figure, rod shaped bacterial species bacterial species are stained purple after gram staining procedure which indicates that that the species is Gram positive as it retains the colour of primary strain crystal violet. Few gram negative bacteria can also be seen.

6.4 Modelling of overall hybrid process using ASPEN ENGINEERING 8.8

The overall process scheme for Rice Straw was simulated using Aspen Engineering 8.8 starting from pyrolysis to fermentation. Flowsheet of the process is shown in the figure given below.

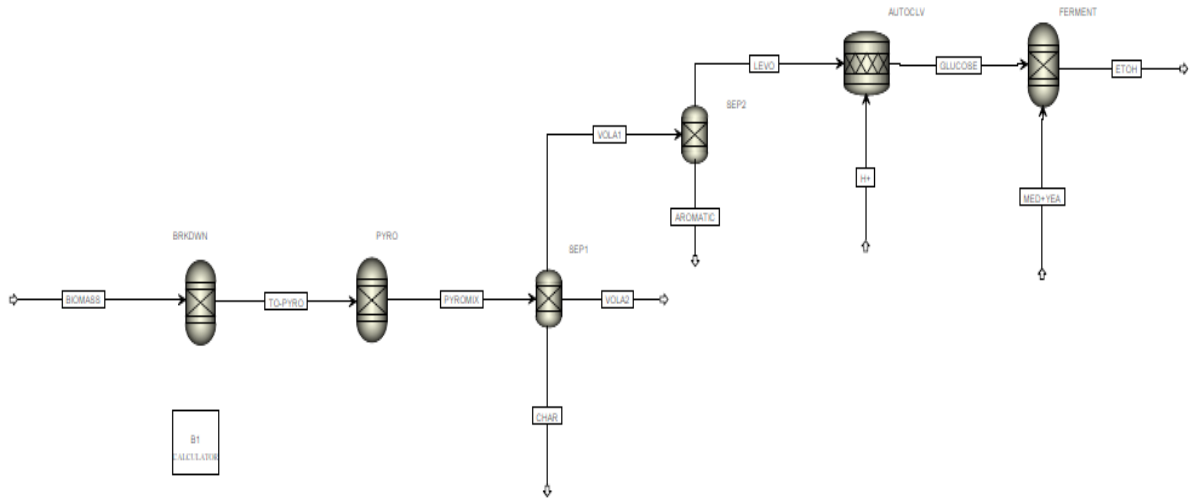


Fig 6.35: Flowsheet of the process using Aspen Engineering 8.8

The description of the blocks that were used in the flowsheet is shown in Table 4.

Table 6.4: Blocks used in Aspen Flowsheet:

Block	Type	Description
Brkdown, pyro, ferment	RYIELD	Generates product from the feed according to the specified yield. Reaction kinetics not needed.
autoclv	RSTOIC	Elements react according to their stoichiometry. Obeys phase equilibrium.
Sep	SEP	Separates according to split fraction.

The first block used is RYIELD, for conversion of the non-conventional biomass into conventional elements using proximate and ultimate analysis data which is given in the Table 5.

Table 6.5: ultimate and proximate analysis of Rice Straw:

Elements	Ultimate analysis (wt. %)					Proximate analysis (wt. %)				
	C	H	O	N	S	moisture	volatiles	Fixed carbon	Ash	HHV (MJ/Kg)
Rice straw (RS)	36.07	5.20	38.80	0.64	0.26	11.69	78.07	6.93	15.00	14.87

Second block was used for pyrolysis also, is also a RYIELD block combined with a SEP block to separate the "PYROMIX" into three parts, i.e. "CHAR", "VOL1" and "VOL2". "CHAR" is pyro-char, which can be further used as adsorbent or for soil amendment. "VOL1" separated is the 80°C condensate stream. "VOL2" can be further condensed to 20°C and this condensate which is rich in acetic acid can be used to develop microbial fuel cell (MFC) for electricity generation, or valuable organic compounds like acetic acid, acetol, propanoic acid, guaiacol, acetaldehyde can the separated from this. The non-condensable gaseous stream can be send to turbine for heat/energy generation. Here we have focused only on "VOL1" stream. "VOL1" is send to another SEP block for separating the aromatic part with levoglucosan. Then the LEVO is hydrolysed in a RSTOIC block using the levoglucosan to glucose conversion equation. Then the glucose is further fermented using another RYIELD block to convert it into ethanol, taking 49 mass% conversion of glucose to ethanol into consideration (luque et al., 2014). The PYROMIX is assumed to be considered to have following components:

Table6.6: Components taken in PYROMIX:

Element	name	formula
C	Carbon	C
H2	hydrogen	H2
N2	Nitrogen	N2

O2	Oxygen	O2
S	Sulphur	S
CO	Carbon monoxide	CO
CO2	Carbon dioxide	CO2
CH4	Methane	CH4
LEVOG-01	Levoglucosan	C6H10O5
PHENOL	Phenol	C6H6O
C2H4O2	Acetic Acid	C2H4O2
H2O	Water	H2O
GLUCOSE	Glucose	C6H12O6
ETOH	Ethanol	C2H60
ACETOL	Acetol	C3H6O2
PROPI-01	Propanoic Acid	C3H6O2
GUAIA-01	Guaiacol	C7H8O2
ACETA-01	Acetaldehyde	C2H40

It is assumed that char is composed of carbon and ash. 20°C condensate is assumed to have following composition, 5.73 mass% acetic acid (Jung et al, 2008), 10 mass% acetol, 2 mass% propanoic acid, 2 mass% guaiacol and 20 mass % acetaldehyde (Oudenhoven et al, 2012). 80°C condensate is assumed to be composed of 40% levoglucosan (mass basis). 42mass % of the total oil is assumed as phenol (Luque et al, 2014). Other part of the oil is taken to be composed of water. Gas is assumed to be composed of 64% CO2, 34.4% CO and 1.6% CH4 in mass basis (Biswas et al, 2017). Another assumption is taken into consideration is that this compositions did not vary with pyrolysis temp. The yield of char, oil and gas is varied at different pyrolysis temperature as per experimental data and simulation of the product composition is observed using aspen. The production ethanol, phenol, acetic acid, acetol, propanoic acid, guaiacol and acetaldehyde found using aspen is given below in Table 7 and plotted against temperature.

Table 6.7: Production of different organic compounds at different temperature using Aspen

Basis: 100kg of biomass

	300°C	350°C	400°C
ETOH	1.114	2.43	2.75
PHENOL	8.39	8.71	8.7
C2H4O2	0.869	0.4194	0.396
ACETOL	1.515	0.73	0.69
PROPI-01	0.303	0.146	0.138
GUAIA-01	0.303	0.146	0.138
ACETA-01	3.03	1.46	1.38

*all units are in kilograms

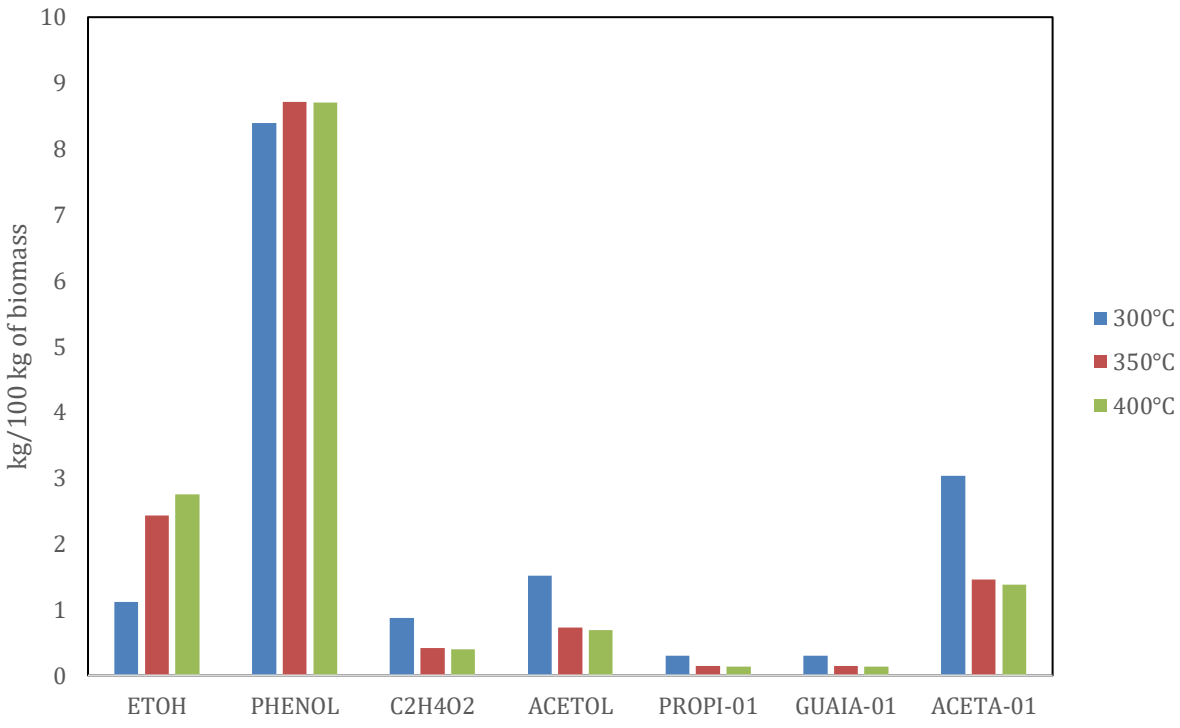


Fig 6.36: production of organics (kg/100kg biomass) against pyrolysis temperature plot

Chapter 7

CONCLUSION AND FUTURE SCOPE OF WORK

7.1 Conclusion:

1) The kinetics for the pyrolysis of RS, JS and MS were determined in the temperature range of 200-400ºC. 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.

2) It is observed that the char yield decreases with increase in pyrolysis temperature and gas yield gradually increases with temperature. Maximum yield of pyro-liquid was found at 300°C which is 31%, 30%, 31.6% for Rice Straw, Jute Stick and Mustard Straw respectively. Maximum yield of char was at 200°C, 70%, 57% and 63.3% for rice straw, jute stick and mustard straw respectively. Maximum pyro-oil yield was 40.83%, 55% and 50% for Rice Straw (at 400°C), Jute Stick (at 400°C) and Mustard Straw (at 350°C) respectively.

3) S. putrifaciens used acetic acid from second condenser liquid for growth.

4) MIC of Rice Straw and Mustard Straw were 10 and 40 vol% respectively for S. putrifaciens. The subsequent acetic acid concentrations was 17ppm and 44 ppm.

5) When glucose (20 g/L) was also added in the media, already having bio-oil, overall growth had been enhanced.

6) Mustard straw bio-oil showed inhibition on S. putrifaciens.

7) For Rice straw μm and Ks of s. putrfaciens was calculated to be 0.207 h^{-1} and 0.029 g/L.

8) First condenser liquid was upgraded with solvent extraction, acid hydrolysis, detoxification prior to fermentation.

9) Sugar content of the hydrolysates were measured after neutralization. It was found that pyro-oil from Jute stick (at 350°C) had the maximum sugar content (41.80 g/L).

10) Altleast 31.67 g/L Ca(OH)2 concentration were required for detoxification.

11) Hydrolysates both with and without detoxification were fermented using two sets of bacteria culture, *C. acetobutylicum* and mixed consortia. Growth did not occur in case of bio-oil which were not detoxified. Thus, detoxification of the hydrolysates must needed for bioconversion.

12) Both C. acetobutylicum and mixed consortia had given growth on detoxified hydrolysates. pH (5.8) fall was higher in case of mixed consortia, indicated more growth in mixed culture than that of single culture.

13) Overall modelling of the pyrolysis-fermentation hybrid process was done using ASPEN ENGINEERING for Rice Straw to determine the maximum ethanol yield for diffenrent pyrolysis temperatures. Maximum 2.75 kg ethanol from 100 kg of biomass can be produced, which were pyrolysed at 673K, the yield of ethanol oil was lower for lower pyrolysis temperatures.

7.2 Future scope of work:

1) Possible scope of alcohol and acid production from bio-oil.

2) MFC can be developed using the second condenser liquid for electricity generation.

3) Various valuable organic acids (such as acetic acid, propanoic acid), phenol, actaldehyde can be produced from the bio-oil.

4) Aspen model can be further developed by integrating MFC for second condenser liquid stream, and turbine with the gaseous stream.

5) Large scale reactor design and modelling for this process.

APPENDIX

Nomenclature:

E = activation energy (kJ/mol)

A = frequency factor (min-1)

k = rate constant (min-1)

kc = rate constant for char formation (min-1)

kv = rate constant for volatile formation (min-1)

kg = rate constant for gas formation (min-1)

koil = rate constant for oil 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))

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

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

Woil = weight of oil at any time during pyrolysis (g)

Wg = weight of gas at any time during pyrolysis (g)

W R= weight of residue (g)

X = concentration of biomass at any time (g/L)

Xo = initial concentration of biomass at any time (g/L)

S = substrate concentration (g/L)

μ = specific growth rate of the microorganisms (h -1)

μm = maximum specific growth rate of the microorganisms

Ks = half-velocity constant

Subscripts:

c = char

v = volatile

oil = oil

g = gas

R =residue

0 = initial condition

The calculation for rate constants, activation energy for pyrolysis following the Mathematical development:

Experimental datasheet of pyrolysis of Rice Straw at 200°C:

T	W+R	W	w	wv	wc	woil	wg
0	1442	10	1	0	0	0	0
5	1441.463	9.46324	0.946324	0.053676	0.125244	0.035784	0.017892
10	1441.434	9.434485	0.943448	0.056552	0.131954	0.037701	0.018851
15	1440.965	8.96482	0.896482	0.103518	0.241542	0.069012	0.034506
20	1440.926	8.92648	0.892648	0.107352	0.250488	0.071568	0.035784
25	1440.198	8.19802	0.819802	0.180198	0.420462	0.120132	0.060066
30	1440.236	8.23636	0.823636	0.176364	0.411516	0.117576	0.058788
35	1440.166	8.1664	0.81664	0.18336	0.42784	0.12224	0.06112
40	1440.157	8.15711	0.815711	0.184289	0.430008	0.122859	0.06143
45	1440.156	8.155825	0.815583	0.184417	0.430307	0.122945	0.061472
50	1440.028	8.028355	0.802835	0.197165	0.460051	0.131443	0.065722
55	1440.025	8.02549	0.802549	0.197451	0.460719	0.131634	0.065817
60	1440.025	8.02549	0.802549	0.197451	0.460719	0.131634	0.065817
65	1439.939	7.939225	0.793923	0.206077	0.480847	0.137385	0.068692
70	1439.7	7.6996	0.76996	0.23004	0.53676	0.15336	0.07668
75	1439.537	7.536655	0.753665	0.246335	0.574781	0.164223	0.082112
80	1439.201	7.20118	0.720118	0.279882	0.653058	0.186588	0.093294
85	1438.904	6.904045	0.690405	0.309596	0.72239	0.206397	0.103199
90	1439.009	7.00948	0.700948	0.299052	0.697788	0.199368	0.099684
95	1439	6.999895	0.699989	0.300011	0.700025	0.200007	0.100004

Experimental datasheet of pyrolysis of Rice Straw at 300°C:

T	W+R	W	w	wv	wc	woil	wg
0	1442	10	1	0	0	0	0

5	1440.497	8.497072	0.849707	0.150293	0.100195	0.077651	0.072642
10	1440.556	8.555592	0.855559	0.144441	0.096294	0.074628	0.069813
15	1438.779	6.77944	0.677944	0.322056	0.214704	0.166396	0.15566
20	1438.445	6.445456	0.644546	0.355454	0.23697	0.183651	0.171803
25	1438.255	6.254608	0.625461	0.374539	0.249693	0.193512	0.181027
30	1437.933	5.932552	0.593255	0.406745	0.271163	0.210151	0.196593
35	1437.789	5.789416	0.578942	0.421058	0.280706	0.217547	0.203512
40	1437.36	5.360008	0.536001	0.463999	0.309333	0.239733	0.224266
45	1437.205	5.204944	0.520494	0.479506	0.31967	0.247745	0.231761
50	1436.68	4.680112	0.468011	0.531989	0.354659	0.274861	0.257128
55	1436.203	4.202992	0.420299	0.579701	0.386467	0.299512	0.280189
60	1436.048	4.047928	0.404793	0.595207	0.396805	0.307524	0.287683
65	1436	4.000216	0.400022	0.599978	0.399986	0.309989	0.28999

Experimental datasheet of pyrolysis of Rice Straw at 350°C:

T	W+R	W	w	wv	wc	woil	wg
0	1458	26	1	0	0	0	0
5	1455.762	23.76221	0.913931	0.086069	0.061154	0.030577	0.055492
10	1453.717	21.71703	0.83527	0.16473	0.117045	0.058522	0.106207
15	1451.848	19.84787	0.763379	0.236621	0.168125	0.084063	0.152558
20	1450.14	18.13958	0.697676	0.302324	0.214809	0.107404	0.194919
25	1448.578	16.57833	0.637628	0.362372	0.257475	0.128737	0.233634
30	1447.151	15.15145	0.582748	0.417252	0.296468	0.148234	0.269018
35	1445.847	13.84739	0.532592	0.467408	0.332106	0.166053	0.301355
40	1444.656	12.65556	0.486752	0.513248	0.364676	0.182338	0.33091
45	1443.566	11.56631	0.444858	0.555142	0.394443	0.197221	0.35792
50	1443.18	11.18	0.43	0.57	0.405	0.2025	0.3675
55	1443.081	11.0812	0.4262	0.5738	0.4077	0.20385	0.36995
60	1443.05	11.05	0.425	0.575	0.408553	0.204276	0.370724
65	1442.803	10.803	0.4155	0.5845	0.415303	0.207651	0.376849

Experimental datasheet of pyrolysis of Rice Straw at 400°C:

T	W+R	W	w	wv	wc	woil	wg
0	1444	12	1	0	0	0	0
5	1443.061	11.06079	0.921733	0.078267	0.048653	0.026442	0.051826
10	1442.195	10.19509	0.849591	0.150409	0.093498	0.050814	0.099595
15	1441.397	9.397152	0.783096	0.216904	0.134832	0.073278	0.143626
20	1440.662	8.661662	0.721805	0.278195	0.172932	0.093985	0.18421
25	1438.781	6.78146	0.565122	0.434878	0.27033	0.146918	0.28796
30	1438.593	6.59298	0.549415	0.450585	0.280093	0.152225	0.29836
35	1438.687	6.68722	0.557268	0.442732	0.275212	0.149572	0.29316
40	1438.499	6.49874	0.541562	0.458438	0.284975	0.154878	0.303561
45	1437.651	5.65058	0.470882	0.529118	0.328911	0.178756	0.350362
50	1437.58	5.5799	0.464992	0.535008	0.332573	0.180746	0.354262
55	1437.509	5.50922	0.459102	0.540898	0.336234	0.182736	0.358162
60	1436.614	4.61394	0.384495	0.615505	0.382611	0.207941	0.407564
65	1436.602	4.60216	0.383513	0.616487	0.383221	0.208273	0.408214

Experimental datasheet of pyrolysis of Jute Stick at 200°C:

T	W+R	W	w	wv	wc	woil	wg
0	1442	10	1	0	0	0	0
5	1441.03	9.02994	0.902994	0.097006	0.128589	0.020304	0.076702
10	1440.582	8.58222	0.858222	0.141778	0.187938	0.029674	0.112104
15	1440.273	8.27308	0.827308	0.172692	0.228917	0.036145	0.136547
20	1440.23	8.23044	0.823044	0.176956	0.23457	0.037037	0.139919
25	1440.241	8.2411	0.82411	0.17589	0.233157	0.036814	0.139076
30	1440.103	8.10252	0.810252	0.189748	0.251526	0.039715	0.150033
35	1440.028	8.0279	0.80279	0.19721	0.261418	0.041277	0.155933
40	1440.049	8.04922	0.804922	0.195078	0.258592	0.04083	0.154248
45	1439.868	7.868	0.7868	0.2132	0.282614	0.044623	0.168577
50	1439.708	7.7081	0.77081	0.22919	0.30381	0.04797	0.18122
55	1439.442	7.4416	0.74416	0.25584	0.339137	0.053548	0.202292
60	1439.207	7.20708	0.720708	0.279292	0.370224	0.058456	0.220836

65	1439.005	7.00454	0.700454	0.299546	0.397073	0.062696	0.23685
70	1438.855	6.8553	0.68553	0.31447	0.416856	0.065819	0.248651
75	1438.877	6.87662	0.687662	0.312338	0.414029	0.065373	0.246965
80	1438.919	6.91926	0.691926	0.308074	0.408377	0.064481	0.243593
85	1438.567	6.56748	0.656748	0.343252	0.455008	0.071843	0.271409
90	1438.61	6.61012	0.661012	0.338988	0.449356	0.070951	0.268037
95	1438.536	6.5355	0.65355	0.34645	0.459248	0.072513	0.273937
100	1438.184	6.18372	0.618372	0.381628	0.505879	0.079876	0.301752
105	1438.141	6.14108	0.614108	0.385892	0.511531	0.080768	0.305124
110	1437.8	5.79996	0.579996	0.420004	0.556749	0.087908	0.332096
115	1437.843	5.8426	0.58426	0.41574	0.551097	0.087015	0.328725
120	1437.693	5.69336	0.569336	0.430664	0.57088	0.090139	0.340525
125	1437.736	5.736	0.5736	0.4264	0.565228	0.089247	0.337153
130	1437.704	5.70402	0.570402	0.429598	0.569467	0.089916	0.339682

Experimental datasheet of pyrolysis of Jute Stick at 300°C:

T	W+R	W	w	wv	wc	woil	wg
0	1442	10	1	0	0	0	0
5	1440.64	8.64	0.864	0.136	0.106857	0.043714	0.092286
10	1440.16	8.16	0.816	0.184	0.144571	0.059143	0.124857
15	1439.36	7.36	0.736	0.264	0.207429	0.084857	0.179143
20	1438.144	6.144	0.6144	0.3856	0.302971	0.123943	0.261657
25	1437.936	5.936	0.5936	0.4064	0.319314	0.130629	0.275771
30	1437.52	5.52	0.552	0.448	0.352	0.144	0.304
35	1437.328	5.328	0.5328	0.4672	0.367086	0.150171	0.317029
40	1437.152	5.152	0.5152	0.4848	0.380914	0.155829	0.328971
45	1437.008	5.008	0.5008	0.4992	0.392229	0.160457	0.338743
50	1436.864	4.864	0.4864	0.5136	0.403543	0.165086	0.348514
55	1436.816	4.816	0.4816	0.5184	0.407314	0.166629	0.351771
60	1436.432	4.432	0.4432	0.5568	0.437486	0.178971	0.377829

Experimental datasheet of pyrolysis of Jute Stick at 350°C:

T	W+R	W	w	wv	wc	woil	wg
0	1442	10	1	0	0	0	0
5	1439.234	7.2336	0.900325	0.099675	0.036866	0.040963	0.058713
10	1436.381	4.38075	0.810584	0.189416	0.070058	0.077842	0.111574
15	1436.196	4.1955	0.729789	0.270211	0.099941	0.111046	0.159165
20	1436.146	4.1461	0.657047	0.342953	0.126846	0.14094	0.202014
25	1435.455	3.4545	0.591555	0.408445	0.151069	0.167854	0.240591
30	1435.38	3.3804	0.532592	0.467408	0.172877	0.192086	0.275323
35	1435.417	3.41745	0.479505	0.520495	0.192512	0.213902	0.306593
40	1435.38	3.3804	0.431711	0.568289	0.210189	0.233544	0.334746
45	1435.331	3.331	0.38868	0.61132	0.226105	0.251228	0.360093
50	1435.269	3.26925	0.349938	0.650062	0.240434	0.267149	0.382913
55	1435.096	3.09635	0.315058	0.684942	0.253335	0.281483	0.403459
60	1435.084	3.084	0.283654	0.716346	0.26495	0.294389	0.421957
65	1435.035	3.0346	0.2835	0.7165	0.265007	0.294452	0.422048
70	1434.862	2.8617	0.275	0.725	0.268151	0.297945	0.427055
75	1434.701	2.70115	0.270115	0.729885	0.269957	0.299953	0.429932

Experimental datasheet of pyrolysis of Jute Stick at 400°C:

T	W+R	W	w	wv	wc	woil	wg
0	1442	10	1	0	0	0	0
5	1439.956	7.9558	0.79558	0.20442	0.061061	0.058406	0.146014
10	1438.9	6.89963	0.689963	0.310037	0.092608	0.088582	0.221455
15	1438.406	6.405615	0.640561	0.359439	0.107365	0.102697	0.256742
20	1437.86	5.860495	0.586049	0.413951	0.123648	0.118272	0.295679
25	1436.941	4.940605	0.49406	0.50594	0.151125	0.144554	0.361385
30	1436.6	4.599905	0.45999	0.54001	0.161302	0.154288	0.385721
35	1436.532	4.531765	0.453176	0.546824	0.163337	0.156235	0.390588
40	1435.135	3.134895	0.313489	0.686511	0.205062	0.196146	0.490365
45	1434.607	2.60681	0.260681	0.739319	0.220836	0.211234	0.528085

50	1434.488	2.487565	0.248756	0.751244	0.224397	0.214641	0.536603
55	1434.419	2.419425	0.241943	0.758058	0.226433	0.216588	0.54147
60	1434.3	2.30018	0.230018	0.769982	0.229995	0.219995	0.549987

Experimental datasheet of pyrolysis of Mustard Straw at 250°C:

T	W+R	W	w	wv	wc	woil	wg
0	1444	12	1	0	0	0	0
5	1443.25	11.24977	0.937481	0.062519	0.107988	0.028418	0.034101
10	1442.844	10.84424	0.903687	0.096313	0.166359	0.043779	0.052535
15	1442.756	10.75637	0.896364	0.103636	0.179007	0.047107	0.056529
20	1442.513	10.51306	0.876088	0.123912	0.214029	0.056323	0.067588
25	1442.452	10.45223	0.871019	0.128981	0.222785	0.058628	0.070353
30	1442.202	10.20215	0.850179	0.149821	0.258781	0.0681	0.08172
35	1441.871	9.870968	0.822581	0.177419	0.306452	0.080645	0.096774
40	1441.746	9.7464	0.8122	0.1878	0.324382	0.085364	0.102436
45	1441.497	9.4968	0.7914	0.2086	0.360309	0.094818	0.113782
50	1440.715	8.715207	0.726267	0.273733	0.472811	0.124424	0.149309
55	1440.668	8.667896	0.722325	0.277675	0.479621	0.126216	0.151459
60	1440.526	8.52596	0.710497	0.289503	0.500051	0.131592	0.157911
65	1440.357	8.356989	0.696416	0.303584	0.524373	0.137993	0.165591
70	1440.276	8.275883	0.689657	0.310343	0.536047	0.141065	0.169278
75	1440.1	8.100154	0.675013	0.324987	0.561341	0.147721	0.177266
80	1439.904	7.904147	0.658679	0.341321	0.589555	0.155146	0.186175
85	1439.83	7.8298	0.652483	0.347517	0.600256	0.157962	0.189555
90	1439.823	7.823041	0.65192	0.34808	0.601229	0.158218	0.189862
95	1439.62	7.620276	0.635023	0.364977	0.630415	0.165899	0.199078
100	1439.6	7.6	0.633333	0.366667	0.633333	0.166667	0.2

Experimental datasheet of pyrolysis of Mustard Straw at 300°C:

T	W+R	W	w	wv	wc	woil	wg
0	1444	12	1	0	0	0	0

5	1442.79	10.79	0.899167	0.100833	0.077108	0.056348	0.044485
10	1442.267	10.2672	0.8556	0.1444	0.110424	0.080694	0.063706
15	1441.51	9.51	0.7925	0.2075	0.158676	0.115956	0.091544
20	1440.918	8.9184	0.7432	0.2568	0.196376	0.143506	0.113294
25	1439.722	7.722	0.6435	0.3565	0.272618	0.199221	0.157279
30	1439.186	7.1856	0.5988	0.4012	0.3068	0.2242	0.177
35	1439.08	7.08	0.59	0.41	0.313529	0.229118	0.180882
40	1438.763	6.7632	0.5636	0.4364	0.333718	0.243871	0.192529
45	1438.6	6.6	0.55	0.45	0.344118	0.251471	0.198529
50	1438.505	6.5052	0.5421	0.4579	0.350159	0.255885	0.202015
55	1438.12	6.12	0.51	0.49	0.374706	0.273824	0.216176
60	1437.844	5.844	0.487	0.513	0.392294	0.286676	0.226324
65	1437.322	5.322	0.4435	0.5565	0.425559	0.310985	0.245515
70	1437.2	5.2	0.433333	0.566667	0.433333	0.316667	0.25

Experimental datasheet of pyrolysis of Mustard Straw at 350°C:

T	W+R	W	w	wv	wc	woil	wg
0	1446	14	1	0	0	0	0
5	1445.38	13.38	0.955714	0.044286	0.022381	0.010952	0.033333
10	1443.85	11.85	0.846429	0.153571	0.077611	0.03798	0.115591
15	1443.84	11.84	0.845714	0.154286	0.077972	0.038157	0.116129
20	1443.27	11.27	0.805	0.195	0.098548	0.048226	0.146774
25	1441.97	9.97	0.712143	0.287857	0.145476	0.07119	0.216667
30	1441.83	9.83	0.702143	0.297857	0.15053	0.073664	0.224194
35	1441.26	9.26	0.661429	0.338571	0.171106	0.083733	0.254839
40	1440.19	8.19	0.585	0.415	0.209731	0.102634	0.312366
45	1439.14	7.14	0.51	0.49	0.247634	0.121183	0.368817
50	1439.1	7.1	0.507143	0.492857	0.249078	0.121889	0.370968
55	1437.88	5.88	0.42	0.58	0.293118	0.143441	0.436559
60	1436.7	4.7	0.335714	0.664286	0.335714	0.164286	0.5

Experimental datasheet of pyrolysis of Mustard Straw at 400°C:

T	W+R	W	w	wv	wc	woil	wg
0	1444	12	1	0	0	0	0
5	1443.216	11.2164	0.9347	0.0653	0.03265	0.026936	0.038364
10	1442.484	10.4844	0.8737	0.1263	0.06315	0.052099	0.074201
15	1441.78	9.78	0.815	0.185	0.0925	0.076313	0.108688
20	1441.12	9.12	0.76	0.24	0.12	0.099	0.141
25	1439.8	7.8	0.65	0.35	0.175	0.144375	0.205625
30	1439.56	7.56	0.63	0.37	0.185	0.152625	0.217375
35	1439.08	7.08	0.59	0.41	0.205	0.169125	0.240875
40	1438.96	6.96	0.58	0.42	0.21	0.17325	0.24675
45	1437.854	5.8536	0.4878	0.5122	0.2561	0.211283	0.300918
50	1437.38	5.38	0.448333	0.551667	0.275833	0.227563	0.324104
55	1437.19	5.19	0.4325	0.5675	0.28375	0.234094	0.333406
60	1437.04	5.04	0.42	0.58	0.29	0.23925	0.34075
65	1436.61	4.61	0.384167	0.615833	0.307917	0.254031	0.361802
70	1436.5	4.5	0.375	0.625	0.3125	0.257813	0.367188
75	1436.41	4.41	0.3675	0.6325	0.31625	0.260906	0.371594
80	1436.32	4.32	0.36	0.64	0.32	0.264	0.376
85	1436.2	4.2	0.35	0.65	0.325	0.268125	0.381875
90	1436.118	4.1184	0.3432	0.6568	0.3284	0.27093	0.38587
95	1436.064	4.0644	0.3387	0.6613	0.33065	0.272786	0.388514
100	1436	4	0.333333	0.666667	0.333333	0.275	0.391667

The table below shows the values needed for calculation of activation energy for Rice Straw:

1/T	lnk	lnkc	lnkv
0.002114	-5.49677	-5.71383	-6.64539
0.001745	-4.16692	-4.55638	-4.14775
0.001605	-4.15665	-4.47414	-4.12894
0.001486	-4.14775	-4.60848	-4.13517

The table below shows the values needed for calculation of activation energy for Jute stick:

1/T	lnk	lnkc	lnkv
0.002114	-5.33914	-5.03595	-5.31852
0.001745	-4.16048	-4.37406	-4.12894
0.001605	-3.92714	-4.90628	-3.91202
0.001486	-3.62309	-4.82831	-3.61563

The table below shows the values needed for calculation of activation energy for Mustard Straw:

1/T	lnk	lnkc	lnkv
0.002114	-5.2591	-4.71053	-5.16729
0.001745	-4.35053	-4.59522	-4.25451
0.001605	-4.21313	-4.91988	-4.24053
0.001486	-4.34281	-5.02069	-4.31999

The calculation for μm and ks for the growth of S. putrefaciens following the Mathematical development:

Growth data of ***S. putrefaciens*** at different acetic acid concentrations with time for Rice Straw bio-oil.

Time(h)	0.07 ppm	0.27 ppm	0.54 ppm	17 ppm
0	0.006	0.005	0.001	0.003
6	0.01	0.012	0.005	0.0036
12	0.023	0.024	0.019	0.016
18	0.104	0.087	0.18	0.039
20	0.34	0.292	0.237	0.081
22	0.368	0.382	0.275	0.165
24	0.39	0.4	0.315	0.2
30	0.392	0.3933	0.321	0.185
36	0.428	0.441	0.313	0.288
42	0.425	0.43	0.318	0.266
48	0.427	0.433	0.317	0.269

54	0.428	0.431	0.321	0.282
60	0.424	0.434	0.321	0.288

Growth data of ***S. putrefaciens*** at different acetic acid concentrations with time for Mustard Straw bio-oil

Time	0.04 ppm	0.35 ppm	0.7 ppm	11 ppm
0	0.005	0.001	0.003	0.009
6	0.016	0.006	0.01	0.016
12	0.05	0.03	0.05	0.02
18	0.327	0.291	0.09	0.056
20	0.359	0.321	0.441	0.146
22	0.375	0.326	0.441	0.16
24	0.397	0.33	0.455	0.17
30	0.411	0.331	0.492	0.202
36	0.409	0.332	0.485	0.256
42	0.408	0.332	0.488	0.275
48	0.413	0.334	0.491	0.263
54	0.411	0.335	0.492	0.272
60	0.411	0.331	0.492	0.272
66	0.411	0.329	0.492	0.273

Growth data of ***S. putrefaciens*** at different acetic acid concentrations with time for Rice Straw bio-oil with glucose.

Time(h)	0.07 ppm	0.54 ppm	17 ppm
0	0.004	0.005	0.001
6	0.034	0.007	0.008
12	0.143	0.011	0.033
18	0.248	0.135	0.144
20	0.35	0.257	0.252
22	0.358	0.32	0.29
24	0.38	0.336	0.292
30	0.399	0.336	0.289

36	0.411	0.333	0.293
42	0.415	0.338	0.296
48	0.417	0.337	0.299
54	0.418	0.341	0.312
60	0.414	0.341	0.318
66	0.412	0.342	0.325
72	0.413	0.355	0.333
78	0.419	0.369	0.357
84	0.421	0.389	0.392
90	0.417	0.397	0.425
92	0.417	0.413	0.443
94	0.423	0.417	0.461
96	0.443	0.425	0.474
102	0.465	0.438	0.488
108	0.478	0.444	0.489
114	0.499	0.459	0.49
120	0.498	0.463	0.491
126	0.493	0.464	0.493
132	0.494	0.463	0.489
138	0.495	0.465	0.488
144	0.496	0.464	0.492

Growth data of ***S. putrefaciens*** at different acetic acid concentrations with time for Mustard Straw bio-oil with glucose

Time(h)	11 ppm	0.7 ppm	0.04 ppm
0	0.011	0.09	0.077
6	0.054	0.35	0.246
12	0.112	0.412	0.308
18	0.176	0.461	0.369
24	0.2	0.475	0.407
30	0.232	0.488	0.418
36	0.259	0.505	0.419

42	0.275	0.508	0.418
48	0.293	0.511	0.423
54	0.302	0.512	0.421
60	0.302	0.512	0.421
66	0.303	0.512	0.421
72	0.311	0.518	0.422
78	0.327	0.521	0.424
84	0.359	0.528	0.423
90	0.397	0.534	0.425
92	0.428	0.546	0.433
94	0.431	0.546	0.458
96	0.458	0.559	0.467
102	0.458	0.565	0.478
108	0.445	0.583	0.484
114	0.443	0.617	0.488
120	0.436	0.643	0.488
126	0.422	0.655	0.487
132	0.4	0.66	0.486
138	0.382	0.662	0.487
144	0.361	0.663	0.487

REFERENCES

- Lewis, F. M. (2016). *U.S. Patent No. 9,416,374.* Washington, DC: U.S. Patent and Trademark Office.
- Cai, J., He, Y., Yu, X., Banks, S. W., Yang, Y., Zhang, X., ... & Bridgwater, A. V. (2017). Review of physicochemical properties and analytical characterization of lignocellulosic biomass. *Renewable and Sustainable Energy Reviews*, *76*, 309-322.
- Sohni, S., Norulaini, N. N., Hashim, R., Khan, S. B., Fadhullah, W., & Omar, A. M. (2018). Physicochemical characterization of Malaysian crop and agro-industrial biomass residues as renewable energy resources. *Industrial crops and products*, *111*, 642-650.
- Biswas, B., Pandey, N., Bisht, Y., Singh, R., Kumar, J., & Bhaskar, T. (2017). Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk. *Bioresource technology*, *237*, 57-63.
- Al Arni, S. (2018). Comparison of slow and fast pyrolysis for converting biomass into fuel. *Renewable Energy*, *124*, 197-201.
- Park, Y. K., Yoo, M. L., Lee, H. W., Park, S. H., Jung, S. C., Park, S. S., & Kim, S. C. (2012). Effects of operation conditions on pyrolysis characteristics of agricultural residues. *Renewable Energy*, *42*, 125-130.
- Bradbury, A. G., Sakai, Y., & Shafizadeh, F. (1979). A kinetic model for pyrolysis of cellulose. *Journal of applied polymer science*, *23*(11), 3271-3280.
- Bandyopadhyay, S., Chowdhury, R., & Biswas, G. K. (1999). Thermal deactivation studies of coconut shell pyrolysis. *The Canadian Journal of Chemical Engineering*, *77*(5), 1028-1036.
- Chowdhury, R., Ghosh, S., Debnath, B., & Manna, D. (2018). Indian Agro-wastes for 2G Biorefineries: Strategic Decision on Conversion Processes. In *Sustainable Energy Technology and Policies* (pp. 353-373). Springer, Singapore.
- Shen, Y., Jarboe, L., Brown, R., & Wen, Z. (2015). A thermochemical–biochemical hybrid processing of lignocellulosic biomass for producing fuels and chemicals. *Biotechnology advances*, *33*(8), 1799-1813.

- Luque, L., Westerhof, R., Van Rossum, G., Oudenhoven, S., Kersten, S., Berruti, F., & Rehmann, L. (2014). Pyrolysis based bio-refinery for the production of bioethanol from demineralized ligno-cellulosic biomass. *Bioresource technology*, *161*, 20-28.
- Westerhof, R. J., Brilman, D. W. F., Garcia-Perez, M., Wang, Z., Oudenhoven, S. R., van Swaaij, W. P., & Kersten, S. R. (2011). Fractional condensation of biomass pyrolysis vapors. *Energy & fuels*, *25*(4), 1817-1829.
- Oudenhoven, S. R. G., Westerhof, R. J. M., Aldenkamp, N., Brilman, D. W. F., & Kersten, S. R. (2013). Demineralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production. *Journal of analytical and applied pyrolysis*, *103*, 112-118.
- Bennett, N. M., Helle, S. S., & Duff, S. J. (2009). Extraction and hydrolysis of levoglucosan from pyrolysis oil. *Bioresource technology*, *100*(23), 6059-6063.
- Jiang, L., Zheng, A., Zhao, Z., He, F., & Li, H. (2015). Comprehensive utilization of glycerol from sugarcane bagasse pretreatment to fermentation. *Bioresource technology*, *196*, 194-199.
- Lian, J., Chen, S., Zhou, S., Wang, Z., O'Fallon, J., Li, C. Z., & Garcia-Perez, M. (2010). Separation, hydrolysis and fermentation of pyrolytic sugars to produce ethanol and lipids. *Bioresource technology*, *101*(24), 9688-9699.
- Chi, Z., Rover, M., Jun, E., Deaton, M., Johnston, P., Brown, R. C., ... & Jarboe, L. R. (2013). Overliming detoxification of pyrolytic sugar syrup for direct fermentation of levoglucosan to ethanol. *Bioresource technology*, *150*, 220-227.
- Zhang, X., Yang, W., & Dong, C. (2013). Levoglucosan formation mechanisms during cellulose pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *104*, 19-27.
- Abdilla, R. M., Rasrendra, C. B., & Heeres, H. J. (2018). Kinetic Studies on the Conversion of Levoglucosan to Glucose in Water Using Brønsted Acids as the Catalysts. *Industrial & engineering chemistry research*, *57*(9), 3204-3214.
- Jung, S. H., Kang, B. S., & Kim, J. S. (2008). Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. *Journal of Analytical and Applied Pyrolysis*, *82*(2), 240-247.
- Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource technology*, *83*(1), 1-11.

- Garcia-Perez, M., Wang, S., Shen, J., Rhodes, M., Lee, W. J., & Li, C. Z. (2008). Effects of temperature on the formation of lignin-derived oligomers during the fast pyrolysis of mallee woody biomass. *Energy & Fuels*, *22*(3), 2022-2032.