STUDIES ON PYROLYSIS OF BIOMASS

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

By

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the dissertation entitled **"STUDIES ON PYROLYSIS OF BIOMASS"** in partial fulfillment of the requirement for the award of the degree Master of Technology in Chemical Engineering with Specialization in **COMPUTER AIDED PROCESS PLANT DESING (CAPPD),** and submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology Roorkee**, under the kind guidance of **Dr. B. Prasad**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute / University.

Place: Roorkee
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CERTIFICATE

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ABSTRACT

Groundnut shell, Eucalyptus and Poplar is pyrolysed in a thermogravimetric analyzer under nitrogen atmosphere to study its pyrolysis behavior for examining its industrial potential as energy resource. This report covered physico-chemical, thermal properties and thermal degradation characteristics in nitrogen atmosphere. The thermal degradation was conducted in a thermogravimetric analyzer from room temperature to 1000 ^{0}C at the heating rates 10, 20, 30 and 40 Kmin^{-1}. The TG and DTG curves exhibited three degradation zones for eucalyptus roots and poplar roots, whereas DTG curves for groundnut shell and eucalyptus stem shows four and five degradation zones respectively. The second, third and fourth zones had the higher value of activation energy than the first zones, whereas values of activation energy for the overall degradation zones is very less.

The kinetic analysis was carried out using several mechanistic models as well Agrawal and Sivasubramanian approximation from global degradation kinetics.
The maximum rate devolatilization and the DTG peak shifted to higher values along with increase in heating rate. The value of various kinetic parameters like activation energy, pre-exponential factor and reaction order calculated for the formation of active complex.

Groundnut shell has a very low activation energy as compared to the other biomass sample showed by Fuoss and Reich approximation and hence groundnut shell is preferable for the Pyrolysis over the other biomass sample.

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INTRODUCTION

HISTORY

The ever increasing energy demands and the fast depleting limited stock of fossil fuels have necessitated the exploration of alternative resources i.e. solar, wind, biomass, ocean etc. Almost 43% of the energy used by world is derived from biomass with over 2 billion people totally reliant on biomass fuels for their energy needs. In India, the energy supplied, from non-conventional energy sources is about 55% of the total energy requirement.

About 3.0 X 10^{21}GJ of solar energy are stored in 2 X 10^{11} tones of organic matter produced annually by photosynthesis. Yet only 14% of the world's total energy comes from biomass. In developed countries only 1 % of the total energy demand is met from biomass.

1.1 BIOMASS

The term biomass generally refers to renewable organic matter generated by plants through photosynthesis in which the solar energy aids in the transformation of carbon dioxide and moisture into carbohydrates and oxygen. Materials having combustible organic matter are also referred to as biomass. Coal is the end product of a sequence of biological and geological processes undergone by biomass itself but is not considered as biomass on a "renewable basis". Biomass a residue is oxygenated hydrocarbons containing C, H, and O. Biomass generally has high moisture and volatile matter constituents. Residues from agricultural and agro-industries, having high carbonaceous content are also referred to as biomass.

1.1.1 AVAILBILITY AND CHARACTERISTICS

India is a large country with a total land area of 328.8 million hectares, with an estimated human population of 967 millions, and a livestock population of about 450 millions living in about 587000 villages (Singh, 1996). The estimated quantity of

agricultural and agro-industrial residues is about 320 million tones with the cattle dung availability being about 240 million tones per year. About 20% of the total land areas is under forest cover, which produces 4 million tones of sawdust (Singh 1996). Biomass characteristics, which depend upon such constituent as lignin, hemicellulose, cellulose, mineral matter and ash, vary from species to species. The compositions of typical biomass species is given below in Table 1.1(Grover, 1996).

TABLE 1.1 **CHARACTERISTICS OF IMPORTANT FUEL WOODS**

Species	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Ash (%)**
Soft wood	41	24	27.8	0.4
Hard wood	39	35	19.5	0.3
Rice straw	30.2	24.5	11.9	16.1
Bagasse	33.6	29	18.5	2.3
Groundnut shell	35.7	18.7	30.2	5.9

1.1.2 CLASSIFICATION OF BIOMASS

Biomass is generally classified as woody and non-woody (powdery) on the basis of its bulk density. For woody biomass, bulk density is more than 250-300 kg/m^3, whereas for non-woody biomass, bulk density is less than 250-300 kg/m^3. Woody biomass is essentially the solid stalk of the main trunk and branches in trees/plants. It is a structural element in the living material. It is dense and has little ash. Even agricultural residues, which may consist of whole plants or branches of plants, can be woody, like cotton stalk and mulberry stalk. Weeds like juliflora pro sop is, lantana camera, usually found in tropical climates can also be treated as woody biomass. Examples of powdery biomass are bagasse, rice husk, rice straw, coir pith, groundnut shells, sawdust etc.

The classification of biomass as woody and non-woody is important, and it is also useful to recognize that the composition of any biomass is nearly the same.

Biomass is found to be composed of volatiles, fixed carbon and ash. Based on ash content the various biomass species can be classified as follows.

Low ash biomass	(Ash content 1-4%)
Medium ash biomass	(Ash content 4-8%)
High ash biomass	(Ash content >8%)

This classification, together with description like powdery, stalk like the one etc is given in Table 1.2 [Grover, 1996].

Table 1.3 [Grover, 1996] Gives the proximate analysis and Table 1.4 [Grover, 1996] provides the comparative assessment of fuel.

TABLE 1.2 CLASSIFICATION OF BIOMASS BASED ON ASH CONTENT

POWDERY MATERIAL

S.No	Biomass low ash	Ash %	Biomass Medium ash	Ash %	Biomass High ash	Ash %
1.	Eucalyptus saw dust	0.4	None	-	Industrial bamboo dust	9.9
2.	Saw dust	1.3	None	-	Jute dust	19.9

COARSE/GRANULAR MATERIAL

S.No	Biomass Low ash	Ash %	Biomass Medium ash	Ash %	Biomass High ash	Ash %
1.	Bagasse	1.8	Bagasse pith	8.0	Tea waste	19.8
2.	Coconut shell	1.9	Cotton shells	4.6	Rice husk	22.4
3.	Groundnut shell	3.6	Sugarcane leaf	7.7	Sunflower	10.1

STALK LIKE MATERIAL

S.No	Biomass Low ash	Ash %	Biomass Medium ash	Ash%	Biomass High ash	Ash %
1.	Com cab	1.2	Congress grass	4.2	Ground paddy straw	15.5
2.	Jute stick	1.2	Dry potato waste	5.8	Rice straw	20.4
3.	Mulburry stick	2.1	Sunflower branch	7.7	Jowar stalk	10.1

TABLE 1.3 PROXIMATE ANALYSES AND CARBON-HYDROGEN CONTENT OF SOME BIOMASS MATERIAL. (Dry basis)

S.No	Biomass	Volatiles	Fixed Carbon	Ash	Carbon	Hydrogen
1.	Bagasse	75.10	16.87	8.03	45.71	5.89
2.	Coconut coir	70.30	26.77	2.93	47.17	6.54
3.	Jute stick	75.33	19.00	5.67	54.77	8.20
4.	Rice husk	60.64	19.90	19.90	40.10	6.03

TABLE 1.4 COMPARATIVE CONSTITUENTS OF FUELS

Component	Biomass	Wood	Coal
Fixed carbon (%)	10-20	15-20	60-80
Volatile matter (%)	60-85	70-80	20-30
Ash content (%)	1-20	1-3	5-40

1.1.3 FEED STOCKS

WOOD

Wood is a predominant fuel in developing countries, and is easily available as firewood for many applications. It competes well with fossil fuels, because it is renewable, and is a cheap source of energy on account of its energy storage capacity. Wood is a composite of cellulose, lignin and hemicellulose (43, 35 and 22%, respectively). A typical analysis of dry wood yields carbon-52%, hydrogen-6.3%, oxygen-40.5% and nitrogen-0.4% (Reddy, 1994). The proximate analysis of wood gives the following components; volatile matter-80%, fixed carbon-19.4% and ash-

0.6%. The calorific value of wood depends on the percentage of carbon and hydrogen. The calorific value of fuel wood lies in between 17.5-22.7MJ/kg. The bulk density of wood lies between 200-220 kg/m^3. In the present study popular wood is used for the pyrolysis, since it is a fast growing energy plantation and is easily available in this part of northern India.

1.1.4 IMPORTANCE OF BIOMASS

Biomass now represents only 3% of primary energy consumption in industrialized countries. However, much of the rural population in developing countries, which represents about 50% of the world's population, is dependent on biomass, mainly in the form of wood, for fuel. Biomass accounts for 35% of primary energy consumption in developing countries, raising the world total to 14% of primary energy consumption.

Biomass has great potential as a renewable energy source, both of the rich countries and for the developing world. Biomass as a fuel is still in the experimental stage and provides only about 0.25% of the total electricity generating capacity in the UK. However, this is likely to increase for a number of reasons. One reason is that European and UK legislation aims to encourage less polluting methods of waste disposal, and one viable option is to burn the waste to generate power. Another reason is that biomass power systems will become more affordable as the technology improves.

Biomass is used in a similar way to fossil fuels, by burning it at a constant rate in a boiler furnace to heat water and produce steam. Pipes carry the steam through the furnace again to raise its temperature and pressure further, and then, it passes through the multiple blades of a turbine, spinning the shaft. The turbine shaft drives an electricity generator which produces an alternating current for use locally or to supply the national grid. Refuse fuels used in power stations would otherwise have to be disposed of a landfill sites or in some other way. Efficient burning reduces them to a relatively small volume of ash while also producing useful electricity of heat energy.

There are also potential benefits in growing biomass especially for fuel. Provided the right crops are chosen, it is possible to use poor quality land which is unsuitable for growing food. Burning biomass produces some pollutants, including dust and the acid rain gases sulfur dioxide (SO_2) and nitrogen oxides (NO_2). Burning wood produces 90% less sulfur than coal. These can all be reduced before releasing the fuel gases into the atmosphere. At the present rate of use, the quantities of atmospheric pollution involved are insignificant compared with other pollution sources, but this would be a factor to consider if the use of biomass increased. Carbon dioxide (CO_2), the greenhouse gas, is also released. However, as this originates from harvested or processed plants, which have absorbed it from the atmosphere in the first place, no additional amounts are involved.

1.1.5 BIOMASS ENERGY

Biomass energy is one humanity's earliest sources of energy. Biomass in used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities. Biomass potential includes wood and animal and plant wastes. Biomass is only an organic petroleum substitute which is renewable. The term 'biomass' refers to forestry, purposely grown agricultural crops, trees and plants and organic, agricultural, agro-industrial and domestic wastes (municipal and solid waste). Biomass is the name given to the plant matter which is created by photosynthesis in which the sun's energy converts water and CO_2 into organic matter. Thus, biomass materials are directly or indirectly a result of plant growth. These include firewood plantations, agricultural residues, forestry residues, animal wastes etc. Fossil fuels can also be termed biomass, since they are the fossilized remains of plants that grew some millions of years ago.

The one renewable energy source on which mankind has relied since the discovery of fire is photosynthesis, the process in which solar energy is converted into an energy rich biomass. In this process, solar energy, absorbed by green plant tissue, provides energy to reduce CO_2 and form carbohydrates, which are then utilized as energy sources and raw materials for all other synthetic reactions in the plant. Thus, solar energy is captured and stored in the plant, thereby providing food, fiber, fuel and shelter for mankind. However, this photosynthesis uses only a small portion of the sun's energy to fix 200 billion tons of carbon into terrestrial and aquatic biomass with an energy content of 3000 billion GJ/y. Yet, only 1/10th of the world's biomass energy is consumed, while the rest is left untapped.

1.1.6 RESOURCES OF BIOMASS

Biomass resources include wood and wastes, agricultural crops and their waste by products, municipal solid waste (MSW), animal wastes, waste from food processing and aquatic plants and algae. The average majority of biomass energy is produced form wood and wood wastes (64%), followed by MSW (24%), agricultural waste (5%) and landfill gases (5%).

Biomass differs from other alternative energy sources in that the resource is varied, and it can be converted to energy through many conversion processes. Biomass resources can be divided into three general categories:

1. Wastes
2. Standing forests
3. Energy crops

Biomass resources that can be used for energy production cover a wide range of materials. Biomass energy can be separated into two categories, namely modern biomass and traditional biomass. Modern biomass usually involves large scale used and aims to substitute for conventional energy sources. It includes wood and agricultural residues, urban wastes and biofuels, such as biogas and energy crops. Traditional biomass is generally confined to developing countries and small scale uses. It includes fuelwood and charcoal for domestic use, rice husks and other plant residues and animal wastes. Examples of biomass energy resources are:

Wastes

- Agricultural production wastes
- Agricultural processing wastes
- Crop residues
- Mill wood wastes
- Urban wood wastes
- Urban organic wastes

Forest Products

- Wood
- Logging residues
- Trees, shrubs and wood residues
- Sawdust, bark etc. from forest clearings

Energy Crops

- Short rotation woody crops
- Herbaceous woody crops
- Grasses
- Starch crops (corn, wheat and barley)
- Sugar crops (cane and beet)
- Forage crops (grasses, alfalfa and clover)
- Oilseed crops (soybean, sunflower, safflower)

Aquatic Plants

- Algae
- Water weed

- Water hyacinth
- Reed and rushes

The demand for energy is increasing at an exponential rate due to the exponential growth of world population. This, combined with the widespread depletion of fossil fuels and gradually emerging consciousness about environmental degradation, suggests that the energy supply in the future has to come from renewable sources of energy. Statistics show that, although total renewable now account for nearly 18% of global primary energy supply, out of this, over 55% is supplied by traditional biomass and about 30% by large hydro. Solar, wind modern biomass, geothermal, small hydro (below 10 MW) and ocean energy all together account for only 12% of total renewable. The new renewable account only for 2 % of the world primary energy supply.

1.1.7 ENERGY FROM BIOMASS

Biomass is not in ideal form for fuel use. The heat content calculated on a dry mass basis must be corrected for the natural water content that can reduce the net heat available by as much as 20% in direct combustion applications. Gasification to low calorific gas carries an additional net energy loss, and conversion to synthetic natural gas and liquid fuels results in still greater reduction of net energy, to perhaps 30% of the original heat content.

To get the maximum energy, the plant materials should be air dried because the amount of energy contained in the plant varies with the amount of moisture content. If the combustible materials are required for the energy recovery process, the amount of water in the plant material will affect the recoverable energy. The variations of calorific value of Indian firewood indicate that with increasing moisture content, the calorific value decreases linearly. Energy can be obtained from biomass in five ways:

- production of crops which yield starch, sugar, cellulose and oil
- solid waste which can be burnt
- anaerobic digesters which produce biogas which can be used to generate heat/electricity
- landfill production for methane

- biofuel production which includes ethanol, methanol, biodiesel and their derivatives.

Ethanol is blended with gasoline in the ratio of 1:9 to produce the fuel gasohol. Ethanol can also be used in fuel cells. The production of biodiesel has also gone up from 11,000 tons in 1991 to 1,286,000 tons in 1997. The raw materials are oils from 84% rapeseed, 13% sunflower, 1% soybean, 1% palm and 1% others. Although wastes are still largely under utilized in some developed countries (such as Sweden) with a high land to population ratio and an active forest industry, their use is increasing rapidly, whilst costs (in real terms) drop significantly, resulting in as much as 15-18% contribution to national energy needs. Predictions suggest that in countries such as New Zealand, biomass mixed with hydro and wind could make the country completely reliant on renewable within the next 26 years, if the right financial support is given. Reports from the US, UK, Sweden, New Zealand and covering the EU indicate the efforts which are being made by governments to establish biomass as a long term resource within the framework of a sustainable, environmentally acceptable, cost effective policy linked to specific fiscal and legislative measures .

1.1.8 AGRICULTURAL RESIDUES

Large quantities of agricultural plant residues are produced annually worldwide and are vastly under utilized. The most common agricultural residue is the rice husk, which makes up 25% of rice by mass. Other plant residues include sugar cane fiber (known as bagasse), coconut husks and shells, groundnut shell and straw. Included in agricultural residue is waste, such as animal manure (e.g. from cattle, chicken and pigs), which is used extensively in developing countries and, in some instances, in developed countries to produce heat or gas.

1.1.9 BENEFITS OF BIOMASS

Biomass is a renewable, potentially sustainable and relatively environmentally benign source of energy. If grown and utilized on a sustainable basis, biomass is carbon dioxide neutral. Thus, the substitution of fossil fuels for energy production with biomass will result in a net reduction in greenhouse gas emissions and the replacement of a non-renewable energy source. Many large power producers in industrialized countries are looking to biomass as a means of meeting greenhouse gas reduction targets. The natural decomposition of biomass produces methane, which is about twenty times more active as a greenhouse gas than carbon dioxide. There is, therefore, an additional greenhouse gas emission benefit in burning biogas, landfill gas and biomass residues to produce carbon dioxide. Biomass fuels have negligible sulfur content and, therefore, do not contribute to sulfur dioxide emissions, which cause acid rain. The combustion of biomass produces less ash than coal combustion, and the ash produced can be used as a soil additive on farm targets. The combustion of agricultural and forestry residues and MSW for energy production is an effective use of waste products that reduces the significant problem of waste disposal, particularly in municipal areas.

1.1.10 ENVIRONMENTAL IMPACTS OF BIOMASS ENERGY

One example is a closed loop system in which carbon dioxide will be taken up by new plant growth at the same rate that it is released by using the harvested biomass for fuel. Such bioenergy crops would make little or no net contribution to atmospheric carbon dioxide as a greenhouse gas. On the other hand, when fossil fuels are burned, carbon is released that has been stored underground for millions of years, making a net contribution to atmospheric greenhouse gases. Therefore, if managed carefully, biomass energy can have significant environmental advantages over the use of fossil fuels. An appropriate level of biomass energy use can have less environmental impacts than our current means of energy production.

The lumber, pulp and paper industries burn their own wood wastes in large furnaces and boilers to supply 60% of the energy needed to run the factories. In our homes, we burn wood in stoves and fireplaces to cook meals and warm our residences.

Biomass is burned by direct combustion to produce steam, the steam turns a turbine and the turbine drives a generator, producing electricity. Because of potential ash build-up (which fouls boilers, reduces efficiency and increases costs), only certain types of biomass materials are used for direct combustion. Gasifiers are used to convert biomass into a combustible gas (biogas). The biogas is then used to drive a high efficiency, combined cycle gas turbine. Heat is used to convert biomass chemically into pyrolysis oil. The oil, which is easier to store and transport than solid biomass material, is then burned like petroleum to generate electricity. Pyrolysis also can convert biomass into phenol oil, a chemical used to make wood adhesives, molded plastics and foam insulation. Wood adhesives are used to glue together plywood and other composite wood products. cross linked and relatively insensitive to impurities. Ablative fast pyrolysis is used to convert solid biomass into liquid pyrolysis oil in high yields while minimizing the formation of char and permanent gases. The liquid pyrolysis oil is then subjected to a solvent extraction process to recover the phenol rich phenolics neutrals (PN) fraction. Depending on the biomass feedstock, 18-20 wt % of the original biomass may be recovered in the PN fraction. This PN fraction can then be formulated into PF resins that are useful as wood adhesives and injection molded plastics. Up to 50% of the phenol in a typical PF resin can be replaced with PN without a substantial decline in the physical properties of the wood adhesives or injection molded plastics. Biomass from a number source, i.e hardwoods, softwoods, annual grasses and wood bark, has been evaluated as feedstocks for the production of PN. The source of the feedstock does have some impact on the quality of the resins or plastics. Softwoods and grasses appear to be attractive feedstocks.

1.1.11 THE FUTURE OF BIOMASS

In the future, biomass has the potential to provide a cost effective and sustainable supply of energy, while at the same time, aiding countries in meeting their greenhouse gas reduction targets. By the year 2050, it is estimated that 90% of the world population will live in developing countries. It is critical, therefore, that the biomass processes used in these countries are sustainable. The modernization of biomass technologies, leading to more efficient biomass production and conversion, is one possible direction for biomass use in developing countries.

In industrialized countries, the main biomass processes utilized in the future are expected to be direct combustion of residues and wastes for electricity generation, bio-ethanol and biodiesel as liquid fuels and combined heat and power production from energy crops. In the short to medium term, biomass waste and residues are expected to dominate biomass supply, to be substituted by energy crops in the longer term. The future of biomass electricity generation lies in biomass integrated gasification/gas turbine technology, which offers high energy conversion efficiencies.

Biomass will compete favorably with fossil mass for niches in the chemical feedstock industry. Biomass is a renewable, flexible and adaptable resource. Crops can be grown to satisfy changing end use needs. The success of the biomass derived chemicals industry will depend on the supply and demand for feedstock, primary chemicals and key intermediates the petrochemical industry cannot make, such as cellulose, lactic acid and levulinic acid. The first thermoplastics and synthetic fibers were made from cellulose derivatives. Acetaldehyde, a major petrochemical key intermediate, can be made from lactic acid. Levulinic acid salts have been proposed to replace ethylene glycol as an engine coolant.

1.2 BIOMASS CONVERSION PROCESSES

Biomass conversion may be conducted on two broad pathways: Chemical Decomposition and Biological Digestion. The conversion technologies for utilizing biomass can be separated into four basic categories: direct combustion processes, thermochemical processes, biochemical processes and agrochemical processes.

Thermochemical decomposition can be utilized for energy conversion of all five categories of biomass materials, but low moisture herbaceous (small grain field residues) and woody (woody industry wastes and standing vegetation not suitable for lumber) are the most suitable. Biological processes are essentially microbic digestion and fermentation. High moisture herbaceous plants (vegetables, sugar cane, sugar beet, corn, sorghum, cotton) marine crops and manure are most suitable for biological digestion.

Extraction is another, mainly mechanical, process for producing an energy carrier from biomass (e.g. rapeseed oil from rapeseed). With regard to the energy carriers produced from biomass, a distinction can be made between the production of heat, electricity and fuels. There are numerous ongoing technological developments in the field of biomass energy conversion. A detailed overview is, however, beyond the scope of this introduction. Such an overview can be found elsewhere, for example in a report by Van den Heuvel.

1.2.1 DIRECT COMBUSTION PROCESS

Combustion is widely used on various scales to convert biomass energy to heat and/or electricity with the help of a steam cycle (stoves, boilers and power plants). Production of heat, power and (process) steam by means of combustion is applied for a wide variety of fuels and from very small scale (for domestic heating) up to a scale in the range of 100 MWe. Co-combustion of biomass in (large and efficient) coal fired power plants is an especially attractive option as well because of the high conversion efficiency of these plants. It is a proven technology, although further improvements in performance are still possible. Net electrical efficiencies for biomass combustion power plants range from 20% to 40%. The higher efficiencies are obtained with systems over 100 MW or when the biomass is co-combusted in coal fired power plants. Direct combustion is the main process adopted for utilizing biomass energy. The energy produced can be used to provide heat and/or steam for cooking, space heating and industrial processes, or for electricity generation. small scale application, such as domestic cooking and space heating, can be very inefficient, with heat transfer losses of 30-90%. This problem can be addressed through the use of more efficient stove technology. On a larger scale, biomass, such as fuelwood, forestry residues, bagasse and MSW, can be combusted in furnaces and boilers to produce process heat, or steam for a steam turbine generator. Power plant size is constrained by the local feedstock availability and is generally less than 25 MW. However, by using dedicated feedstock supplies, such as short rotation plantations or herbaceous energy crops, the size can 1:>e increased to 50-75 MW, gaining significant economics of scale. In developing countries, power generation is usually required in smaller increments, and agricultural residues, such as rice husk and nutshells, can easily meet feedstock requirements.

1.2.2 THERMO CHEMICAL CONVERSION PROCESS

Thermochemical conversion processes can be subdivided into gasification, pyrolysis, and direct liquefaction. The last two processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights. With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase.

PYROLYSIS

Pyrolysis is the thermochemical process that converts biomass into liquid (bio-oil or bio-crude), charcoal and non-condensable gases, acetic acid, acetone and methanol by heating the biomass to about 750 K in the absence of air. The process can be adjusted to favor charcoal, pyrolytic oil, gas or methanol production with a 95.5% fuel-to-feed efficiency. Pyrolysis can be used for the production of bio-oil if flash pyrolysis processes are used, and it is currently at the pilot stage.

Pyrolysis produces energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method, most capable of competing with and eventually replacing non-renewable fossil fuel resources: the conversion of biomass to crude oil can have efficiency up to 70% for flash pyrolysis processes. The so-called bio-crude can be used in engines and turbines. Its use as feedstock for refineries is also being considered some problems in the conversion process and use of the oil need to be overcome. These include poor thermal stability and corrosivity of the oil. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications.

Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon rich gas mixture, an oil-like liquid and a carbon rich solid residue. Traditionally in developing countries, the solid residue produced is charcoal, which has a higher energy density than the original fuel and is smokeless and, thus, ideal for domestic use. The traditional kilns are simply mounds of wood covered with earth, or pits in the ground. However, the process of carbonization is very slow and inefficient in these kilns and more sophisticated kilns are replacing the traditional ones. Chemical decomposition through pyrolysis is the same technology used to refine crude fossil fuel oil and coal. Biomass conversion by pyrolysis has many environmental and economic advantages over fossil fuels, but coal and oil production dominate because costs are kept lower by various means, including government protection.

Pyrolysis of wood to produce charcoal was a major industry in the 1800s, supplying the fuel for the industrial revolution, until it was replaced by coal. In the late 19th century and early 20th century, wood distillation was still profitable for producing soluble tar, pitch, creosote oil, chemicals and non-condensable gases often used to heat boilers at the facility.

The wood distillation industry used pyrolytic reactors in a process called destructive distillation. The operation was performed in a fractionating column (a tall still) under high temperature (from 750 to 1350 K). Charcoal was the main fuel product, and methanol production was about 1-2% of volume, or 6 gallons per ton. This traditional method was replaced by the synthetic process developed in 1927 (Dembrisis, 2001). The synthetic process utilizes a pyrolytic reactor, operating as a gasifier by injecting air or pure oxygen into the reactor core to completely burn the biomass to ash. The energy contained in the biomass is released in the gases formed. After purification, the synthic gas, hydrogen and carbon monoxide in a 2 to 1 ratio, is altered by catalyst under high pressure and temperature to form methanol. This method will produce 100 gallons of methanol per ton of feed material .Pyrolysis of wood has been studied as a zonal process with zone A (easily degrading zone) occurring at temperatures up to 473 K. When temperatures of 473-533 K are attained, the wood is said to be in zone Band is evolving water vapor, carbon dioxide, formic acid, acetic acid glyoxal and some carbon monoxide. The reactions to this point are mostly endothermic, the products are largely non condensable and the wood is becoming charred. Pyrolysis actually begins between 535 and 775 K, which is called zone C. The reactions are exothermic, and unless heat is dissipated, the temperature will rise rapidly. Combustible gases, such as carbon monoxide from cleaving of the carbonyl group, methane, formaldehyde, formic acid, acetic acid, methanol and hydrogen are being liberated and charcoal is being formed. The primary products are beginning to react with each other before they can escape the reaction zone. If the temperature continues to rise above 775 K, a layer of charcoal will be formed that is the site of vigorous secondary reactions and is classified as zone D. Carbonization is said to be complete at temperatures of 675-875 K. The thermal degradation properties of hemicelluloses, celluloses and lignin can be summarized as follows:

Thermal degradation of hemicelluloses > of cellulose >>> of lignin

If the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. For high' char production, a low temperature, low heating rate process would be chosen. If the purpose is to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred.

GASIFICATION

Gasification is a form of pyrolysis, which is performed at high temperatures in order to optimize gas production. The resulting gas, known as producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen

Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency and to reduce the investment costs of biomass electricity generation through the use of gas turbine technology. High efficiencies (up to about 50%) are achievable using combined cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine. Economic studies show that biomass gasification plants can be as economical as conventional coal fired plants. Commercial gasifiers are available in a range of sizes and types and run on a variety of fuels, including wood, charcoal, coconut shells and rice husks. Power output is determined by the economic supply of biomass, which is limited to 80 MW in most regions.

SUPERCRITICAL FLUID EXTRACTION

Conversion by supercritical fluid extraction of biomass to liquids has been demonstrated with the use of a number of processing configurations. These different processing techniques tend to emphasize different mechanism subsets within the large group of potential chemical mechanisms by which biomass is converted to primary products and thereafter further converted by varying degrees to final products.

LIQUEFACTION

Liquefaction is a low temperature, high-pressure thermochemical process using a catalyst. The process produces a marketable liquid product. Liquefaction takes place at moderate temperatures at high pressure with the addition of hydrogen. The interest in liquefaction is low because the reactors and fuel feeding systems are more complex and more expensive than for pyrolysis processes.

HYDRO THERMAL UPGRADING PROCESS

Another way to produce bio-crudes is the hydro thermal upgrading (HTU) process. HTU converts biomass in a wet environment at high pressure to partly oxygenated hydrocarbons.

1.2.3 BIOCHEMICAL PROCESS

BIOGAS GENERATION

Anaerobic digestion is the decomposition of biomass through bacterial action in the absence of oxygen. It is essentially a fermentation process and produces a mixed gas output of methane and carbon dioxide. The product generated by the decay, in the absence of air, of sewage or animal waste is known as biogas. The anaerobic digestion of MSW buried in landfill sites produces a gas known as landfill gas.

Biogas is most commonly produced by using animal manure mixed with water, which is stirred and warned inside an airtight container, known as a digester. Digesters range in size from around 1 m^3 for a small household unit to as large as 2000 m^3 for a large commercial installation. The biogas produced can be burnt directly for cooking and space heating, or used as fuel in internal combustion engines to generate electricity.

The methane gas produced in landfill sites eventually escapes into the atmosphere. However, the landfill gas can be extracted from existing landfill sites by inserting perforated pipes into the landfill. In this way, the gas will travel through the pipes under natural pressure for use as an energy source, rather than simply escaping into the atmosphere to contribute to greenhouse gas emissions. Generally used for electricity generation, using large internal combustion engines. One of the larges landfill gas plants in the world is a 46 MW plant in California.

ALCOHOLIC FERMENTATION

Ethanol can be produced from certain biomass materials which contain sugars, starch or cellulose. The best-known source of ethanol is sugar cane, but other materials can be used, including wheat and other cereals, sugar beet, Jerusalem artichoke and wood. The choice of biomass is important as feedstock costs typically make up 55-80 % of the final alcohol-selling price. Starch based biomass is usually cheaper than sugar based materials but requires additional processing. Similarly, cellulose materials, such as wood and straw, are readily available but require expensive preparation.

A process known as fermentation produces ethanol. Typically, sugar is extracted from the biomass crop by crushing, mixed with water and yeast and kept warm in large tanks called fomenters. The yeast breaks down the sugar and converts it to methanol. A distillation process is required to remove the water and other impurities in the diluted alcohol product (10-15% ethanol). The concentrated ethanol (95% by volume with a single step distillation process) is drawn off and condensed to a liquid form.

Methanol can be used as a supplement or substitute for petrol in cars. Brazil has a successful industrial scale ethanol project which produces ethanol from sugar cane for blending with petrol. Some vehicle adaptations are required for full petrol substitution.

Crop residues are often used to supply the external heat required for the process. There is a significant energy loss in the distillation stage, particularly the complex secondary distillation process required to achieve ethanol concentrations of 99%.

1.2.4 AGROCHEMICAL PROCESS

Seed crops, which contain a high proportion of oil, can be crushed and the oils extracted and used directly to replace Diesel (called biodiesel) or as a heating oil. The energy content of vegetable oils are 39.3-40.6 MJ/kg. There are a wide range of crops that can be used for biodiesel production, but the most common crop is rapeseed. Other raw materials used are palm oil, sunflower oil, soya bean oil and recycled frying oils. The cost of the raw material is the most important factor affecting the overall cost of production. There are currently 85 biodiesel plants around the world (including one in Malaysia using palm oil) with a combined capacity of over 1.28 million tons. In the Philippines, Diesel is blended with coconut oil and used in tractors and lorries.

There are a number of benefits associated with biodiesel, including a reduction in greenhouse gases of at least 3.2 kg of carbon dioxide-equivalent per kilogram of biodiesel, a 99% reduction of sulfur oxide emissions, a 39% reduction in particulate matter, a high biodegradability and energy supply security

1.2.5 HYDROGEN FROM BIOMASS

Hydrogen is a clean burning fuel. It is not a primary fuel it must be manufactured from water. With either fossil or non-fossil energy sources. Hydrogen is produced from pyroligneous oils produced from the pyrolysis of lignocelluloses biomass .Gasification of solid wastes and sewage is a recent innovation. The synthesis gas formed with air or oxygen is reformed to hydrogen. The solid waste concept solves two problems: (1) disposal of urban refuse and sewage and (2) a source of hydrogen fuel for hydrogen powered vehicles. Hydrogen from biomass has generally been based on the following reactions

Solid waste + Air $\rightarrow$ $CO + H_2$

Biomass + H_2O + Air $\rightarrow$ $H_2 + CO_2$

Cellulose + H_2O + Air $\rightarrow$ $H_2 + CO + CH_4$

1.3 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is extensively used to understand the pyrolytic characteristics and determine the kinetic parameters. Many TGA studies on the pyrolytic kinetics of wastes from domestics industrial and agriculture activities have been reported. The kinetic parameters including activation energy, frequency factor and reaction order were measured. These data are important to efficient design ,operation, and modeling of pyrolysis and related thermochemical conversion system for biomass.

1.4 AIMS AND OBJECTIVES

The kinetic data of pyrolysis of many biomass residues are not available. Thermogravimetric analysis in the presences of an inert gas like helium, nitrogen is carried out to study the kinetics of thermal degradation.

In view of the limited kinetic data of groundnut shell, poplar and eucalyptus, the present study has been undertaken with following aims and objective.

1. To carry out proximate and ultimate analyses of groundnut shell, poplar and eucalyptus.

2. To carry out thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) of groundnut shell, poplar and eucalyptus at different heating rates under flowing nitrogen atmosphere.

3. To determine kinetic parameters of the pyrolysis and thermal degradation in air utilizing integral and differential methods of analysis.

CHAPTER-II

LITERATURE REVIEW

2.1 PROXIMATE ANALYSIS

Proximate analysis consists of the determination of moisture, volatile matter and ash in a sample of biomass. Moisture is undesirable in industrial biomass. It reduces the heating value when the biomass is burned, the moisture is evaporated and this entails loss of heat, since the latent heat of evaporation cannot be recovered, while the steam produced, escapes as superheated steam with the wastes gases. The loss is seldom very great; each one percent of moisture causes a loss of approximately one-tenth of a percent of the heat of combustion of the biomass. When biomass is so treated, the organic matter decomposes, yielding water of decomposition, oxides of carbon, tarry vapors and gases, including hydrogen, methane, other hydrocarbon, ammonia, hydrogen sulphide and nitrogen. This mixture is known as volatile. Sometimes the terms volatile hydrocarbon or "volatile combustible matter" are used; both terms are objectionable because they are inaccurate and misleading. The volatiles contains other constituents besides hydrocarbon while, in addition, there may be an appreciable quantity of carbon dioxide and combined water from mineral matter.

Biomass yields volatile, which are the products of the decomposition of the biomass the percentage decomposition depends on the temperature to which the biomass has been heated; the composition is influenced by the rate of heating and the ultimate temperature reached. High volatiles are advantageous. For the same amount of heat release per unit of combustion volume, the loss of unburned carbon is lower with high volatiles than with low volatiles, and in addition ease and stability of ignition are favored by high volatiles.

The fixed carbon, with consists chiefly carbon, contains minor proportions of hydrogen, nitrogen, sulphur and oxygen also. It is always less than total carbon in the biomass as determined by combustion analysis.

The desired pyrolysis charactestics are high heating rate, low mineral content, low moisture and uniform size. Several investigators have reported their results of proximate analysis of Groundnut shell. These are reported in Table 2.1

Table 2.1 **Proximate Analysis of groundnut shell and eucalyptus**

Investigator	Biomass	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Higher heating value MJ/kg	Ash deformation temperature ^0C	Ash fusion temp. ^0C
Ramesh Kate (2001)	Groundnut shell	68.12	24.97	6.91	17.20	1180-1200	1220-1250
Raveendran et.al (1994)	Ground nut shell	83.00	13.92	5.4	18.65	_	_
M.Guerrero et.al (2004)	eucalyptus	74.91	16.38	0.98	_	_	_

2.2 ULTIMATE ANALYSIS

Ultimate analysis of any biomass samples provides information on the elemental composition of the biomass. Normally, carbon, hydrogen and nitrogen are analyzed and the balance of oxygen is obtained by subtraction of the sum of carbon, hydrogen and nitrogen from 100 as a percentage. Ultimate analysis of different biomass given in Table 2.2

Table 2.2 **Ultimate Analysis of Groundnut shell and Eucalyptus**

Investigators	Biomass	Hydrogen	Nitrogen	Carbon	Oxygen
Ramesh Kate(2001)	Groundnut shell	6.68	0.78	47.67	44.87
Raveendran et.al (1994)	Groundnut shell	5.7	0.8	48.3	39.4
M.Guerrero et.al (2004)	Eucalyptus	6.16	0.28	48.65	44.91

2.3 THERMAL DEGRADATION KINETICS IN OXIDIZING ATMOSPHERE

Prasad B. et.al (2004) studied the global degradation kinetics of pine needles in air for determining the kinetic parameters under non isothermal condition. They suggested that at low heating rate, only three degradation zones were found. The second, third and fourth zones had higher values of activation energy than the first zone. Agrawal and Sivasubramaian method was found to be most consistent. For the total degradation zone the orders of reaction were found in the range of 0.00 – 2.50 by using Agrawal and Sivasubramanian approximation, the activation energy in the range of 34.60- 85.34 kJ/mol and preexpontial factor in the range of 3.29 X 10^4 to 5.98 X 10^6 mg^{1-n} min^{-1}.

Singmsetti and Rao (2000) studied the pyrolysis of rice husk for determining the kinetic parameters under isothermal and non isothermal heating conditions. Analysis of the isothermal data showed that the reaction followed second order kinetics and that the activation energy was 53 kJ/mol in the lower temperature zone and 75-110 kJ/mol in the higher temperature zone. It was also found that a kinetic compensations effect existed between the activation energies and the frequency factor.

They found that the transition temperature and the maximum reaction rates were dependent on the heating rate.

Nassar (1995) carried out studies on thermal degradation kinetics of nonwood plants by using TG and DT analysis under oxidizing and inert atmosphere. He found that the thermal curves of rice straw and hulls were very similar, but bagasse shows a different curve similar to that of for hardwood. He reported that the rate of thermal degradation of nonwood plants was faster than wood because of the porous structure of biomass sample. Kinetics studies were based on weight loss obtained from TG analysis. A dual mechanism concept similar to wood was found for nonwood plants. Two values of activation energy were obtained with a transition temperature at 335 ^{0}C. Rice straw and hulls have low values of activation energy due to the porous structure and presence of higher percentage of silica, while activation energies of bagasse were found to be close to that of hardwood. The presence of inorganic impurities in the cellouse material had an effect on the kinetics of thermal decomposition.

Determination of the kinetic parameters of three verities of oat straw in an oxidizing atmosphere (15% oxygen and 85% nitrogen) using thermogravimetric analysis from ambient temperature to a temperature of 700 ^{0}C using heating rates 20 ^{0}C/min was carried out by Ghaly et al. (1993). They found that the kinetics parameters for the two reaction zones separately by applying thermo-analytical techniques to the reaction kinetics. They reported higher thermal degradation rates in the first reaction zone. The activation energies were found to be in the range of 83-102 and 58-75 kJ/mol for the first and second reaction zones, respectively.

Determination of kinetics parameters of four varieties of rice husk (Lemont, ROK 14, CP 4, and Parameters Potho)in an air atmosphere using thermogravimetric analysis from ambient temperature to a temperature of 700 ^{0}C, and a heating rate 20 ^{0}C/min was carried out by Ghaly et al.(1999). They found kinetic parameters for each reaction zones separately. Higher thermal degradation rates were reported in the first reaction zone. The activation energies were found to be in the range of 37-55 and 18-21 kJ/mol for the first and second reactions zones, respectively. The pre exponential facture were found to be in the range of 4.3 X 10^4-6.4 X 10^4 min^{-1} in the first reaction zones and 4.5 X 10^2 -1.5 X 10^3 min^{-1}in the second reaction zone. The order of reaction were in the range of 1.2-1.6 and 0.4-0.5 for the first zone and second zone, respectively.

The reaction kinetics of paddy husk at heating rates between 10 and 100 ^{0}C/min and under atmosphere of air and oxygen-nitrogen mixture (5:95) has been evaluated from experimentally obtained TGA data Jain et.al (1999). The limitations of the existing TGA models were discussed by them and a supposed by modified and although the correct Coats and Redfern (1964) approximation to the integral method was used for the correlation of the data. They got the optimum values of kinetic parameters with the optimum values of regression coefficient in the case of gasification as shown in Table 2.3 at two different ranges of temperature.

Table 2.3 **Kinetic Parameters of Paddy Husk at 10 and 100 ^{0}C/min in Air Jain et.al (1999).**

Range of Temperature ^{0}C	n	E (kJ/mol)	A (s^{-1})	R^2
260-310	1.00	313.540	1.790×10^{26}	0.9942
310-500	1.50	175.500	8.000×10^{11}	0.9871

Global degradation kinetics of wood and agriculture residues in air at a heating rate of 20 ^{0}C/min was carried out by Di Blasi and Caranca (1999). They reported negligible effects of reaction exothermicity when they divided TGA curves into three reaction zones. They found that the first, very fast step could be attributed to the degradation of all the main components, the very slow second stage to lignin and hemi cellouse degradation, while the third was the combustion of the solid residual. The amount of volatiles released in the first stage was higher for woods (75% to 77 % of the total solids against 50 to 60% of the residues) and the process was found to be displaced towards higher temperatures and thus associated with higher activation energies (values of about 75 to 100 kJ/mol for woods and 72 to 78 kJ/mol for residues. In all cases, devolatilization rates were to found to be very slow and almost constant in the second stage, with small amounts of volatiles released (6 to 9 % for woods and 5 to 6 % for residues)and comparable activation energies (86 to 92 kJ/mol for woods and 83 to 87 kJ/mol for residues). Combustion for chars from agriculture residues again was found to start at lower temperature and was describes by activation energies of 73 to 80 kJ/mol against 71 to 90 kJ/mol for woods.

Combustion of woods chars gives rise to a new peak in the reaction rate. The peak rate temperatures vary from 683 K (oak) to 703 K (pine). Wheat straw and olive husk present a peak in the combustion at temperature of 656 to 663 K, whereas for the other residues this is displaced towards higher values (683 to 686 K), close to those observed for woods. Its was found that agriculture residues degrade at lower temperature than woods. The volatilization process also gives rise to higher char yields, making combustion (and or gasification) proportionally more important. The reactivity in air of resulting chars appears to be higher for wheat straw and olive husk.

Nut shells and rise husk present reactivities comparable to those of woods, whereas gape residues were found to be slightly less active. Again the catalytic action of ashes may have been responsible for the higher reactivity and lower values for activation energies estimated for agriculture residue. It has been found that the chemical composition of biomass may explain the appearance of different reaction zones, the basic characteristics of the global degradation mechanism and other minor features.

Bilbao et.al (1993) studied the kinetics of thermal decomposition of cellulose and other biomass material. They reported that in the following temperature intervals

$T_f < T_{f1}$: the solid temperature increases without weight loss.

$T_{f1} < T_f < T_{f2}$: a slight weight loss can be observed. This is mainly due to the loss of moisture, as well as the evolution of CO and CO_2 in the first stages of cellouse decomposition.

$T_{f2} < T_f < T_{f3}$: no significant weight loss is observed.

$T_f > T_{f3}$: the main weight loss takes place in this interval

The variation of the specific reaction rate with temperature was assumed to follow Arrhenius equation. The specific reaction rate for pine were obtained as,

$T<290\ ^0C$	$k_{s1.5}\ (min^{-1}) = 0.017$(average value)
$290<T<325\ ^0C$	$k_{s1.5}\ (min^{-1}) = 3.61 \times 10^4 \exp(-16400/RT)$
$T>325\ ^0C$	$k_{s1.5}\ (min^{-1}) = 9.96 \times 10^{17} \exp(-25900/RT)$

The above equation can be used for the correction of the temperature gap between the solid and the system when high heating rates are to be used.

2.4 THERMOGRAVIMETRIC EVALUATION OF THE KINETICS OF THERMAL DEGRADATION OF BIOMASS

The application of thermoanalytical techniques are useful for calculating the energy of activation and order of reaction for the thermal degradation of biomass. The thermal behavior of biomass is frequently studied by measuring the weight loss of material as a function of time or temperature. This information, coupled with a reaction mechanism, is then used to estimate activation energies and frequency factor for Arrhenius type reaction rate expressions.

Freeman and Benjamin (1958) proposed that the plot of

$$(\Delta \ln d\omega / dt)/(\Delta \ln Wr) vs. \Delta(T^{-1})/(\Delta \ln Wr)$$

should result in straight lines with intercepts (-n) and slopes of (-E/R) for any unique physical or chemical reaction.

The method proposed by Piloyan and Novikava as given is valid for $0.08 < \omega < 0.5$.

$$\ln(\frac{\omega}{T^2}) = \ln\frac{AR}{\beta E} - \frac{E}{RT}$$

Where,

ω is the degree of decomposition, A is the preexpontial factor, β is the heating rates, and other symbols have this usual meanings. The plots of y = log (ω/T^2) against x= 1/T, the slope gives the activation energies, and the preexponetial factor may be calculated from the intercept.

The equation derived by Horowitz and Metzger (1964) can be written as

$$\ln[-\ln(1-\omega)] = \frac{E}{RT_s^2} \qquad \text{When n=1}$$

$$\ln[\frac{1-(1-\omega)^{1-n}}{1-n}] = \frac{E\theta}{RT_S^2} \qquad \text{When } n \neq 1$$

T_s, is the peak temperature as taken from the DTG curve, $\theta = T - T_s$. A plot of $y=\ln[\frac{1-(1-\omega)^{1-n}}{1-n}]$ against $x=\theta$ (when n=1) and $y=\ln[\frac{1-(1-\omega)^{1-n}}{1-n}]$ against $x=\theta$ (when $n \neq 1$) will give a straight line for the correct order of reaction. the pre-exponential factor is calculated from the intercept using the following expressions,

$$A = \frac{\beta E_a}{RT_S^2}\exp(\frac{E_a}{RT_S^2}) \qquad \text{When n=1}$$

$$A = \frac{\beta E_a}{RT_S^2} n^{-1} C_S \exp(\frac{E_a}{RT_S}) \qquad \text{When n =1}$$

Coats and Redfern (1964) proposed the integral method, which could be applied to TG data assuming a correct order of reaction. The correct order is assumed to lead the best-fit linear plot from which the activation energy and the preexponetial factor could be determined. The equations commonly used are follows

$$\ln[\frac{-\ln(1-X)}{T^2}] = \ln[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)] - \frac{E}{RT} \qquad \text{for n=1}$$

$$\ln\left[\frac{-\ln\{1-(1-X)^{1-n}\}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad \text{For } n \neq 1$$

It is possible to use a computational approach to select a value of n which gives best straight line through the points on the assumption that the order is constant through the reaction.

Reich and Stivala (1980) have devolved an iterative method to determine kinetic parameters. They reported the following relationship:

$$\ln\left[\frac{1-(1-\omega_i)^{1-n}}{1-(1-\omega_{i+1})^{1+n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right] = -\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_{i+1}}\right)$$

The plot of y= $\ln\frac{1-(1-\omega_i)^{1-n}}{1-(1-\omega_{i+1})^{1+n}}\left(\frac{T_{i+1}}{T_i}\right)^2$ against X= $(\frac{1}{T_i}-\frac{1}{T_{i+1}})$ will give a straight line. The slope is (-E/R) and intercept is nearest to zero.

A new integral approximation formula for kinetic analysis of non-isothermal TGA data was studied by Lee and Beck (1984) and by Chung –Hsiung Li (1985). However, the best approximation for the integral of the exponential term was given by Agrawal and Sivasubramanian (1987).They reported that

$$\int_0^T \exp(-E/RT)dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-5(RT/E)^2}\right]\exp(-E/RT)$$

For both methods as proposed by Coats and Redfern (1964) and Agrawal and Sivasubramanian (1987) the determination of activation energy E, the preexponetial factor n, is valid to give the best fit between Y=-ln $\frac{\{1-(1-X)^{1-n}}{T^2(1-n)}$ for $n \neq 1$ and

$-\ln\frac{[-\ln(1-X)]}{T^2}$ for n=1, (to be obtained from TGA curve) and 1/T. The slope of the curve in both the cases –E/R. The frequency factor A is obtained from the intercept that is,

$$\{-\ln(\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right])\} \qquad \text{for Coats and Redfern.}$$

For Agrawal and Siva Subramanian (1987) approximation, the intercept is

$$I=-\ln(\frac{AR}{\beta E}\left(\frac{1-2RT/E}{1-5(RT/E)^2}\right)).$$

From the intercept A can be calculated. It was found that the Agrawal and Sivasubramanian (1987) method gave the best fit values of E and A for the full range of activation energies whereas the Coats and Redfern (1964) method gave good estimates only at lower E values.

The kinetics and the reaction order of simple decomposition reactions by using DTA curves were carried out by Kissinger (1957). He found that the dominant factor controlling the shape and position of the differential thermal analysis peak is the nature of the reaction itself. The determination of activation energies of chemical reaction by differential thermal analysis was studied by Piloyan, Ryabchikov and Novikova (1966) for both isothermal and non isothermal reactions. They derived the following equation for isothermal reaction for 0.05< X <0.8 and for heating rates between 10 and 40 ^{0}C/min.

$$\ln \Delta t = C - \frac{E}{RT}$$

Where the values of Δt are taken directly from DTA curve in units of length (cm or mm) and x is the fraction reacted. We can get here the activation energies from the slope value and frequency factor from intercept point.

The above equation is used for isothermal reaction, and for non-isothermal reaction we can determine the activation energy for a sample decomposition reaction regardless of reaction order by making differential thermal analysis patterns at a number of heating rates by using the following equation as given by Kissinger (1957):

$$\frac{d(\ln\frac{\beta}{T_m{}^2})}{d(\frac{1}{T})}=-\frac{E}{R}$$

Where T_m is the peak temperature in K, and is the heating rate. Thus, a plot of ln $\ln(\frac{\beta}{T^2{}_m})$ against $1/T_m$ will give activation energy.

Another method of analyzing thermal degradation data, developed independently by Fuoss and by Reich (2003), focuses on the inflection point, which is the point where the reaction rate is maximum. While this technique requires only a single thermogram, it has the disadvantage that the order of the reaction must be known *a priori*. For the purposes of the present study, n is known to be 1 and this method can be applied. The activation Energy can be found quite simply from the expression

$$E_a=\frac{-\left[nRT^2\left(\frac{dW}{dT}\right)_{\max}\right]}{W_{\max}}$$

Where W_{max} and T_{max} are the weight and temperature at the inflection point, respectively,

and $\left(\frac{dW}{dT}\right)_{MAX}$ is the slope at that point. The pre-exponential factor is then found from

$$A=\left(\frac{\beta}{W_{\max}}\right)\left(\frac{dW}{dT}\right)_{\max} e^{E_a}/RT_{\max}$$

Where β is the heating rate.

Lappas et.al (2002) study for biomass flash pyrolysis in a circulating fluid bed (CFB) reactor with continuous solids regeneration. The unit is capable of performing conventional and catalytic biomass pyrolysis with the proper solid selection. Both conventional and catalytic. Flash pyrolysis conditions were achieved and liquid product yields of, 70 wt% (on biomass feed) were obtained. Solid materials included silica sand, a commercial fluid catalytic cracking catalyst and a ZSM-5 additive is used.Reactor temperature is maintained at 400-600 ^{0}C. Reactor pressure is 1.6-3.3 atm. Biomass feed rate is 2-30 g/min. Lignocell HBS 150-500 is used as a biomass feedstock

Bridgewater (1998) Study the design considerations faced by the developers of fast pyrolysis, upgrading and utilization processes in order to successfully implement the technologies. Aspects of design of a fast pyrolysis system include feed drying; particle size; pretreatment; reactor configuration; heat supply; heat transfer; heating rates; reaction temperature; vapors residence time; secondary cracking; char separation; ash separation; liquids collection. Each of these aspects is reviewed and discussed.

Demirbas (2001) study the three different biomass samples were subject to the direct and catalytic pyrolysis in order to obtained hydrogen rich gaseous products at desired temperature The samples both untreated and impregnated with catalyst, were pyrolysed at 770, 925, 975, and 1025K temp.The largest hydrogen rich gas yield were obtained from olive husk, cotton cocoon shell and tea waste using about 13% $ZnCl_2$ as a catalyst at about 1025 K were 70.3, 59.9, and 60.3 % respectively. Reactor used is stainless steel cylindrical reactor.

Babu and Chaurasia (2004) parametric study of thermal and thermodynamic properties on pyrolysis of biomass in thermally thick regime

In this study, a simultaneous chemical kinetics and heat transfer model is used to predict the effects of the most important thermal and thermodynamic properties (thermal conductivity, heat transfer coefficient, emissivity and heat of reaction number) of the feedstock on the convective-radiant pyrolysis of biomass fuels. The Runge-Kutta fourth-order method is used for the chemical kinetics model equations.

Simulations are performed considering cylindrical pellets of equivalent radius ranging from 0.003 to 0.011 m and temperatures ranging from 303 to 900K. Sensitivity analysis is conducted to find the most dominant properties affecting the pyrolysis and found that the highest sensitivity is associated with the emissivity and thermal conductivity of the biomass.

Gillu and Demirbas (2000) study the pyrolysis of biomass to produce methanol. The experiment is carried out in tubular reactor. The liquid product obtained from the pyrolysis of the biomass samples were fractionated by means of gas chromatograph into their tar, methanol, acetone etc. Methanol is obtained from hazelnut shell is 7.8 (%by weight of dry and ash basis) at 295 to 850 K The pyrolysis treatment is conducted by from ambient temp 295K to 475,575,675,775,875, 1075. Heating rate is 2.4 K/s, Solid Residence Time 300-400 sec, Particle size is 0.6 and 1.2mm In the catalytic run 3 % of pulverized K_2CO_3 of the sample used

Gercel (2002) studied the effect of a sweeping gas flow rate on the fast pyrolysis of biomass. Sunflower (Helianthus annus L.) pressed bagasse pyrolysis experiments were performed in a fixed-bed tubular reactor. The effects of nitrogen flow rate and final pyrolysis temperature on the pyrolysis product yields and chemical compositions have been investigated. The maximum bio-oil yield of 46.62 wt% was obtained in a nitrogen atmosphere with a nitrogen flow rate of 25 cm^3 min^{-1} and at a pyrolysis temperature of 550°C with a heating rate of 300°C min^{-1}. The chemical characterization showed that the oil obtained from sunflower-pressed bagasse may be potentially valuable as fuel and chemical feedstocks.

Shiguang et.al (2003) Fast pyrolysis of two typical biomasses (legume straw and apricot stone) in a free-fall reactor was studied. The total ratio of CO and H_2 in the gas product reaches 65.4 mol% for legume straw and 55.7 mol% for apricot stone, respectively. Effects of sample particle size and pyrolysis temperature on the fast pyrolysis of the biomass were also studied. The results of this study show that the fast pyrolysis of biomass produces more volatile than the slow pyrolysis at the same temperature. The results also show that smaller particle size of biomass and higher fast pyrolysis temperature (700-800 ^{O}C) are in favor of hydrogen-rich gas

CHAPTER- III

EXPERIMENTAL WORK

3.1 SAMPLE PREPARATION

For the physico-chemical and thermal characterization of groundnut shell, eucalyptus and poplar, a sample of approximately 1 kg was oven dried and ground in a laboratory ball mill. The ground material was further classified by using two IS sieves. The samples so obtained were of the size range of 180+600 μ m. This sieved sample was stored in airtight plastic containers for further use.

3.2 PHYSICO-CHEMICAL ANALYSIS OF THE SAMPLE

3.2.1Proximate Analysis

The proximate analysis of sieved biomass sample was carried out as per procedure laid in IS: 1350 (PART1)-1984 and the desired weight of sample was put in a silica crucible and dried in an oven at a temperature of 105 ^{0}C for one hour .After on hour, the sample was kept in a desicator, cooled and there after weighed. The weight difference was taken as the moisture content of the sample. The same sample was kept in a muffle furnace at a temperature of 925 ^{0}C for 7 min for the determination of the volatile matter of the sample by weight difference. Ash content was found by weight difference obtained putting the sample in the muffle furnace for 1 hour at 800 ^{0}C. All the weights were measured by an electronic balance after desiccating the sample until cooling to room temperature.

3.2.2 Bulk Density

The bulk density of the sample was determined by using the bulk density apparatus (Micro Scientific Works) by filling 50 ml cylinder to about 50 ml mark by the dried sample and keeping the cylinder on the bracket and inserting the knurled ring from the top of the cylinder and tighting it gently by turning it till the cylinder was held on the bracket. Then the timer was set to around 3 min to get 100 stokes required as per the standard requirement. After 100 stokes the reading on the cylinder was noted. The bulk density was calculated by dividing the weight of the powder by the volume.

3.2.3 Ultimate Analysis

Take 1-2 mg Tungsten oxide and placed in aluminum foil and weight in a balance and after that that aluminum foil tear off and add 1-3 mg sample and weight in a balance and closed the aluminum foil and placed in a CHN analyzer for the 15 minutes for the determination of carbon, hydrogen, nitrogen and oxygen.

3.3 THERMAL ANALYSIS

Perkin Elmer (Pyris Diamond) thermogravimetric analyzer was used in the present study to continuously monitor weight changes in groundnut shell, eucalyptus and poplar samples due to drying, devolatilization, gasification and combustion as the sample followed a liner-heating program. This instrument was available in the IIC, I.I.T Roorkee and was chosen on the basis of its sensitivity (0.1 μ g max), range of heating rates (10 to 40 Kmin^{-1}), connivance of operation, and ability to use any type i.e. inert (nitrogen), oxidizing (oxygen or air), in static and or in following mode. Fig. 3.1 shows schematic diagram of the thermal analysis system. The furnace area was separated from the weighing chamber to minimize any effect on the weighing mechanism. The micro balance operated on a mull-balance principle. The micro balance was near a precession of 0.1 μ g. The furnace temperature was controlled in such a way that the sample temperature followed a desired temperature-time profile. The precision of the temperature measurement is ± 2 ^{0}C. The equipment was capable of handling samples up to 20 mg. The flow path of the purge gas is shown in Fig 3.1. The purge gas maintained a positive pressure through the weighing chamber in order to protect the balance mechanism from the volatiles evolved. The sample was placed in a platinum crucible and the sample was heated by both radiation and convection by means of the purge gas entering the furnace chamber. Chromel alumel thermocouples were positioned just below the crucible. The low material mass of this furnace configuration allowed rapid temperature equilibrium. The continuous record of weight loss and temperature was obtained.

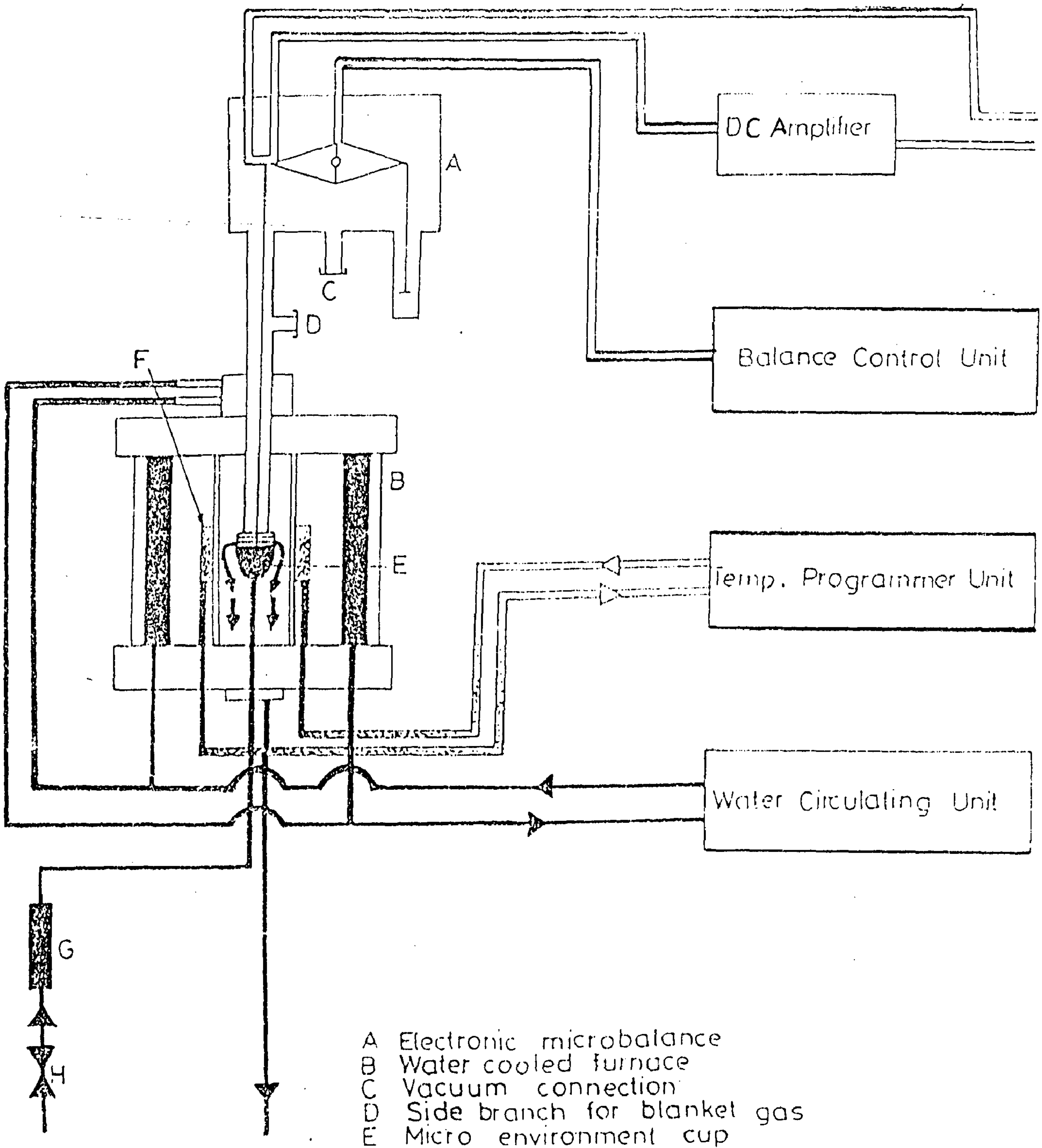
The instrument also provided with the continuous recording of the DTG and DTA curves, in terms of % weight loss per minute and in mv (for DTA). The mv recording could be converted to obtained temperature difference between the alumina sample and the biomass sample at any temperature under temperature programmed heating rate (10 to 40 $Kmin^{-1}$).

3.1 THERMOGRAVIMETRIC OPERATING CONDITION

The principle experimental variables, which could affect the degradation results in a TGA, are the pressure, the purge gas flow rate, the heating rate, the weight of the sample and the sample size fraction. In the present study, the operating pressure was kept slightly positive, the purge gas (nitrogen) flow rates was maintained (for most experimental runs) at 400 ml/min and the heating rate was varied from 10 to 40 ^{0}C/min.

TheTG, DTG and DTA curves were obtained for 10, 20, 30 and 40 ^{0}C/min heating rates for each purge gas. Some experiments were also carried out at 40 ^{0}C/min heating rates with varying purge gas flow rates is 400 ml/min.

The sample size fraction chosen in the experiments ensured that the influence of heterogeneity of the sample was minimized .The uniformity of the sample was maintained by using the sample from the stored lot of size fraction -180+600 μm and same type . The samples were uniformly spread over the crucible base. Around 10 mg samples were used in all the experiments.



A Electronic microbalance
B Water cooled furnace
C Vacuum connection
D Side branch for blanket gas
E Micro environment cup
F Furnace winding
G Flow meter
H Control valve

ig. 3.1 Schematic Diagram of Thermal Analysis System

CHAPTER- IV

RESULT AND DISCUSSION

4.1 RESULTS

4.1.1 Physico-Chemical and Thermal Degradation Characteristics

The proximate analyses and ultimate analyses of Groundnut shell, Poplar and Eucalyptus materials are given in Table 4.1 and 4.2 respectively. From table 4.1 it may be seen that groundnut shell have got maximum volatile matter i.e.72.13%.The volatiles content in poplar and eucalyptus is around 68%.The ash content in all the three biomass residues studied is about 6.0 %. Thus they fall in medium ash containing biomass as classified by Grover (1996).Fixed carbon is minimum i.e. 22 % in groundnut shell and eucalyptus (roots) have the highest content of fixed carbon. Gangawati et.al reported volatile matter, fixed carbon and ash content of press mud as 54.0-58.0 %; 25.7-20.2 and 12.9-18.21 % respectively. It may be seen that the ash content of the biomass residues studied is quite low in comparison to press mud. The ultimate analysis is presented in table 4.2 for the three biomass residues shows that carbon content varies from 47.32 to 49.32 %, groundnut shell has the highest value. The oxygen content is lowest at 41.86 % in poplar, whereas groundnut shell and eucalyptus (root) are having around 45 % Hydrogen content is highest in poplar (6.98) followed by eucalyptus roots (6.49%) and groundnut shell (5.18 %).

The thermal characteristics as depicted by the TG, DTG, and DTA curves for the 10, 20, 30, and 40 K min^{-1} heating rates are shown in Fig.4.1-4.4 for the eucalyptus, poplar and groundnut shell. During thermal degradation under nitrogen atmosphere given material looses moisture followed by release of volatiles. With increase in heating rate there was slight decrease in drying zone which may be attributed to loss of surface tension bound water of the ground samples, but it was not very significant. It is clear from Fig4.1-4.4 that the pyrolysis of given material takes place in three steps. The first step shows the degradation of hemicelluloses, the second step shows the degradation of cellulose content of the given material and the third step, which is the slowest step, shows the degradation of char. The lignin decomposition occurs throughout the degradation zone.

TGA and DTG curves at different heating rates in nitrogen atmosphere revealed that three stages existed in the pyrolysis process.

The first stage was from the starting temperature to the temperature of initial devolatilization (T_i). The second stage was from T_i to the end of main devolatilization (T_e). The third stage was from T_e to the final temperature 1000 ^{0}C. The temperature of maximum reaction rate was referred as T_m. Slight weight loss appeared in stage I. It could be due to the elimination of water (Dehydration). Stage II was characterized by a major weight loss, which correspond to the main pyrolysis process (devolatilization). Most of the volatiles were released in this stage. It proceeded with high rate and let to the formation of the pyrolysis products. During stage three, a slow continued loss of weight revealed that the carbonaceous matters in the solid residue continuously decomposed at a very slow rate and the solid residue reached on asymptotic value.

The instantaneous maximum and average reaction rate in stage II for biomass were increased as the heating rate increased. The decomposition of poplar roots started earlier than the eucalyptus roots and also ended earlier than that of a eucalyptus roots.

The initial temperature for decomposition of poplar roots at different heating rates are 225- 250 ^{0}C and for the eucalyptus roots the initial temperature for the decomposition is 230-245 ^{0}C. While the final temperature is 505 ^{0}C to 570 ^{0}C and 550 to 610 ^{0}C respectively. This implies that the main pyrolysis reaction including depolymeisation, decorboxylation and cracking took place over the temperature range 225 to 505 ^{0}C.

Table 4.1 Proximate Analysis of Groundnut shell, Poplar and Eucalyptus (Dry basis)

Biomass	Volatile matter (%)	Ash (%)	Fixed carbon(%)
Groundnut shell	72.13	5.85	21.633
Poplar	68.73	6.61	24.362
Eucalyptus roots	68.11	6.06	25.505

Table 4.2 **Ultimate analysis of Groundnut shell, Poplar and Eucalyptus roots**

Biomass	Carbon	Nitrogen	Hydrogen	Oxygen
Groundnut shell	49.32	0.88	5.18	44.62
Poplar	47.32	0.78	6.98	41.86
Eucalyptus roots	47.92	0.67	6.49	44.92

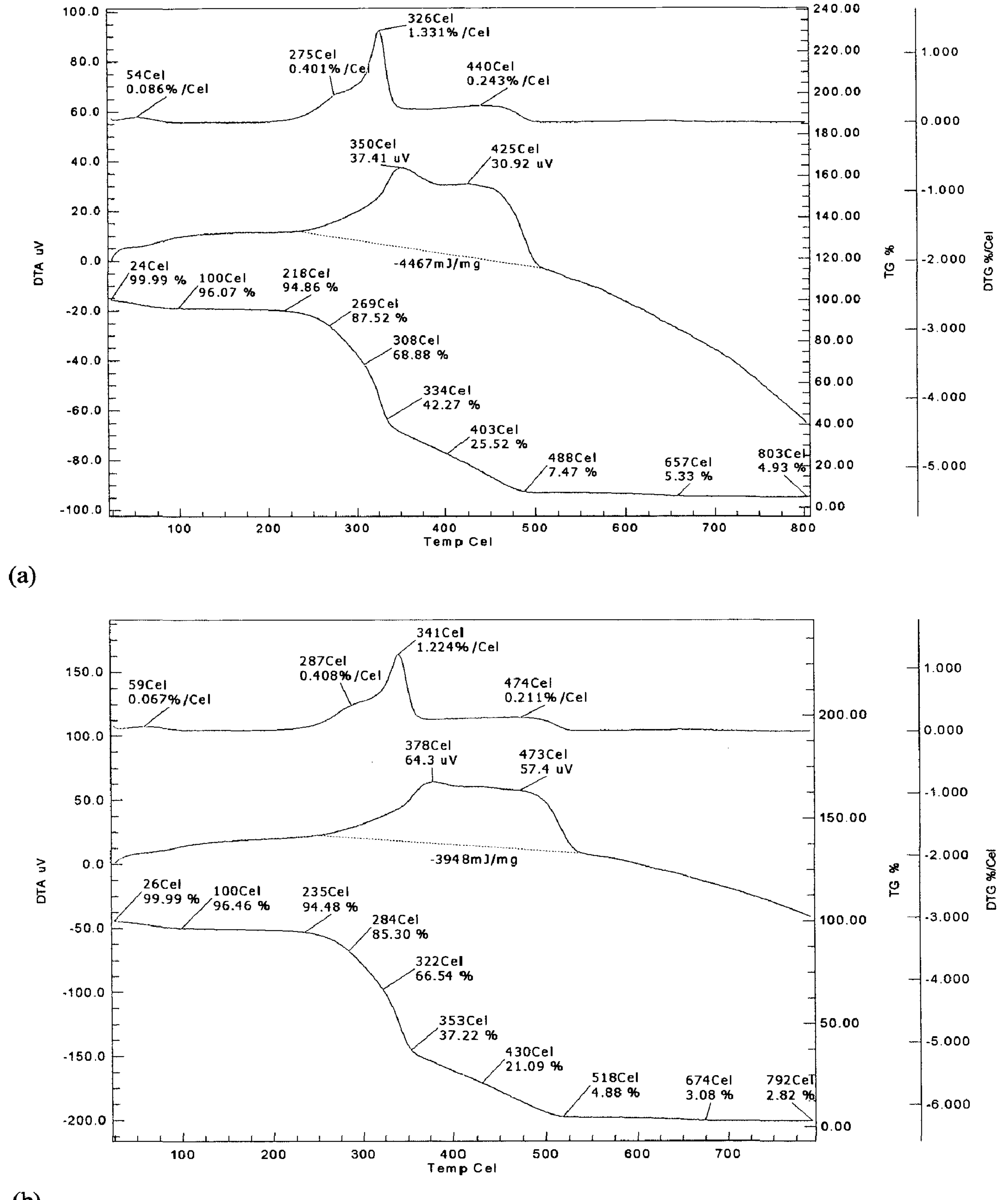
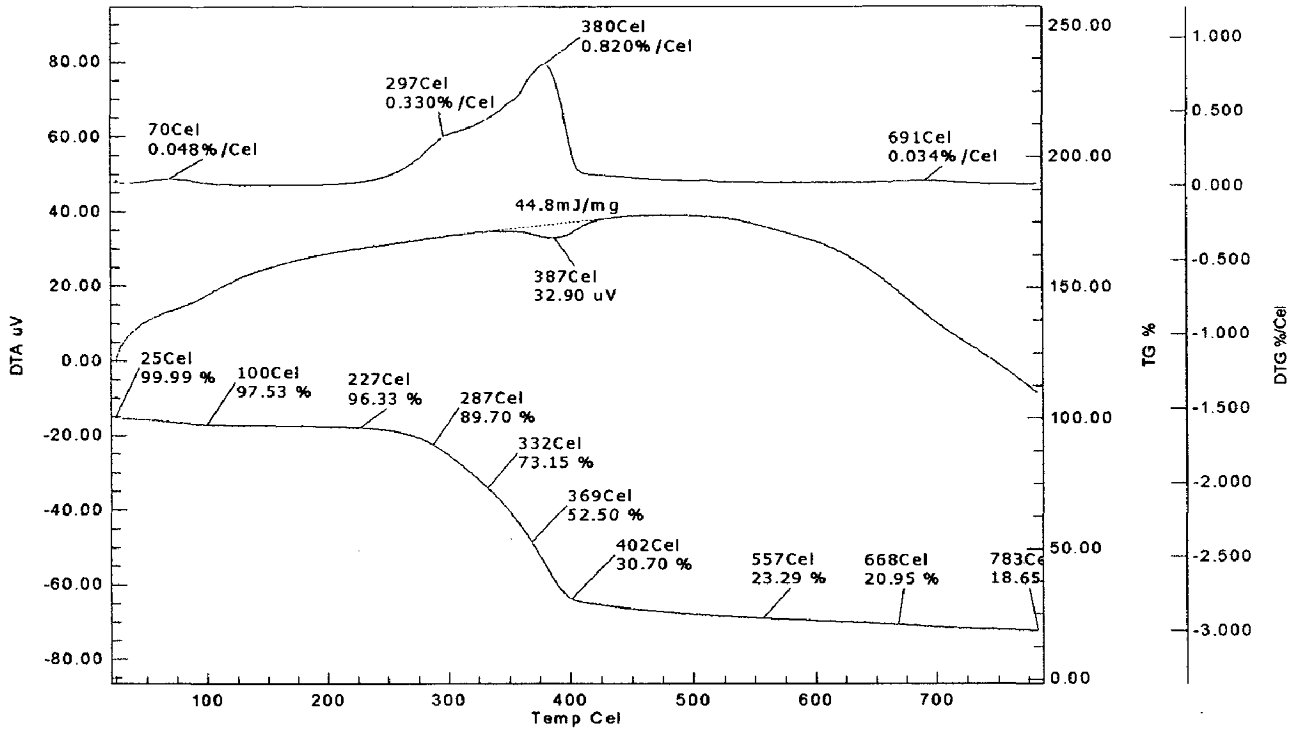
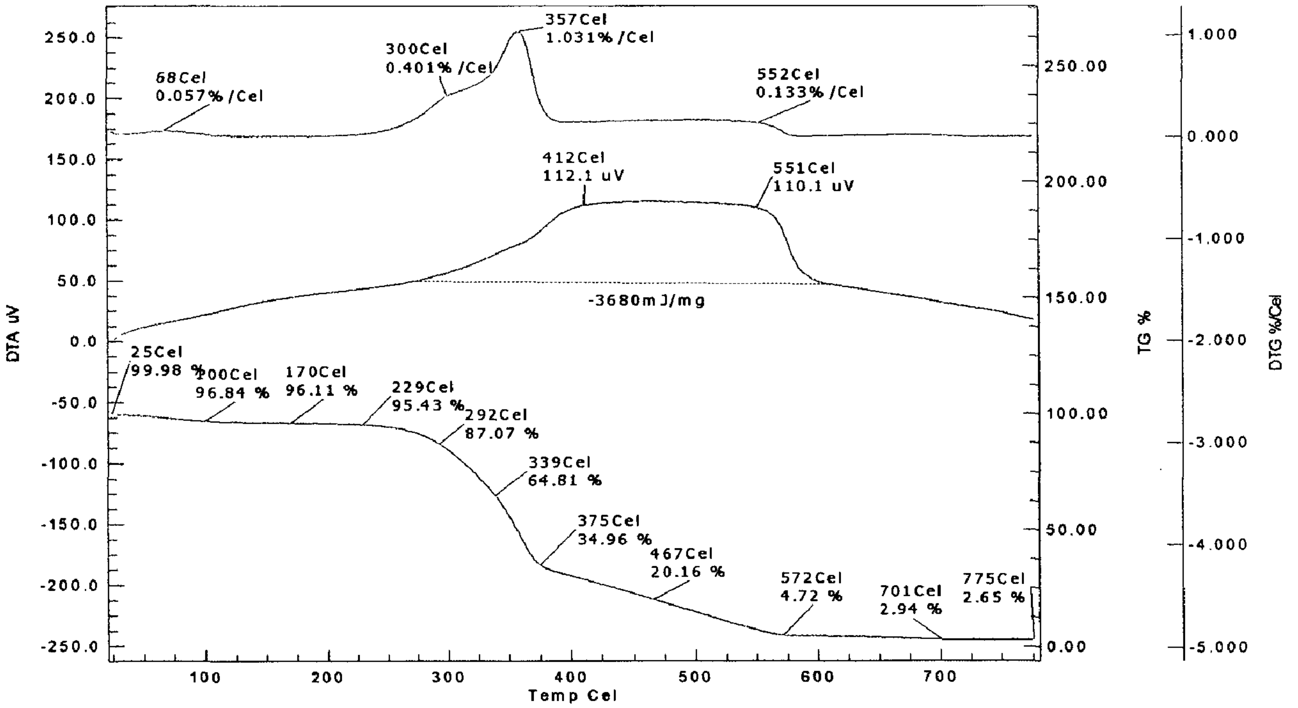


Fig. 4.1: Thermal Degradation of Eucalyptus Roots at different heating rate under nitrogen atmosphere (a) 10 Kmin^{-1} (b) 20 Kmin^{-1}



(c)



(d)

Fig. 4.1: Thermal Degradation of Eucalyptus Roots at different heating rate under nitrogen atmosphere (c) 30 Kmin^{-1} (d) 40 Kmin^{-1}

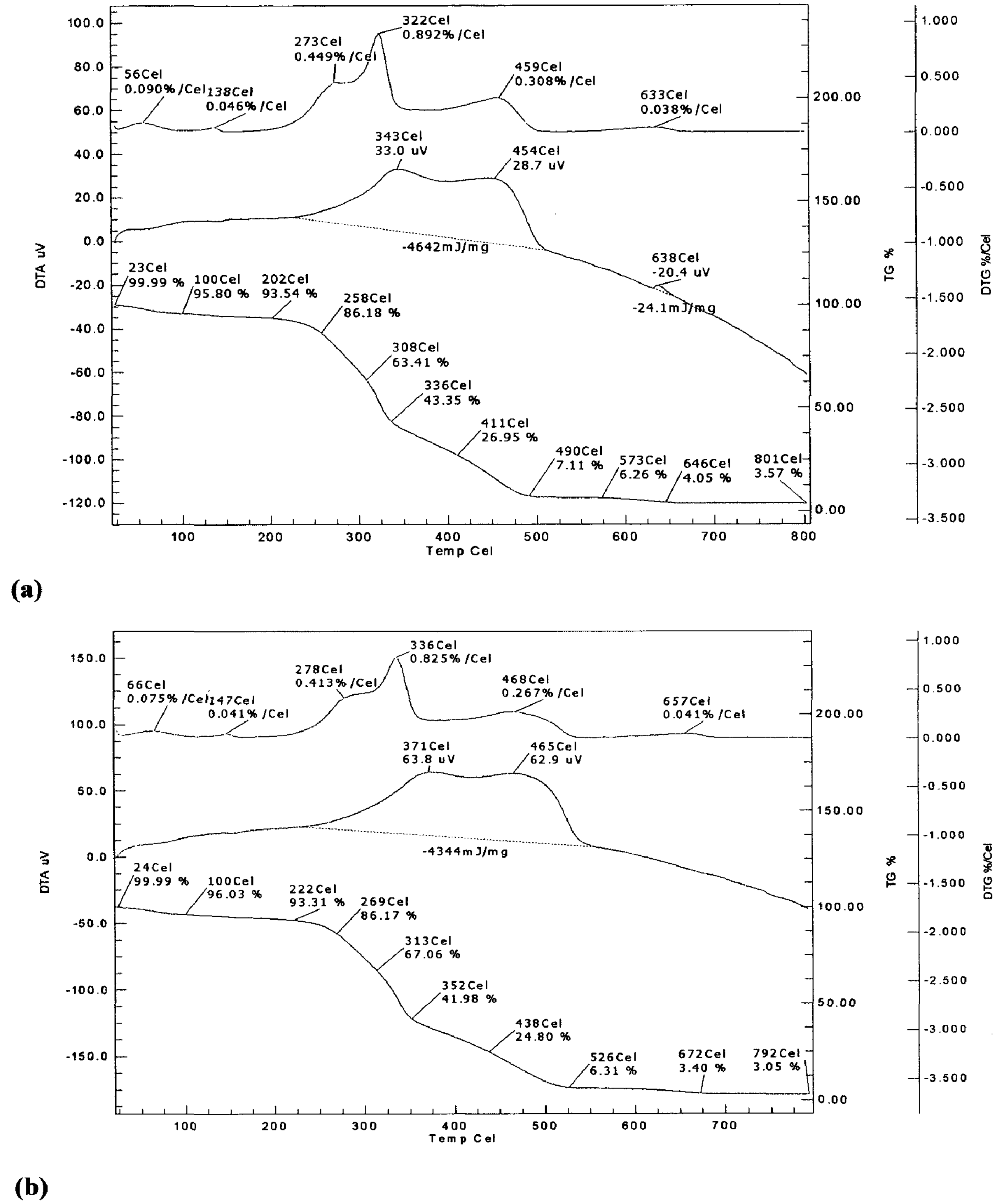


Fig.4.2: Thermal Degradation of Eucalyptus Stem at different heating rate under nitrogen atmosphere (c) 10 Kmin^{-1} (d) 20 Kmin^{-1}

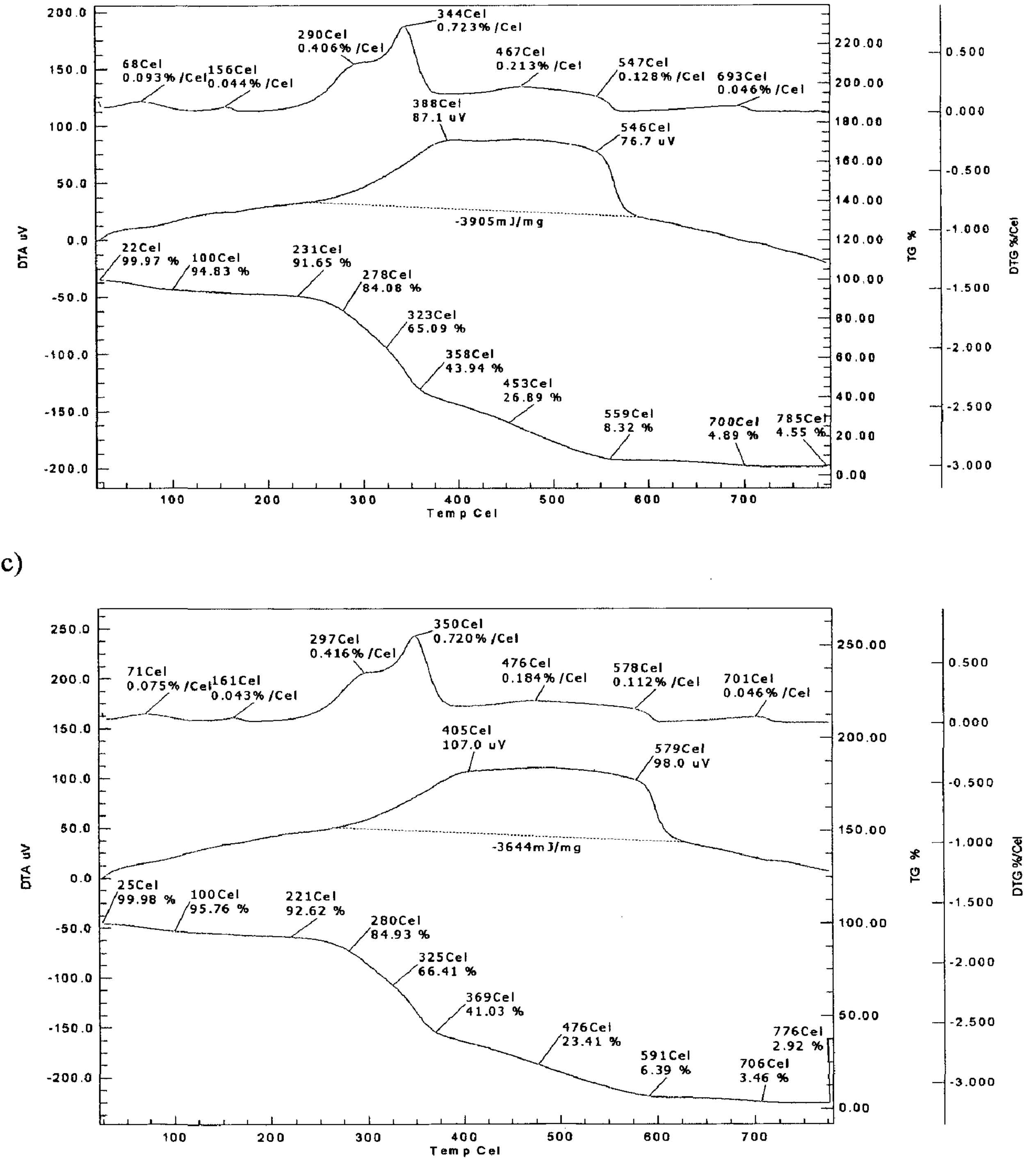


Fig.4.2: Thermal Degradation of Eucalyptus Stem at different heating rate under nitrogen atmosphere (c) 30 Kmin^{-1} (d) 40 Kmin^{-1}.

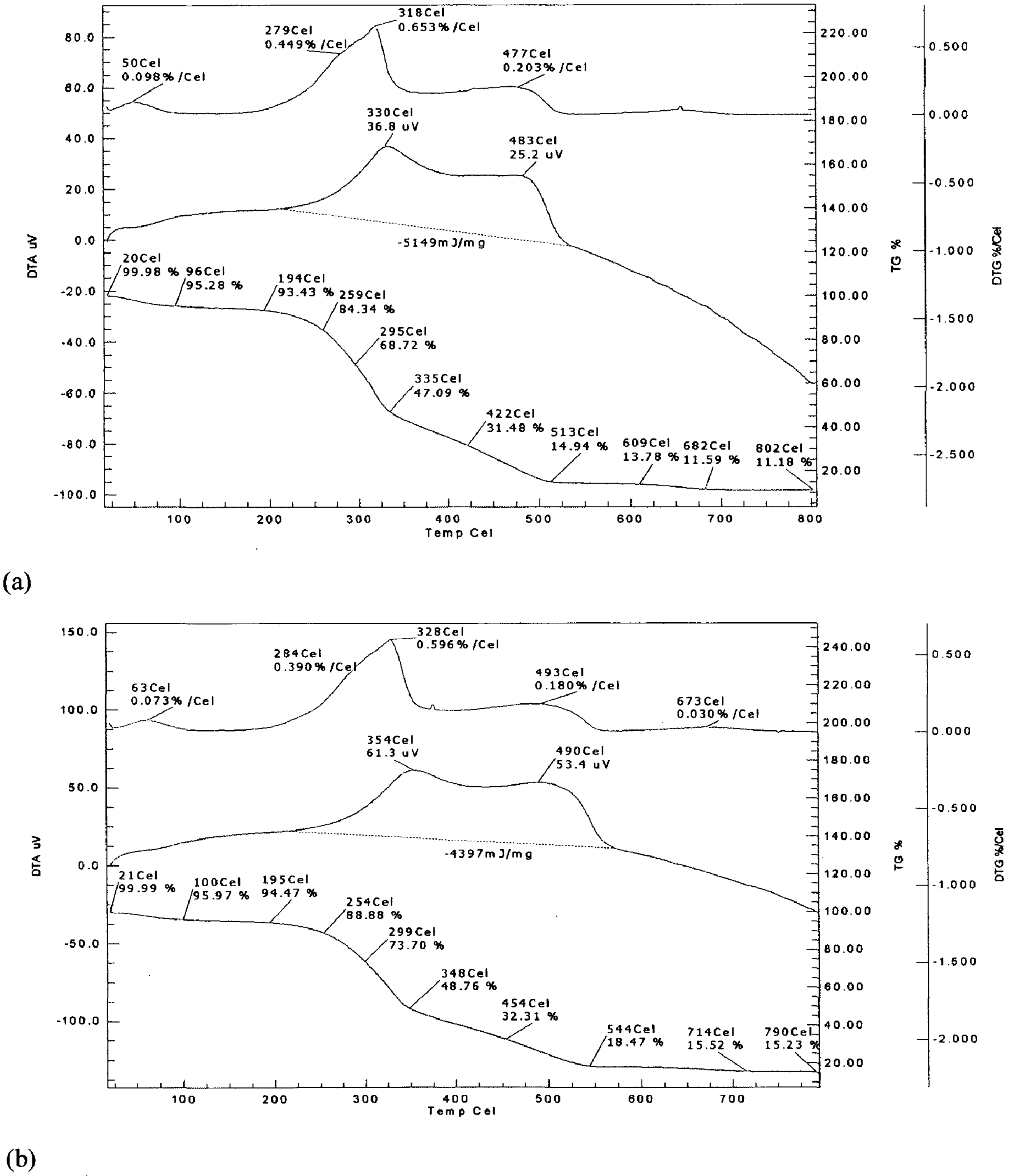
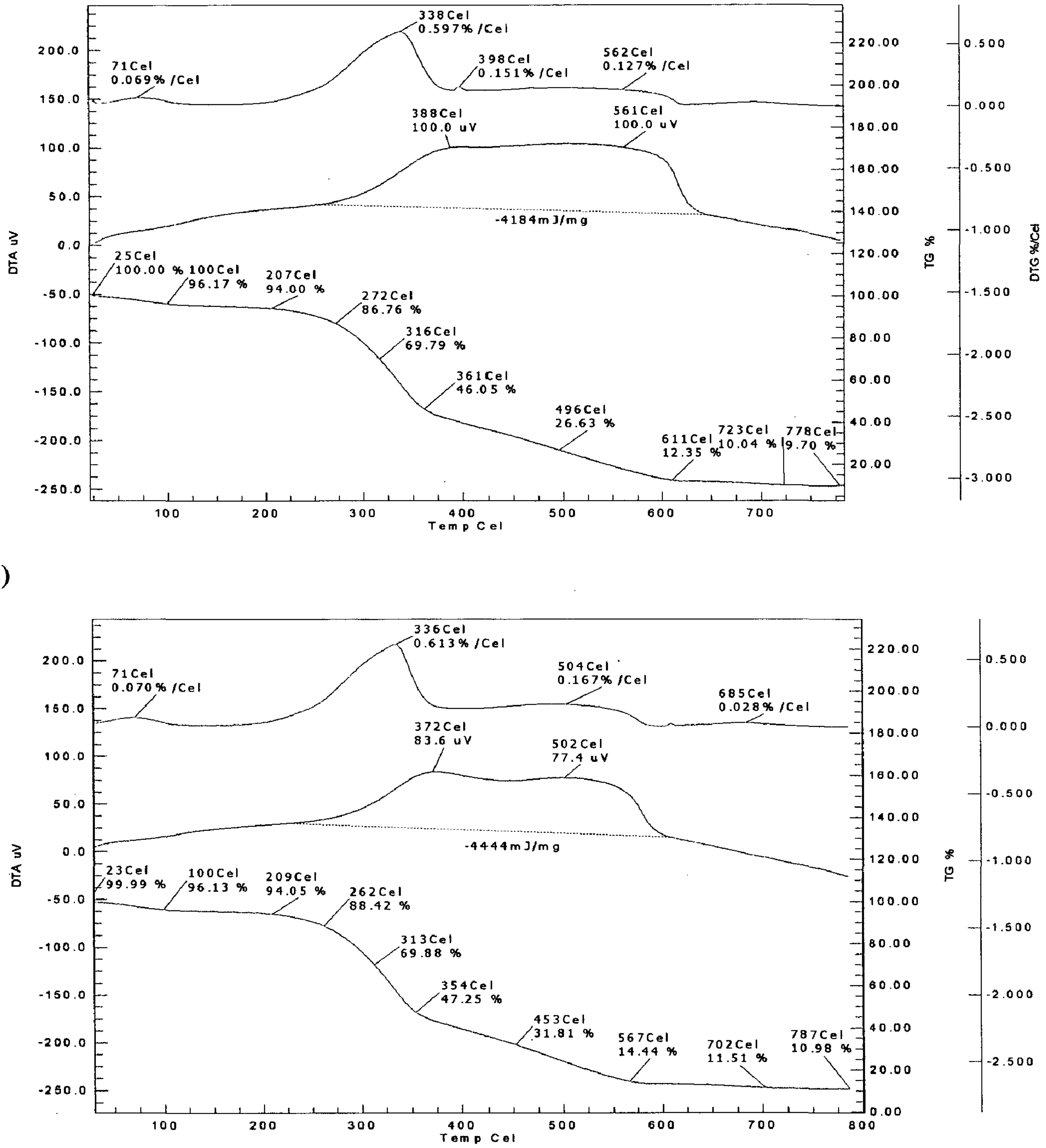


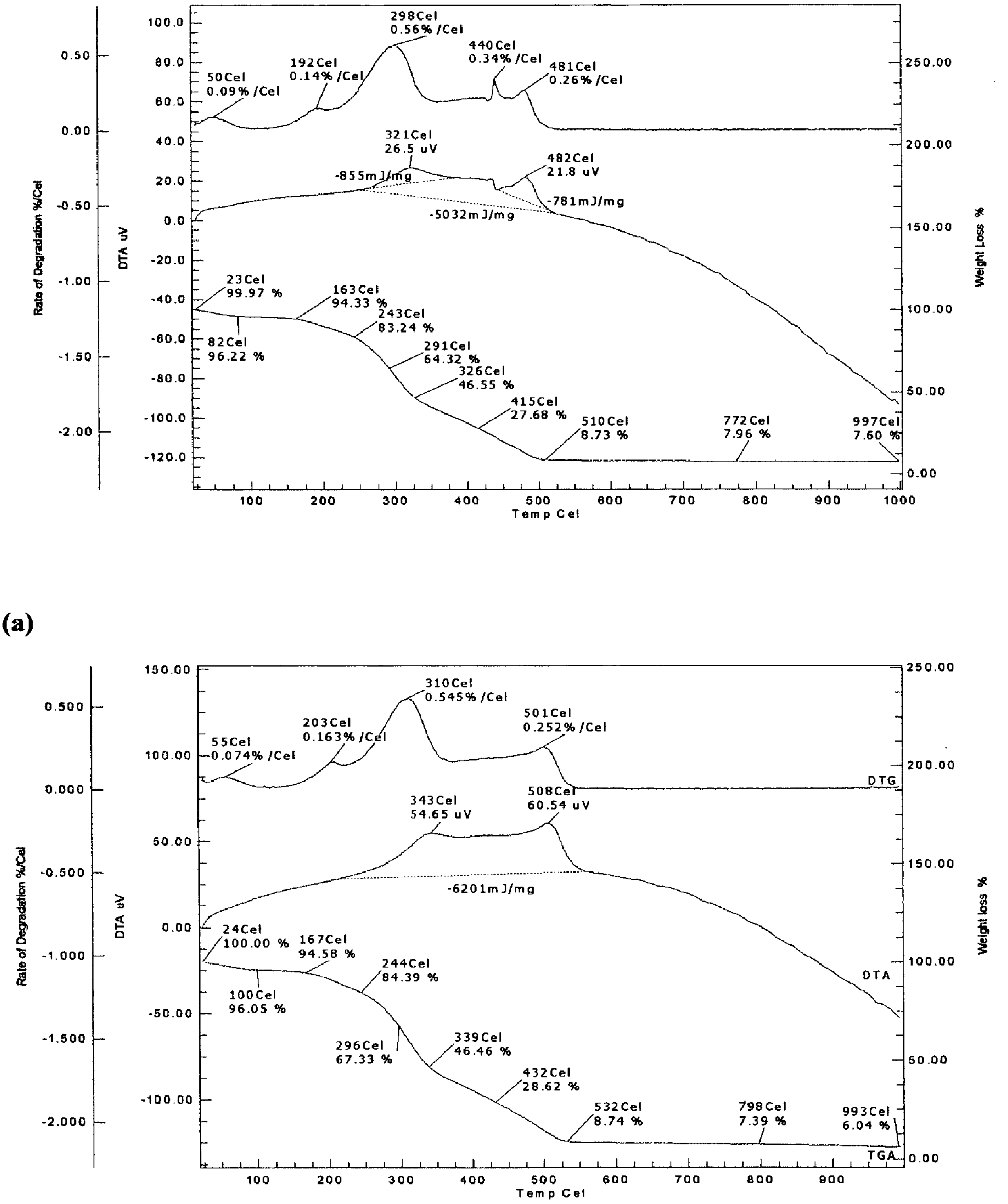
Fig.4.3: Thermal Degradation of Poplar Roots at different heating rate under nitrogen atmosphere (a) 10 Kmin^{-1} (b) 20 Kmin^{-1}



(c)

(d)

Fig.4.3: Thermal Degradation of Poplar Roots at different heating rate under nitrogen atmosphere (a) 30 Kmin^{-1} (b) 40 Kmin^{-1}



(b)

Fig. 4.1: Thermal Degradation of Groundnut shell at different heating rate under Nitrogen atmosphere (a) 10 $Kmin^{-1}$ (b) 20 $Kmin^{-1}$

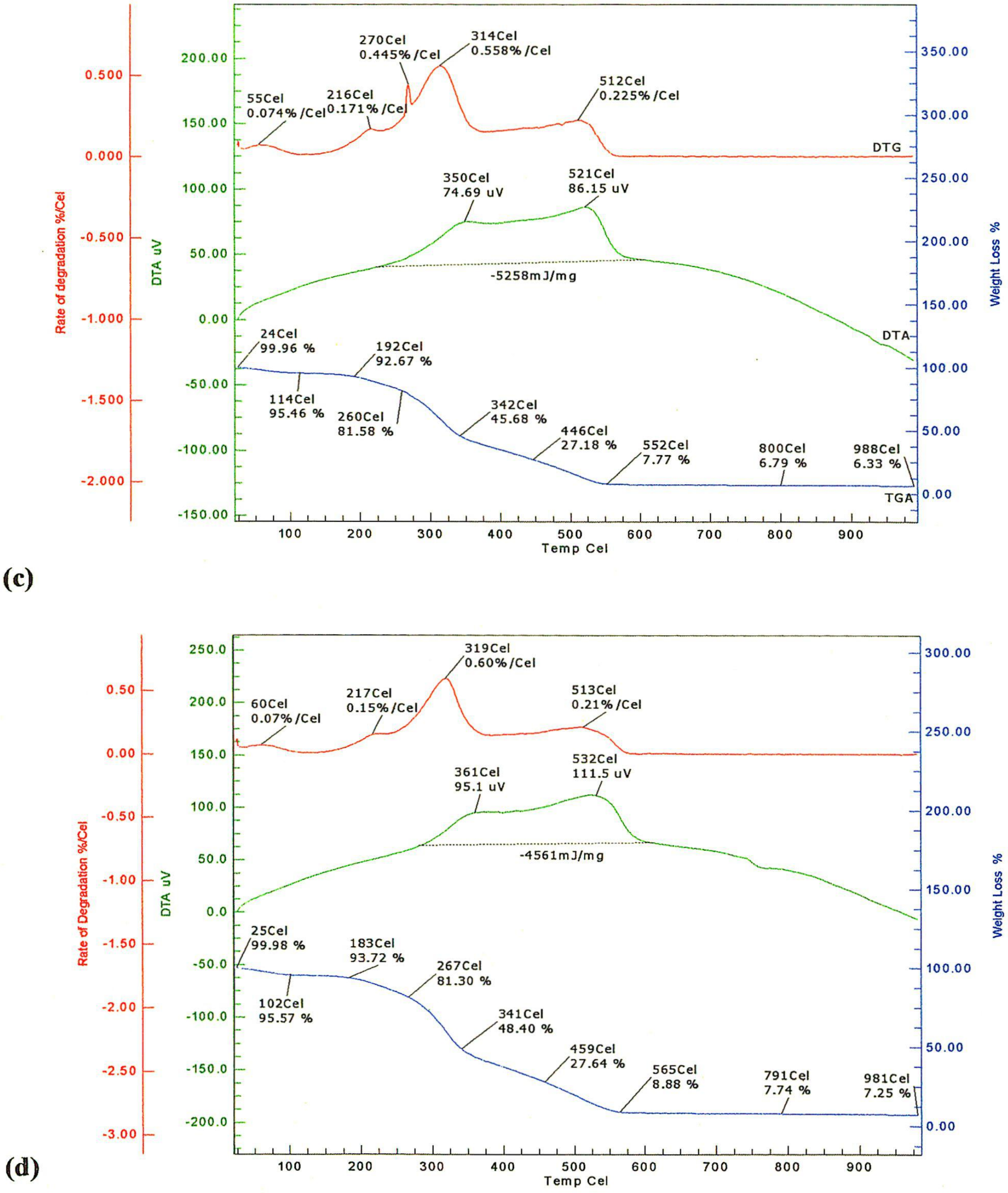


Fig. 4.1: Thermal Degradation of Groundnut shell at different heating rate under nitrogen atmosphere (c) 30 Kmin^{-1} (d) 40 Kmin^{-1}

Table 4.3 TEMPERATURE CHARTERSTICS OF BIOMASS

Biomass	Heating Rate K min^{-1}	Temperature ^{0}C		
		T_i	T_m	T_e
Groundnut shell	10	163	299	510
	20	167	310	534
	30	198	314	552
	40	205	318	565
Poplar roots	10	212	318	478
	20	225	340	505
	30	243	346	530
	40	250	346	570
Eucalyptus roots	10	202	322	490
	20	230	336	550
	30	240	344	570
	40	245	350	610
Eucalyptus stem	10	202	322	513
	20	222	336	528
	30	231	344	560
	40	221	350	610

4.1.2 Products of Pyrolysis.

The yield of initial moisture, volatile matter and final residue obtained from TGA of different biomass are presented in Table 4.4. The yield of initial moisture is calculated as the weight loss in stage I and total volatile yield is calculated as the weight loss in both the stage II and stage III. The initial moisture yield of poplar roots at different heating rates 4.81%, 6.59% 6.67%, and for the eucalyptus roots 6.69% 7.10% and 7.38%. The difference may have been caused by the different heating times and temperature. The total volatile yield is 90.06%, for poplar roots and 86.76%for eucalyptus roots at 40 K min^{-1}. As the heating rates increased the volatile yield decreases. The final residue consists of ash and char. The total residue at 800 ^{0}C for the different heating rates as shown in table 4.4. The amount of total residue for the eucalyptus roots are 3.05, 4.55 and 2.92% for 20, 30 and 40 K min^{-1} respectively.

Table 4.4 **The distribution of volatiles released during pyrolysis**

Heating rate K min^{-1}	Biomass	Initial moisture (%)	Total volatile yield (%)	Volatile evolution between T_e and 800 ^{0}C	Final Residue at 800 ^{0}C
10	Groundnut shell	5.64	86.37	2.13	7.60
20		5.32	84.87	2.7	6.04
30		6.38	83.98	1.44	6.33
40		7.29	83.36	1.63	7.225
10	Poplar roots	4.9	88.92	4.38	4.10
20		4.81	90.13	5.19	5.06
30		6.59	90.7	4.54	2.71
40		6.67	90.06	3.34	0.07
10	Eucalyptus root	5.13	87.39	2.54	4.93
20		6.69	90.26	3.26	3.05
30		7.1	87.1	3.77	4.55
40		7.38	86.76	3.47	2.92
10	Eucalyptus Stem	6.45	86.43	3.54	3.57
20		6.68	87.00	3.26	3.05
30		8.32	85.78	3.77	4.55
40		7.36	86.84	2.939	2.92

The distribution of volatiles released during pyrolysis is shown in Table4.5. The weight loss of the initial samples due to release of the volatiles in the temperature range (a) < 200 °C, (b) 200-285 °C, (c) 285 –320 °C, (d) 320-500 °C, and (e) > 500 °C, is reported in Table4.6 (a-c)

Table 4.5 (a) Distribution of volatiles released during thermal degradation of Groundnut shell in nitrogen atmosphere

Heating rate (K min^{-1})	Weight loss (%)					Total volatile matter including moisture (%)	PTFV as percentages of total volatiles released at 320-500 ^{0}C
	< 200 ^{0}C	200 - 285^{0}C	285 - 320^{0}C	320 - 500^{0}C	> 500 ^{0}C		
10	8.65	29.86	17.90	35.83	1.13	91.24	47.54
20	8.32	22.45	17.18	34.46	5.96	92.74	53.13
30	7.29	19.97	16.90	26.20	6.87	92.23	62.02
40	6.26	15.20	14.90	26.10	11.75	94.81	62.73

Table 4.5 (b) Distribution of volatiles released during thermal Degradation of Poplar in nitrogen atmosphere.

Heating rate (K min^{-1})	Weight loss (%)					Total volatile matter including moisture (%)	PTFV as percentages of total volatiles released at 320-500 °C
	< 200 °C	200 - 285°C	285 - 320°C	320 - 500°C	> 500 °C		
10	3.11	10.38	42.19	34.9	3.14	91.52	47.54
20	3.68	16.45	29.45	40.74	4.68	89.75	53.13
30	5.88	7.84	23.23	51.77	6.41	92.73	62.02
40	7.87	8.9	21.32	52.84	8.74	96.71	62.73

Table 4.5 (c) Distribution of volatiles released during thermal degradation of Eucalyptus in nitrogen atmosphere

Heating rate (K min^{-1})	Weight loss (%)					Total volatile matter including moisture (%)	PTFV as percentages of total volatiles released at 320-500°C
	< 200 °C	200 - 285°C	285 - 320°C	320 - 500°C	> 500 °C		
10	4.68	12.08	31.252	44.77	2.28	92.42	47.54
20	4.88	9.82	19.32	58.11	2.39	95.11	53.13
30	5.92	7.08	17.84	59.91	3.21	83.23	62.02
40	3.98	6.99	16.84	59.91	4.21	95.26	62.73

For the temperature range less than 500 °C, the region manifests the intense loss of weight at rapid rates with release of volatiles of different nature both tar forming and non-tar forming. For the temperatures greater than 500 °C, the weight loss trend is irregular. The total volatile matter including moisture released during thermal degradation was approximately 95% of the original biomass sample taken. Due to lignin degradation above 320 ^{0}C mainly combustible gases and high molecular weight components are given as volatiles, which upon condensation are responsible for the formation of tar. Therefore, these volatiles released between 320-500°C are called Potential Tar Forming Volatiles (PTFV).

At low heating rates, the residence time is more the evolution of uncracked gases is reduced. However, at higher heating rates the evolution of uncracked volatiles is more. This seen from the data for maximum rate of volatilization presented in Table-4.6 (a-d), for DTG peak temperatures at different heating rates.

Table 4.6 (a) Thermal degradation characteristics of Groundnut shell in nitrogen

Characteristics	Heating rate K min^{-1}				
	10	20	30	40	100
Drying characteristics					
Drying range (^{O}C)	14 - 189	24 - 198	24 - 202	25 - 212	20 - 218
Moisture removal (%)	5.64	5.32	6.38	7.29	7.34
Maximum rate of drying (wt % loss min^{-1})	1.3	2.1	3.0	4.0	5.0
Pyrolysis characteristics					
Temperature of initial degradation	172	192	212	238	229
T_{1max}(^{O}C)	190	203	216	219	--
T_{2max}(^{O}C)	299	310	314	318	373
T_{3max}(^{O}C)	480	501	512	560	538
Maximum rate of volatilization					
Wt %/ ^{0}C	0.563	0.543	0.558	0.595	94
mg min^{-1}	0.198	0.33	0.61	0.77	3.3276

Table 4.6 (b) Thermal degradation characteristics of poplar roots in nitrogen

Characteristics	Heating rate K min^{-1}			
	10	20	30	40
Drying characteristics				
Drying range (^{O}C)	24 - 219	21 - 214	23 - 235	26 - 220
Moisture removal (%)	4.29	4.81	6.59	6.67
Maximum rate of drying (wt % loss min^{-1})	2.1	2.32	4.02	4.79
Pyrolysis characteristics				
Temperature of initial degradation	218	225	243	250
T_{1max}(^{O}C)	318	328	339	344
T_{2max}(^{O}C)	429	445	478	522
T_{3max}(^{O}C)	639	648	660	667
Maximum rate of volatilization				
Wt %/ ^{0}C	0.947	0.891	0.878	0..869
mg min^{-1}	0.56	1.22	1.64	2.24

Table 4.6 (c) Thermal Degradation characteristics of Eucalyptus roots in nitrogen atmosphere

Characteristics	Heating rate K min^{-1}			
	10	20	30	40
Drying characteristics				
Drying range (^{O}C)	19 - 209	26 - 231	25 - 226	25 - 227
Moisture removal (%)	5.98	6.69	7.1	7.38
Maximum rate of drying (wt % loss min^{-1})	1.68	2.39	3.83	4.23
Pyrolysis characteristics				
Temperature of initial degradation	218	235	227	231
T_{1max}(^{O}C)	275	287	297	300
T_{2max}(^{O}C)	326	341	380	357
T_{3max}(^{O}C)	440	474	511	552
Maximum rate of volatilization				
Wt %/ ^{0}C	1.331	1.224	0.820	1.013
mg min^{-1}	0.432	0.562	0.949	1.978

Table 4.6(d) Thermal Degradation characteristics of Eucalyptus stems in nitrogen atmosphere

Characteristics	Heating rate K min^{-1}			
	10	20	30	40
Drying characteristics				
Drying range (^{O}C)	23 - 198	24-218	22 - 228	25- 221
Moisture removal (%)	6.54	6.68	8.32	7.36
Maximum rate of drying (wt % loss min^{-1})	1.98	2.04	3.66	3.04
Pyrolysis characteristics				
Temperature of initial degradation	202	222	231	221
T_{1max}(^{O}C)	273	278	290	297
T_{2max}(^{O}C)	322	336	344	350
T_{3max}(^{O}C)	459	468	467	476
Maximum rate of volatilization				
Wt %/ ^{0}C	0.892	0.825	0.723	0.720
mg min^{-1}	0.66	1.22	1.75	2.10

With increase in the heating rate, the DTG peak temperature also increases. This lateral shift of initial, final and peak temperature of degradation with increase in heating rate is due to the combined effect of heat transfer and the kinetics of decomposition resulting in delayed decomposition. The DTG curves characterize the componential decomposition of given biomass. The transition temperature (T_i) between endothermic drying (probably associated with the evolution of light volatiles) and the exothermic reaction (associated with the cracking of C-C bonds in inert atmosphere) are listed in Table4.3. The transition and final temperature of degradation show upward trend with an increase in the heating rate.

4.1.3 Kinetic Parameters of Thermal Degradation of given Biomass Material

The pyrolysis process may be represented by the following scheme:

Biomass $\longrightarrow$ solid residue (char) +volatiles

The pyrolysis reaction rate may be expressed by the following nth order rate equation

$$\frac{-dX}{dt} = k'(1-X)^n \qquad 1.1$$

Where X= $(W_0-W_t)/(W_0-W_\infty)$

$k'=k(W_0-W_\infty)$

under non-isothermal conditions for a constant heating rates of β ^{0}C/min and with the rate constant expressed in Arrhenius form, Eq 1.1 can be written as

$$\frac{dX}{dt} = \beta\frac{dX}{dt} = A(1-X)^n e^{-E/RT} \qquad 1.2$$

Eq 1.2 may be integrated to obtained

$$\int_0^X \frac{1}{(1-X)^n}dX = \frac{A}{\beta}\int_{T_0}^T \exp(-E/RT)dT \qquad 1.3$$

Right hand side of the above equation can not be integrated analytically. Integral approximation for non-isothermal kinetics have been derived by Coats and Redfern (1964) and bettered by Agrawal and Subramanian (1987). Their approximation of the exponential integrands is given as follows.

Coats and Redfern approximation

$$\int_0^T \exp(-E/RT)dT = \frac{RT^2}{E}(1-\frac{2RT}{E})\exp(-E/RT) \qquad 1.4$$

The approximation of Agrawal and Subramanian is

$$\int_0^T \exp(-E/RT)dT = \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-5(RT/E)^2}\right]\exp(-E/RT) \qquad 1.5$$

By applying Coats and Redfern approximation for the pyrolysis of given biomass material at any heating rate, β (^{0}C/min), i.e. from eq 1.4 and eq. 1.5 we can get

$$y = -(E/R)(1/T) + \ln[\{(AR/\beta E)\}\{1-(2RT)/E\}] \qquad 1.6$$

Where, y=ln (-ln (1-X)/T^2) for n=1

and y=ln [{1-(1-X)$^{1-n}$}/{(1-n)T^2}] for $n \neq 1$

The method of of liner least squares is then applied to equation 1.6 to minimize the sum of the squares of the difference between the experimental and calculated values of y.

Since the second term on the right hand side of equation 1.6 is almost invariant with temperature, we can plot y against 1/T to get a straight line. In order to avoid inaccuracies in calculation, E and RT have been rescaled and reparameterized as follows: b=E/1,000

T=RT/1,000

And $a = \ln\left(\left[\frac{AR}{\beta E}\right]\left\{1-2\frac{t}{b}\right\}\right)$

So y=-(b/t) +a

The sum of the squares of the deviation is

$$S_L = \sum_{j=1}^{j} d_i^2$$

Thus

$$S_L = \sum_{i=1}^{n} (y_i - a + b/t_i)^2 \qquad 1.7$$

For the determination of the best values of a and b, we must differentiate equation 1.7 with respect to a and b equate them to zero, i.e.

$$\frac{\partial S}{\partial a} = 0 and \frac{\partial S}{\partial b} = 0$$

Hence, equating them to zero and simplifying, we get the following linear equation

$$j.\, a + b \sum x = \sum y$$

$$a \sum x + b \sum x^2 = \sum xy$$

These equations are called normal equation for least square line.

The solution of the linear form S_L and the best values of a and b (in the least square sense) are:

$$a = \frac{pl - qm}{jl - m^2},\quad b\frac{pm - qj}{jl - m^2} \quad R = \frac{jp - mp}{\sqrt{jl - m^2}\sqrt{jl - p^2}}$$

where $m = \sum 1/t_i, l = \sum 1/t_i^{\,2}, p = \sum y_{i,} q = \sum (y_i / t_i) and z = \sum y_i^{\,2}$

We find that y and r (reaction rate) have the same dependent variables, i.e. X_i, T_i, such that $r = \left(\frac{\partial r}{\partial X_i}\right) X_i + \left(\frac{\partial r}{\partial T_i}\right) T_i$

Kinetic Parameters were found by using the integral and differential techniques. The order of reaction, n, the activation energy, E and pre-exponential factor, A as obtained by different methods viz., Fuoss and Reich, Agrawal and Sivasubramanian (1987), Freeman and Carroll (1958) and Coats and Redfern (1964).

Kinetic parameters were determined by using TGA and DTG curves and applying integral and differential techniques for each degradation zone. The kinetic parameters were determined as the best fit values by using the experiment data. Table shows the kinetic parameters of given biomass material pyrolysis at different heating rates under nitrogen flow rate of 400 ml/min.

Table 4.7.1 Kinetic Parameters of (pyrolysis) Thermal Degradation of given Biomass material under Non Iso-thermal condition in Nitrogen atmosphere using Fuoss and Reich (2003) approximation.

Biomass	**Heating Rate K min^{-1}**	**E kJ/mol**	**A min^{-1}**	**n**
Poplar roots	10	18.379	143.45	1
	20	21.818	417.85	1
	30	23.109	535.05	1
	40	28.9	655.97	1
Eucalyptus roots	10	33.60	92044.4	1
	20	30.3413	25896	1
	30	25.35	1970.19	1
	40	24.82	4013.73	1
Eucalyptus steam	10	14.6942	171.39	1
	20	15.0682	323.818	1
	30	14.250	436.40	1
	40	15.941	629.526	1
Groundnut shell	10	6.5060	87.76	1
	20	8.2158	209.76	1
	30	8.630	316.89	1
	40	8.025	377.5	1

From the table Fuoss and Reich shows that the value of activation energy for ground nut shell pyrolysis is 8.02 kJ mol^{-1} lower than that of given biomass. This indicates that groundnut shell is preferable for the pyrolysis over the other biomass material

Table 4.7.2 Kinetic Parameters of Groundnut shell using **Freeman and Carroll** (1958)

Heating rates 10 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp Zone ^0C	$\dfrac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\dfrac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
143-900	-6.502	0.0199	19.95	27.892	0.013	0.9377
	-3.0983	0.00231				
	1.3848	0.00048				
	0.1300	0.000506				
143-267	-10.76	0.0932	3.23	58.98	Negative value	0.8972
	-1.028	0.001267				
	3.99	0.549				
	-0.0025	1.137				
267-392	-24.36	0.0301	5.43	165.32	0.00032	0.9823
	-4.875	0.748				
	-7.025	0.00446				
392-570	-13.089	1.92	8.072	88.73	Negative value	0.9673
	-3.280	0.00976				
	0.280	0.972				
	-0.793	0.000674				

Table 4.7.3 Kinetic Parameters of Groundnut shell using **Freeman and Carroll** (1958)

Heating rates 20 Kmin^{-1} Nitrogen flow rate 400 ml/min

Temp Zone ^{0}**C**	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
167-293	-11.32	0.009327	4.512	156.32	0.068	0.9321
	-1.398	0.01267				
	3.78	0.549				
	-0.025	1.137				
293-420	-16.962	0.0152	7.7905	118,98	0.073	0.9991
	-2.818	0.0000744				
	-6.812	0.00446				
420-720	-26.787	0.0193	11.1716	98.67	0.08	0.9735
	-5.385	0.00526				
	-2.6017	0.000563				
167-720	-1.398	0.0198	8.76	112.36	0.074	0.8823
	-7.360	0.1374				
	3.796	0.000452				
	0.0875	0.00387				

Table 4.7.4 Kinetic Parameters of Groundnut shell using **Freeman and Carroll** (1958)

Heating rates 30 Kmin^{-1} Nitrogen flow rate 400 ml/min

Temp Zone ^{0}**C**	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
183-263	-15.47	0.0144	6.6512	69.0587	0.028	0.963
	-3.28	0.0242				
	-10.77	0.0182				
263-297	-11.97	0.00140	2.4942	78.730	0.0059	0.7380
	-4.50	0.006				
	-0.63	0.00447				
297-363	-0.7458	0.00124	13.3024	460.78	0.15	9.459
	-0.9836	0.00171				
	0.4356	0.0003965				
363-700	-0.246	0.0011	4.157	89.390	0.00091	7.390
	-0.371	0.00040				
	-1.60	0.000144				
183-700	-15.64	0.0144	7.482	174.32	0.004	9.723
	-9.108	0.00876				
	-1.1107	0.00254				
	-0.496	0.00070				
	-1.604	0.000144				

Table 4.7.5 Kinetic Parameters of Groundnut shell using **Freeman and Carroll** (1958)

Heating rates 40 Kmin^{-1}. Nitrogen flow rate 400 ml/min.

Temp Zone ^{0}**C**	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
240-341	-1.695	0.00760	13.30	43.28	0.017	0.7891
	-5.2415	0.00289				
	-4.3486	0.00064				
170-240	-6.507	0.0078	10.808	72.05	0.012	0.8326
	-6.097	0.0097				
	-4.232	0.0112				
341-700	-0.5716	0.00113	35.75	102.82	0.32	0.9807
	-0.3786	0.00041				
	-0.329	0.0000489				
170-700	-6.50	0.00781	9.9768	82.9432	0.00091	0.9806
	-4.613	0.00468				
	-0.6546	0.000793				

Table 4.7.6 Kinetic Parameters of Eucalyptus roots using **Freeman and Carroll** (1958)

Heating rates 10 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp Zone ^0C	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E kJ/mol**	**$Amin^{-1}$**	**n**	**R^2**
197-273	-14.208	0.00947	8.923	112.84	0.0673	0.8892
	-7.389	0.863				
	1.398	3.4832				
	-0.890	0.0090				
273-360	-2.0472	0.0009692	13.32	98.76	0.11	-
	9.044	0.00135				
	0.9146	0.0010732				
360-498	-0.1614	0.0003545	70.349	67.387	0.192	0.9993
	0.875	0.000232				
	0.2980	0.0003				
197-700	0.2394	0.000650	9.8342	239.370	0.0984	0.9978
	1.2023	0.0007019				
	0.778	0.000465				

Table 4.7.7 Kinetic Parameters of Eucalyptus roots using **Freeman and Carroll** (1958)

Heating rates 20 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}C	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** $\mathbf{min^{-1}}$	**n**	$\mathbf{R^2}$
226-319	-11.962	0.02152	6.09	79.83	0.032	0.9720
	-0.818	0.000744				
	-6.812	0.0446				
319-412	-0.4535	0.000392	153.2	134.23	1.39	0.8975
	0.32	0.000257				
	3.582	0.000212				
412-760	1.01	0.000683	9.320	123.84	0.098	0.9322
	0.237	0.000196				
	-0.3320	0.0000149				
226-760	-0.372	0.0093	6.780	68.85	0.041	0.8832
	-12.678	0.00084				
	2.347	0.0931				
	-0.0032	0.00831				

Table 4.7.8 Kinetic Parameters of Eucalyptus roots using **Freeman and Carroll** (1958)

Heating rates 30 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min.

Temp Zone ^{0}C	$\dfrac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\dfrac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
242-337	-16.962	0.0152	7.789	184.73	0.13	0.9989
	-2.818	0.0000744				
	-6.812	0.00446				
337-422	-0.4535	0.000392	186.83	87.23	0.68	0.8932
	0.6972	0.000274				
	3.582	0.000252				
242-760	-17.05	0.0153	9.840	779.97	1.02	0.9807
	-0.8849	0.000360				
	2.234	0.000288				
	0.5046	0.000445				

Table 4.7.9 Kinetic Parameters of Eucalyptus roots using **Freeman and Carroll** (1958)

Heating rates 40 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}C	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E kJ/mol**	**Amin^{-1}**	**n**	**R^2**
237-340	-44.193	0.0193	19.49	426.24	0.0068	0.9667
	-5.385	0.00526				
	-2.60179	0.000563				
340-389	-1.1875	0.000546	222.15	45.025	0.16	-
	1.3070	0.000362				
	6.0734	0.000344				
389-560	1.200	0.000683	11.299	41.73	negative value	9729
	0.427	0.000196				
	-0.3320	0.0000149				
	-18.885	0.0101				
237-700	-1.882	0.00099	16.220	58.90	0.12	0.9946
	0.872	0.000425				
	0.299	0.0001343				

Table 4.7.10 Kinetic Parameters of Eucalyptus stem using **Freeman and Carroll** (1958)

Heating rates 10 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp Zone ^0C	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** $\mathbf{min^{-1}}$	**n**	$\mathbf{R^2}$
102-210	-3.825	0.0406	12.68.71	43.10	0.039	9.998
	-4.1	0.08260				
	-3.913	.05419				
210-347	-27.67	0.01410	4.157	79.46	0.005	0.997
	-1.485	0.001212				
	3.137	0.00073				
102-700	-3.825	0.0406	29.90	54.32	0.01	0.897
	-5.2	0.00722				
	0.874	0.832				
	1.12	0.000358				
	0.136	0.0000708				

Table 4.7.11 Kinetic Parameters of Eucalyptus stem using **Freeman and Carroll** (1958)

Heating rates 20 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}C	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^{2}**
123-227	-29.23	0.0049	13.39	68.09	0.019	0.9832
	1.132	0.0826				
	-3.913	0.05419				
127-360	-0.993	0.00125	14.79	148.38	0.023	0.9944
	0.4255	0.00026				
	1.31	0.00032				
360-570	-31.512	0.08	2.976	57.78	0.00068	0.9726
	-10.846	0.0135				
	-1.4652	0.00136				
123-700	-3.913	0.05419	1.983	38.79	0.0001	0.9913
	0.3498	0.000358				
	0.324	0.000037				
	-1.604	0.000144				

Table 4.8.12 Kinetic Parameters of Eucalyptus stem using **Freeman and Carroll** (1958)

Heating rates 30 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}**C**	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
198-372	-29.190	0.01939	14.3228	77.34	0.15	0.9702
	-1.4008	0.00131				
	6.029	0.000714				
372-559	-1.353	0.00125	21.369	47.43	0.584	0.8766
	0.4255	0.00026				
	2.131	0.0000672				
559-760	-0.1183	0.000321	12.329	39.42	0.018	-
	0.1809	0.000133				
	-0.1534	0.000213				
127-760	-16.84	0.07407	3.270	44.61	0.0078	0.9108
	-5.645	0.00705				
	1.57481	0.000979				
	0.4535	0.000207				

Table 4.7.13 Kinetic Parameters of Eucalyptus stem using **Freeman and Carroll** (1958)

Heating rates 40 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min.

Temp Zone ^{0}**C**	$\dfrac{\Delta\ln\frac{d\alpha}{dT}}{\Delta\ln(1-\alpha)}$	$\dfrac{\Delta(\frac{1}{T})}{\Delta\ln(1-\alpha)}$	**E** **kJ/mol**	**A** $\mathbf{min^{-1}}$	**n**	$\mathbf{R^2}$
138-221	-31.512	0.8	1.98	77.34	-	0.911
	-37.67	0.239				
	-33.74	0.137				
221-383	-9.9174	0.00573	19.172	196.19	0.018	0.9556
	-1.4665	0.00136				
	2.739	0.000706				
383-620	-0.1100	0.000893	13.3093	48.93	0.011	0.9867
	0.5506	0.000410				
	1.1391	0.000126				
620-760	-0.1415	0.000109	68.642	32.30	0.0001	0.999
	0.442	0.0000384				
	0.0779	0.0000829				
138-760	-31.512	0.08	3.264	77.30	0.038	0.9588
	-10.846	0.0135				
	-1.4652	0.00136				
	1.494	0.00082				
	0.3820	0.000187				

Table 4.7.14 Kinetic Parameters of Poplar roots using **Freeman and Carroll** (1958)

Heating rates 10 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}**C**	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
219-333	-14.607	0.00691	23.80	16.05	0.083	0.9569
	-1.1079	0.00127				
	5.926	0.000312				
333-462	-0.0871	0.000916	12.67	83.30	0.023	-
	-1.3875	0.0002452				
	2.882	0.000195				
462-800	-0.1452	0.0004	3.92746	49.38	0.0076	0.9901
	-0.30452	0.0000678				
	-0.232	0.000190				
219-800	-3.7142	0.00133	61.74	22.67	0.39	0.8136
	0.5693	0.000410				
	5.87135	0.000249				

Table 4.7.15 Kinetic Parameters of Poplar roots using **Freeman and Carroll** (1958)

Heating rates 20 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}**C**	$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\frac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^{2}**
223-339	-13.390	.00530	24.03	53.67	0.001	0.9914
	0.7668	.000632				
	-1.230	.000831				
339-512	-0.0569	0.000135	8.930	87.50	0.068	0.8941
	-1.032	0.0002452				
	1.675	0.000923				
223-760	-2.459	0.002214	15.90	68.90	0.0015	-
	6.061	0.00053				
	0.3498	0.000358				
	0.324	0.000037				

Table 4.7.16 Kinetic Parameters of Poplar roots using **Freeman and Carroll** (1958)

Heating rates 40 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp Zone ^{0}**C**	$\dfrac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)}$	$\dfrac{\Delta(\frac{1}{T})}{\Delta \ln(1-\alpha)}$	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
228-363	-11.0662	0.00729	13.32	159.420	1.03	0.9949
	-1.155	0.000817				
	0.1787	0.000530				
363-560	-0.0349	0.00055	6.448	76.11	0.352	0.999
	0.324	0.000087				
	0.1441	0.00032				
228-700	-3.459	0.002324	31.91	59.30	0.21	0.9237
	6.261	0.00053				
	0.3498	0.000558				
	0.324	0.000087				

Table 4.7.17 Kinetic Parameters of Groundnut shell using **Agrawal and Sivasubramanian.**

Heating rates 10 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	**-ln**$[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** min^{-1}	**n**	R^2
143-900	9.677	0.00699	2.26	22365.41	1	0.9623
	10.63	0.00411				
	10.80	0.003436				
	10.837	0.00306				
	10.95	0.00208				
143-236	11.32	0.0078	0.7630	5824.40	1	0.9982
	9.02	0.0069				
	11.91	0.00450				
	10.32	0.0032				
236-377	9.802	0.0068	1.5862	9372.30	1	0.9372
	8.802	0.00304				
	10.32	0.00390				
	11.98	0.00280				
377-480	11.0443	0.00194	3.206	17340.69	1	0.9213
	11.38	0.00165				
	11.342	0.00157				
	10.874	0.001388				

Table 4.7.18 Kinetic Parameters of Groundnut shell using **Agrawal and Sivasubramanian**

Heating rates 40 Kmin^{-1} Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
170-240	10.32	0.00546	0.674	24900.199	1	0.955
	10.59	0.00456				
	10.64	0.00444				
	10.75	0.4166				
240-341	10.75	0.004166	2.1986	14780	1	0.9867
	10.93	0.00374				
	11.12	0.00314				
	11.0443	0.00293				
341-700	11.0443	0.00293	.172	19870.32	1	0.999
	11.38	0.00210				
	11.342	0.00197				
	10.874	0.00174				
170-700	10.32	0.00546	2.525	69952.28	1	0.9588
	10.59	0.00456				
	11.128	0.00314				
	11.342	0.00197				

Table 4.7.19 Kinetic Parameters of Groundnut shell using **Agrawal and Sivasubramanian**

Heating rates 30 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	- **$\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
183-263	10.1960	0.00546	3.2739	2036.32	1	0.8992
	10.486	0.00462				
	10.85	0.00380				
263-297	10.852	0.00380	3.0572	4800.22	1	0.9632
	10.8557	0.00370				
	10.932	0.00353				
	11.005	0.00336				
297-363	11.005	0.00336	5.3033	41007.98	1	0.9932
	11.02	0.00318				
	10.08	0.00295				
	9.980	0.00181				
363-700	9.980	0.00181	2.032	52615.79	1	0.9432
	11.230	0.002212				
	11.2495	0.00195				
	11.196	0.00182				
183-700	10.196	0.00546	2.3510	68790.58	1	0.9647
	10.48	0.00462				
	10.85	0.00370				
	11.02	0.00318				
	11.249	0.00195				
	11.196	0.00182				

Table 4.7.20 Kinetic Parameters of Groundnut shell using **Agrawal and Sivasubramanian.**

Heating rates 20 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^{0}**C**	**-ln**$[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** **min**$^{-1}$	**n**	**R**^{2}
167-243	12.32	0.0078	0.930	3120.56	1	0.9772
	9.02	0.0069				
	10.091	0.00450				
	10.12	0.0032				
243-358	9.872	0.0067	2.68	4912.972	1	0.9863
	8.702	0.00204				
	9.32	0.003490				
	11.98	0.00780				
358-760	12.0443	0.00294	4.480	13558.09	1	-
	11.38	0.00465				
	11.342	0.00357				
	10.874	0.001388				
167-760	10.067	0.00799	3.210	22728.31	1	0.9991
	11.03	0.004311				
	11.80	0.00436				
	10.837	0.00706				
	10.01	0.002308				

Table 4.7.21 Kinetic Parameters of Eucalyptus stem using **Agrawal and Sivasbramanian.**

Heating rates 10 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^0C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^1**	**n**	**R^2**
102-210	8.596	0.0098	2.3075	6672.80	1	0.9756
	9.171	0.007246				
	9.996	0.00476				
210-347	9.996	0.00476	2.969	8368.3	1	.8592
	10.482	0.00366				
	10.6125	0.00310				
	10.6411	0.002923				
347-513	10.6411	0.002923	1.865	9810.32	1	0.9332
	10.83	0.00243				
	10.9417	0.00217				
	10.813	0.00194				
513-720	10.813	0.00194	5.8759	14227.29	1	-
	11.085	0.00165				
	11.192	0.00157				
	11.175	0.001388				
102-720	8.596	0.0098	2.6623	14927	1	0.9937
	9.171	0.0072				
	10.6125	0.00310				
	10.94	0.00217				
	11.192	0.00157				
	11.175	0.001388				

Table 4.7.22 Kinetic Parameters of Eucalyptus stem using **Agrawal and Sivasubramanian.**

Heating rates 30 Kmin^{-1}. Nitrogen flow rate 400 ml/min.

Temp zone ^{0}C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
127-198	8.97153	0.00787	2.576	2961.28	1	0.9951
	9.3714	0.00641				
	9.8467	0.00505				
198-372	9.8467	0.00505	3.373	5672.30	1	0.9921
	10.570	0.00344				
	10.737	0.00290				
	10.785	0.002688				
372-559	10.785	0.002688	2.4665	41890.945	1	0.7064
	11.0914	0.00214				
	11.0985	0.001828				
	11.0127	0.00179				
559-760	11.0127	0.00179	5.715	150270	1	0.9985
	11.1635	0.00156				
	11.255	0.00144				
127-760	8.97153	0.00787	3.06719	52615.79	1	0.9966
	9.3714	0.00641				
	10.737	0.00290				
	11.0914	0.00214				
	11.255	0.00144				

Table 4.7.23 Kinetic Parameters of Eucalyptus stem using **Agrawal and Sivasubramanian**.

Heating rates 40 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min.

Temp zone ^0C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
138-221	9.196	0.0072	2.923	11380	1	0.9972
	9.501	0.0062				
	10.131	0.00452				
221-383	10.131	0.00452	3.0942	22031.9	1	0.9893
	10.62	0.003366				
	10.78	0.00285				
	10.83	0.0026				
383-620	10.83	0.0026	3.1345	38133.630	1	0.941
	11.0992	0.0021				
	11.20	0.00173				
	11.1920	0.00161				
620-760	11.1920	0.00161	3.218	61858	1	0.9966
	11.122	0.00142				
	11.101	0.00138				
138-760	9.196	0.0072	3.046	75885.78	1	0.9583
	9.501	0.0062				
	10.594	0.00336				
	11.0992	0.00285				
	11.122	0.00142				

Table 4.7.24 Kinetic Parameters of Eucalyptus roots using **Agrawal and Sivasubramanian.**

Heating rates 10 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^0C	**$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A**	**n**	**R^2**
275-360	10.462	0.00363	2.678	6853.37	1	0.9399
	10.562	0.00306				
	10.686	0.00277				
360-498	10.686	0.0027	0.2981	8974.853	1	0.9321
	10.696	0.00227				
	10.712	0.00200				
275-700	10.462	0.0036	2.6026	12394.28	1	0.9228
	10.72	0.00227				
	11.1695	0.00142				

Table 4.7.25 Kinetic Parameters of Eucalyptus roots using **Agrawal and Sivasubramanian.**

Heating rates 30 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^0C	**-ln**$[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** $\mathbf{min^{-1}}$	**n**	$\mathbf{R^2}$
242-337	10.249	0.00413	3.357	18087.361	1	0.9267
	10.626	0.0030				
	10.793	0.00296				
337-422	10.793	0.00296	3.991	24011.75	1	0.8993
	11.923	0.00263				
	10.692	0.00248				
	10.658	0.00236				
422-760	10.658	0.00236	5.317	31582.91	1	0.9703
	11.299	0.00149				
	11.249	0.0014				
	11.255	0.00138				
242-760	10.2496	0.00413	2.913	56771.15	1	0.9504
	10.626	0.0030				
	10.726	0.00263				
	10.702	0.00236				
	11.249	0.0014				

Table 4.7.26 Kinetic Parameters of Eucalyptus roots using **Agrawal and Sivasubramanian.**

Heating rates 40 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min.

Temp zone ^0C	**$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
237-340	10.354	0.0042	3.680	23623.675	1	0.9959
	10.641	0.0036				
	10.777	0.0033				
	10.906	0.00294				
340-389	10.906	0.00294	2.377	33076.684	1	0.902
	10.890	0.00280				
	10.798	0.0026				
	10.82	0.00257				
389-560	10.822	0.00257	1.901	52980.32	1	-
	11.104	0.00196				
	11.072	0.0018				
	10.896	0.00178				
560-700	10.896	0.00178	4.665	68937.80	1	0.9615
	11.032	0.0016				
	11.098	0.00142				
237-700	10.35	0.0042	2.147	71308.9	-	0.9217
	10.77	0.0033				
	10.890	0.00280				
	11.07	0.0018				
	11.098	0.00142				

Table 4.7.27 Kinetic Parameters of Poplar roots using **Agrawal and Sivasubramanian**.

Heating rates 10 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^0C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
219-333	10.226	0.00456	2.263	5451.77	1	0.9235
	10.561	0.00374				
	10.67	0.0031				
	10.638	0.0030				
333-463	10.638	0.0030	1.898	8300.89	1	0.8932
	10.80	0.0025				
	10.77	0.00233				
	10.70	0.00216				
219-800	10.226	0.00456	2.293	11540.07	1	0.9788
	10.672	0.0031				
	10.771	0.00233				
	11.09	0.00156				

Table 4.7.28 Kinetic Parameters of Poplar roots using **Agrawal and Sivasubramanian**

Heating rates 40 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	-ln[$\frac{-\ln(1-\alpha)}{T^2}$]	**1/T**	**E** **kJ/mol**	**A** **min^{-1}**	**n**	**R^2**
228-363	10.273	0.00438	2.781	22728.54	1	0.9508
	10.739	0.0033				
	10.793	0.00290				
	10.794	0.00275				
363-560	10.794	0.00275	1.686	36205.631	1	0.8999
	11.077	0.00191				
	10.918	0.00178				
228-700	10.27	0.00438	0.198	5995.520	1	
	10.7838	0.00290				
	10.794	0 .00275				
	11.077	0.00195				
	10.918	0.00178				

Table 4.7.29 Kinetic Parameters of Poplar roots using **Agrawal and Sivasubramanian**

Heating rates 30 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^0C	**$\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A min^{-1}**	**N**	**R^2**
223-343	8.97153	0.00787	13.39	11380	1	0.9832
	9.3714	0.00641				
	9.8467	0.00505				
	9.8467	0.00505				
343-528	10.570	0.00344	14.79	22031.9	1	0.9944
	10.737	0.00290				
	10.785	0.002688				
	10.785	0.002688				
528-760	11.0914	0.00214	2.976	38133.630	1	0.9726
	11.0985	0.001828				
	11.0127	0.00179				
223-760	8.97153	0.00787	1.983	61858	1	0.9913
	9.3714	0.00641				
	10.737	0.00290				
	11.0914	0.00214				
	11.255	0.00144				

Table 4.7.30. Kinetic Parameters of Groundnut shell using **Coats and Redfern (1964)**

Heating rates 10 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^0C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
143-900	9.677	0.00699	2.26	2196.41	1	0.9623
	10.63	0.00411				
	10.80	0.003436				
	10.837	0.00306				
	10.95	0.00208				
143-236	11.32	0.0078	0.7630	78240.40	1	0.9982
	9.02	0.0069				
	11.91	0.00450				
	10.32	0.0032				
236-377	9.802	0.0068	1.5862	11372.30	1	0.9372
	8.802	0.00304				
	10.32	0.00390				
	11.98	0.00280				
377-480	11.0443	0.00194	3.206	17340.69	1	0.9213
	11.38	0.00165				
	11.342	0.00157				
	10.874	0.001388				

Table 4.7.31. Kinetic Parameters of Groundnut shell using **Coats and Redfern (1964)**

Heating rates 40 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^0C	**- $\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
170-240	10.32	0.00546	0.5974	14800.199	1	0.9556
	10.59	0.00456				
	10.64	0.00444				
	10.75	0.4166				
240-341	10.75	0.004166	2.0398	18780	1	0.9867
	10.93	0.00374				
	11.12	0.00314				
	11.0443	0.00293				
341-700	11.0443	0.00293	0.172	188700.32	1	0.999
	11.38	0.00210				
	11.342	0.00197				
	10.874	0.00174				
170-700	10.32	0.00546	2.525	69952.28	1	0.9588
	10.59	0.00456				
	11.128	0.00314				
	11.342	0.00197				

Table 4.7.32 Kinetic Parameters of Groundnut shell using **Coats and Redfern (1964)**

Heating rates 30 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	**$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
183-263	10.1960	0.00546	3.2739	2036.32	1	0.8992
	10.486	0.00462				
	10.85	0.00380				
263-297	10.852	0.00380	3.0572	4800.22	1	0.9632
	10.8557	0.00370				
	10.932	0.00353				
	11.005	0.00336				
297-363	11.005	0.00336	5.3033	41007.98	1	0.9932
	11.02	0.00318				
	10.08	0.00295				
	9.980	0.00181				
363-700	9.980	0.00181	2.032	52615.79	1	0.9432
	11.230	0.002212				
	11.2495	0.00195				
	11.196	0.00182				
183-700	10.196	0.00546	2.3510	68790.58	1	0.9647
	10.48	0.00462				
	10.85	0.00370				
	11.02	0.00318				
	11.249	0.00195				
	11.196	0.00182				

Table 4.7.33 Kinetic Parameters of Groundnut shell using **Coats and Redfern (1964)**

Heating rates 20 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^0C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
167-243	12.32	0.0078	0.930	8120.56	1	0.9772
	9.02	0.0069				
	10.091	0.00450				
	10.12	0.0032				
243-358	9.872	0.0067	2.68	6912.972	1	0.9863
	8.702	0.00204				
	9.32	0.003490				
	11.98	0.00780				
358-760	12.0443	0.00294	4.480	13558.09	1	-
	11.38	0.00465				
	11.342	0.00357				
	10.874	0.001388				
167-760	10.067	0.00799	3.210	22728.31	1	0.9991
	11.03	0.004311				
	11.80	0.00436				
	10.837	0.00706				
	10.01	0.002308				

Table 4.7.34 Kinetic Parameters of Eucalyptus stem using **Coats and Redfern (1964)**

Heating rates 10 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^{0}**C**	-**ln**$[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** **min**$^{-1}$	**n**	**R**^{2}
102-210	8.596	0.0098	2.3075	6672.80	1	0.9756
	9.171	0.007246				
	9.996	0.00476				
210-347	9.996	0.00476	2.969	8368.3	1	0.8592
	10.482	0.00366				
	10.6125	0.00310				
	10.6411	0.002923				
347-513	10.6411	0.002923	1.865	9810.32	1	0.9332
	10.83	0.00243				
	10.9417	0.00217				
	10.813	0.00194				
513-720	10.813	0.00194	5.8759	14227.29	1	-
	11.085	0.00165				
	11.192	0.00157				
	11.175	0.001388				
102-720	8.596	0.0098	2.6623	14927	1	0.9937
	9.171	0.0072				
	10.6125	0.00310				
	10.94	0.00217				
	11.192	0.00157				
	11.175	0.001388				

Table 4.7.35 Kinetic Parameters of Eucalyptus stem using **Coats and Redfern (1964)**

Heating rates 30 $Kmin^{-1}$. Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** min^{-1}	**n**	R^2
127-198	8.97153	0.00787	2.576	2961.28	1	0.9951
	9.3714	0.00641				
	9.8467	0.00505				
198-372	9.8467	0.00505	3.373	5672.30	1	0.9921
	10.570	0.00344				
	10.737	0.00290				
	10.785	0.002688				
372-559	10.785	0.002688	2.4665	41890.945	1	0.7064
	11.0914	0.00214				
	11.0985	0.001828				
	11.0127	0.00179				
559-760	11.0127	0.00179	5.715	150270	1	0.9985
	11.1635	0.00156				
	11.255	0.00144				
127-760	8.97153	0.00787	3.06719	52615.79	1	0.9966
	9.3714	0.00641				
	10.737	0.00290				
	11.0914	0.00214				
	11.255	0.00144				

Table 4.7.36 Kinetic Parameters of Eucalyptus stem using **Coats and Redfern (1964)**

Heating rates 40 $\mathrm{Kmin^{-1}}$ Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	**$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A $\mathrm{min^{-1}}$**	**N**	**R^2**
138-221	9.196	0.0072	2.923	11380	1	0.9972
	9.501	0.0062				
	10.131	0.00452				
221-383	10.131	0.00452	3.0942	22031.9	1	0.9893
	10.62	0.003366				
	10.78	0.00285				
	10.83	0.0026				
383-620	10.83	0.0026	3.1345	38133.630	1	0.941
	11.0992	0.0021				
	11.20	0.00173				
	11.1920	0.00161				
620-760	11.1920	0.00161	3.218	61858	1	0.9966
	11.122	0.00142				
	11.101	0.00138				
138-760	9.196	0.0072	3.046	75885.78	1	0.9583
	9.501	0.0062				
	10.594	0.00336				
	11.0992	0.00285				
	11.122	0.00142				

Table 4.7.37 Kinetic Parameters of Eucalyptus roots using **Coats and Redfern (1964)**

Heating rates 10 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** min^{-1}	**n**	R^2
275-360	10.462	0.00363	2.678	6853.37	1	0.9399
	10.562	0.00306				
	10.686	0.00277				
360-498	10.686	0.0027	0.2981	8974.853	1	0.9321
	10.696	0.00227				
	10.712	0.00200				
275-700	10.462	0.0036	2.6026	12394.28	1	0.9228
	10.72	0.00227				
	11.1695	0.00142				

Table 4.7.38 Kinetic Parameters of Eucalyptus roots using **Coats and Redfern (1964)**

Heating rates 30 Kmin^{-1}. Nitrogen flow rate 400 ml/min

Temp zone ^{0}**C**	-**ln**$[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** **min**$^{-1}$	**n**	**R**^{2}
242-337	10.249	0.00413	3.357	18087.361	1	0.9267
	10.626	0.0030				
	10.793	0.00296				
337-422	10.793	0.00296	3.991	24011.75	1	0.8993
	11.923	0.00263				
	10.692	0.00248				
	10.658	0.00236				
422-760	10.658	0.00236	5.317	31582.91	1	0.9703
	11.299	0.00149				
	11.249	0.0014				
	11.255	0.00138				
242-760	10.2496	0.00413	2.913	56771.15	1	0.9504
	10.626	0.0030				
	10.726	0.00263				
	10.702	0.00236				
	11.249	0.0014				

Table 4.7.39 Kinetic Paramèters of Eucalyptus roots using **Coats and Redfern (1964)**

Heating rates 40 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^0C	**$-\ln[\frac{-\ln(1-\alpha)}{T^2}]$**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
237-340	10.354	0.0042	3.680	9362.675	1	0.9959
	10.641	0.0036				
	10.777	0.0033				
	10.906	0.00294				
340-389	10.906	0.00294	2.377	33076.684	1	0.902
	10.890	0.00280				
	10.798	0.0026				
	10.82	0.00257				
389-560	10.822	0.00257	1.901	52980.32	1	-
	11.104	0.00196				
	11.072	0.0018				
	10.896	0.00178				
560-700	10.896	0.00178	4.665	68937.80	1	0.9615
	11.032	0.0016				
	11.098	0.00142				
237-700	10.35	0.0042	2.147	71308.9	1	0.9217
	10.77	0.0033				
	10.890	0.00280				
	11.07	0.0018				
	11.098	0.00142				

Table 4.7.40 Kinetic Parameters of Poplar roots roots using **Coats and Redfern (1964)**

Heating rates 10 $Kmin^{-1}$Nitrogen flow rate 400 ml/min

Temp zone ^0C	**-ln[$\frac{-\ln(1-\alpha)}{T^2}$]**	**1/T**	**E kJ/mol**	**A min^{-1}**	**n**	**R^2**
219-333	10.226	0.00456	2.263	5451.77	1	0.9235
	10.561	0.00374				
	10.67	0.0031				
	10.638	0.0030				
333-463	10.638	0.0030	1.898	6370.89	1	0.8932
	10.80	0.0025				
	10.77	0.00233				
	10.70	0.00216				
219-800	10.226	0.00456	2.293	11640.07	1	0.9788
	10.672	0.0031				
	10.771	0.00233				
	11.09	0.00156				

Table 4.7.41 Kinetic Parameters of Poplar roots using **Coats and Redfern (1964)**

Heating rates 40 $Kmin^{-1}$ Nitrogen flow rate 400 ml/min

Temp zone ^{0}C	**-ln**$[\frac{-\ln(1-\alpha)}{T^2}]$	**1/T**	**E** **kJ/mol**	**A** $\mathbf{min^{-1}}$	**N**	$\mathbf{R^2}$
228-363	10.273	0.00438	2.781	6272.54	1	0.9508
	10.739	0.0033				
	10.793	0.00290				
	10.794	0.00275				
363-560	10.794	0.00275	1.686	36205.631	1	0.8999
	11.077	0.00191				
	10.918	0.00178				
228-700	10.27	0.00438	0.198	55995.520	1	0.998
	10.7838	0.00290				
	10.794	0 .00275				
	11.077	0.00195				
	10.918	0.00178				

4.2 DISCUSSION

4.2.1 DEGRADATION CHARATERISTICS

The optimum value of heating rate for pyrolysis according to the largest value of total volatile matter realesed and the lowest value of PTFV was found to be in 10 K min^{-1}. In the case of pyrolysis, the moisture removed was in the range of 19-205 ^{0}C and maximum rate of drying is in the range of 1.3-5.0 wt % min^{-1} for the Groundnut shell, 2.1-4.79 wt % min^{-1} for the Poplar roots, 1.68-4.23 wt % min^{-1} for the eucalyptus roots and 1.98-3.04 wt % min^{-1} for the eucalyptus stem. The temperature of maximum devolatilization rate as obtained from DTG peaks were in the range of T_{1max}=318-344 ^{0}C, T_{2max}=429-522, for the poplar roots, T_{1max} =322-350, T_{2max}=459-578, T_{3max}=633-701, for the eucalyptus steam, and T_{1max}= 299-318 ^{0}C T_{2max}=480-507 ^{0}C, for the Ground nut shell. The maximum rate of degradation is found to be 0.561 to 1.331 (% weight/ ^{0}C) for the given biomass sample.

4.2.2 KINETIC PARAMETER:

The activation energy and pre exponential factor obtained from this study are in the range of 1.5 to 300 kJ/mol and 10^{2}> 10^{8}. The result of least square method showed that the kinetic parameters for the entire degradation zone for the pyrolysis of given biomass material at heating rates 96.68 % confidence for the value of activation energy and the regression coefficient is 0.99. In the case of pyrolysis in general we found that the second zone of degradation had the largest value of activation energy, while overall activation energy is the lowest in comparisons to the value obtained in the various zone. Comparison of E value for different temperature zone indicates that the second reaction zone had the highest activation energy, however, it should be noted that the comparisons of this nature has no meant as the best fit value at different order of reaction. As the increase in the order of reaction increased the activation energy for any temperature zone.

For the entire zone of pyrolysis of given biomass material, the order of reaction is found in the range of 0.000-2.50, the activation energy is in the range of 1.5 to 300 kJ/mol

and the pre-exponential factor in the range of 2284-80,750 $\min^{-1}$ with the regression coefficient in the range of 0.899-0.99.

The approximation of Agrawal and Siva Subramanian (1987) has been found to be near numerically integrated value than the value obtained by Coats and Redfern (1964). However, both the methods gave the same value of E and A at any best fit n value with a confidence levels of 97% by using the linear least square method for regression of data. Freeman and Carroll method has an advantage as it gives the kinetic parameters in one single step. At the same order of reaction the frequency factor increased with the activation energy increase.

From the table 4.7.1 Fuoss and Reich shows that the value of activation energy for ground nut shell pyrolysis is 8.02 kJ/mol lower than that of given biomass. This indicates that groundnut shell is preferable for the pyrolysis over the other biomass material

CHAPTER-V

CONCLUSION

Proximate analysis of groundnut shell, Eucalyptus, Poplar is carried out and it was found that the groundnut shell is a potential source of energy. Thermal Degradation of given biomass material in nitrogen atmosphere at different heating rates as carried out in a Perkin Elmer (Pyris Diamond) TG apparatus. Three degradation zones were found in the case of thermal degradation of poplar roots and eucalyptus roots, where as four degradation zones found in groundnut shell and five degradation zones is found in a eucalyptus stem. The second and third zone was the fastest degradation zones and gave the highest activation energy, whereas the activation energy of overall degradation zones is less. TG, DTG and DTA curved showed the number of distinct zones during thermal degradation process of the biomass. Two zones of thermal degradation were very prominent and third zone of char degradation in case of pyrolysis in nitrogen atmosphere was not very prominent. The first zones showed the degradation of hemicellouse and the second zone exhibited the degradation of cellouse. The lignin degradation occurred throughout the degradation zone. The kinetic parameters were determined by using four different method for given biomass sample and at different heating rates. Agrawal and sivasubramanian (1987) method was found to be most constient. Groundnut shell has low value of activation energy as compared to other given biomass sample shows by Fuoss and Reich approximation. The relative simplicity of the Agrawal and Sivasubramanian model gives it the potential for applications in the design of large scale biomass pyrolysis facility in the remote areas. The result of the least square regression showed that the kinetic parameters of the total degradation zones for the pyrolysis of given biomass sample at 10 $Kmin^{-1}$ heating rates had 96.68 confidence for the value of activation energy and the regression coefficient is 0.99.

RECOMMENADATIONS

1) The ultimate analysis, proximate analysis of the given biomass sample should be carried out.
2) The kinetic parameters should be determined by using better mechanistic models as suggested by some workers should be attempted.

NOMENCLATURE

DTA	Differential thermal analysis
DTG	Differential thermal gravimetric analysis
F.C	Fixed carbon (%)
HHV	Higher heating value
LHV	Lower heating value
MJ	Mega Joule
PTFV	Potential tar forming materials
TGA	Thermal gravimetric analysis
V.M	Volatile matter released

NOTATIONS

A	Frequency factor, min^{-1}
E	Activation energy, kJ/mol
k	kinetic constants
n	Reaction order
R	Universal gas constant
R^2	The optimum value of regression coefficient
t	Time, min
T	Absolute temperature, K
T_i	Transition temperature, K
T_m	Temperature at maximum rate of degradation
T_e	Temperature at completion of devolatilization
α	Fractional conversion
W	Residual weight fraction,
W_0	Initial weight of the biomass sample, mg

W_t	Weight of biomass at any time, mg
W_∞	Weight of biomass at the completation of Pyrolysis, mg

GREEK LETTERS

ω	Decomposition fraction of solid at time t
β	Heating rate, $Kmin^{-1}$
α	Fractional conversion

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