BIO-FUELS FROM BIOMASS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering

By
SUDEEP MOHAPATRA
LALIT MOHAN SAHU

Department of Chemical Engineering
National Institute of Technology
Rourkela
2007

BIO-FUELS FROM BIOMASS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering
By
SUDEEP MOHAPATRA
LALIT MOHAN SAHU

Under the Guidance of
Dr. R.K.SINGH

Department of Chemical Engineering
National Institute of Technology
Rourkela
2007

National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that the thesis entitled, “BIO-FUELS FROM BIOMASS” submitted by Sri Sudeep Mohapatra and Lalit Mohan Sahu in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

Dr. R.K.SINGH
Dept.of Chemical Engineering
National Institute of Technology
Rourkela - 769008

ACKNOWLEDGEMENT

We take this opportunity to express our gratitude to all those who motivated, encouraged and helped us in the project work. We are grateful to our supervisor, Prof. Dr. R.K. Singh, for his kind support, guidance and encouragement throughout the project work, also for introducing to us this topic, which has been very interesting and has given us great insight to the future work on this area. We also wish to thank Dr .P .Rath, Head of Department of Chemical Engineering, for his encouragement, patience and resourcefulness throughout the development of this project. We would like to take the chance to express our appreciation to our family members. Their continuous love and support gave us the strength for pursuing our dream. Special thanks to our friends and other members of the department for being so supportive and helpful in every possible way.

CONTENTS

ABSTRACT

Biofuels are alcohols, ethers, esters and other chemicals made from cellulosic biomass, large portions of municipal solid and industrial wastes. Biofuels are renewable since they are produced from biomass i.e. from organic matter such as plants . Biomass does not add carbon dioxide to the atmosphere as it absorbs the same amount of carbon in growing as it releases when consumed as a fuel. Biomass recycles carbon from the air and spares the use of fossil fuels, reducing the need to pump additional fossil carbon from ground into the atmosphere.

Pyrolysis of biomass consists of heating solid biomass in the absence of air to produce solid, liquid and gaseous fuels. In this experimental work rapid pyrolysis of wood and some agricultural residues at high temperature (400ºC – 700ºC) is carried out. The composition of the biomass influences the product distribution. Longer residence time in rapid pyrolysis increases the time for contact between tar and char which makes the char less reactive. The main product obtained by the rapid pyrolysis of wood is bio-oil which acts as an alternative to petroleum products.

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

INTRODUCTION –

Humans live in the twenty-first century. They have traveled very far from their beginning, the cradle of life, their provenance. They have shed their nomadic traditions, their fight for survival with the nature and no longer are beggars at the doors of the supreme force. Having equipped themselves with the ultimate force called **SCIENCE**, they are in a position to challenge the unknown, to challenge what is called destiny and eternity. They have moved from the jungles and caves to sprawling acres called cities filled with all kinds of luxuries and amenities which they couldn't even dream of earlier. They have humbled the unfathomable. Due to science the earth is now a place with huge industries and towering skyscrapers. Science has led to massive industrialization and urbanization which has made people's life an ecstasy. And its a well known fact that for running industries or managing the cities, one needs power:-" **Energy**" . We need energy or power to do even the simplest of work and we get it by substances called **FUELS**-the store house of energy.

Conventionally fuels are either obtained from Coal or from Petroleum or from Natural Gas. There are other sources of energy as well like solar, wind, nuclear energy which are the answer to a small percentage of world's energy needs. Fuels can be classified into two broad categories-

1) Non- renewable Sources of Energy
2) Renewable Sources of Energy

Non- renewable sources as the name suggest are those which cannot be renewed or regenerated. Coal, Petroleum and Natural Gas come under this category. We can call these as fossil fuels as well. If once these sources are exhausted; we cannot obtain these by any means as these are formed by the natural process which takes millions of years. Around 85-90% of worlds total energy demand is met by this type.

Renewable energy on the other hand consist of those sources which can be either renewed or are present in huge and vast which will take a lot of years to consume them. They are perennial in nature and are renewed by the nature itself. Wind energy, solar energy, biomass energy, energy possessed by running water etc. Though these have huge potentials, due to lack of available technology and the inconveniences in handling them, a very small fraction of these have been utilized till date.

As man is progressing accompanied by urbanization and industrialization, two very serious menaces are raising their ugly faces which threaten the very existence of life on earth. First of all with such rapid development, nations and people are facing energy shortage. We have used our energy sources to such an extent that there is a danger of their complete extinction which might be just a few years away. Day by day the huge, once considered perennial storages of coal are diminishing. The story of petroleum isn't different altogether. As the world is advancing, the energy crisis is deepening. The prices of petrol and diesel are sky rocketing day by day. Similarly coals prices are reaching astronomical prices. Secondly the use of fossil fuels has led to extensive pollution. It has resulted in severe air as well as water pollution. Moreover the use of fossil fuels result in generation of large amounts of Carbon Dioxide and other Green House gases which are leading to global warming. The twin problem of pollution mainly due to the effluents and the release of Green House gases is a thing to worry about. Unless some thing is done quickly, we have to face the implications and consequences which are well known to each one of us. We have to sort this out as quickly as possible otherwise no one can save the earth from the hellish doomsday.

One of the solutions lies in looking for other avenues of fuels, alternate sources of energy, unconventionally sources of energy. Thus now a day man is trying hard to find ways to tap the best out of the renewable sources. A lot of work is being done to utilize Solar, Wind energy, Hydel energy, Geo thermal energy and the energy stored in biomass. Our endeavor is to find out and obtain fuels from biomass which could be a solution to tomorrow's answer.

CHAPTER 2

LITERATURE REVIEW

2.1 WHAT IS BIOMASS?

Biomass is the term used to describe all the organic matter, produced by photosynthesis that exists on the earth's surface. Biomass is a renewable energy resource derived from the carbonaceous waste of various human and natural activities. It is derived from numerous sources, including the by-products from the timber industry, agricultural crops, raw material from the forest, major parts of household wastes and wood.

With its zero emission of CO_2, biomass is one of the most potentially rich resources of energy that is yet to be tapped to the utmost extent. The source of all energy in biomass is the sun, thus biomass acts as a kind of chemical energy store. Biomass is constantly undergoing a complex series of physical and chemical transformations and being regenerated while giving off energy in the form of heat to the atmosphere.

Biomass does not add carbon dioxide to the atmosphere as it absorbs the same amount of carbon in growing as it releases when consumed as a fuel. Biomass recycles carbon from the air and spares the use of fossil fuels, reducing the need to pump additional fossil carbon from ground into the atmosphere. Biomass comes from green plants which actively absorbs carbon dioxide from the atmosphere and converts it into sugars, which are then stored in long molecules like cellulose. Eventually this plant carbon is returned to the atmosphere by natural decay process including the breakdown of cellulose. We can intervene in this process by breaking down cellulose to glucose in bio mass processing plants, and then converting the sugars to ethanol, which is a substitute for gasoline. Using ethanol made from biomass, sugars reduce the need for fossil fuels like gasoline. Ethanol can also be used to power fuel cells and is easier to store and distribute than gaseous hydrogen.

Its advantage is that it can be used to generate electricity with the same equipment or power plants that are now burning fossil fuels. Biomass is an important source of energy and the most important fuel worldwide after coal, oil and natural gas.

2.2BIO-FUELS FROM BIOMASS

Traditionally the extraction of energy from biomass is split into 3 distinct categories:

SOLID BIOFUELS

These include the use of trees, crop residues, animal and human wastes (although not strictly a solid biomass source, it is often included in this category for the sake of convenience), household or industrial residues which are used for direct combustion to provide heat. Often the solid biomass will undergo physical processing such as cutting, chipping, briquetting, etc. but retains its solid form. Also compressed peat and dry bagasse come under this category which can be burnt to get heat as a form of energy.

LIQUID BIOFUELS

These are obtained by subjecting organic materials to one of various chemical or physical processes to produce a usable, combustible, liquid fuel. Biofuels such as vegetable oils or ethanol are often processed from industrial or commercial residues such as bagasse (sugarcane residue remaining after the sugar is extracted) or from energy crops grown specifically for this purpose. Biofuels are often used in place of petroleum derived liquid fuels. Liquid biofuels basically consist of liquid extracted from biomass and used for the production of other useful chemicals. This liquid stream consists of bio fuels called **BIO-OIL** .It is dull black-brown liquid and remains in liquid form at room temperature. This consists of many chemicals mainly ethanol, acetone, acetic acid etc.

GASEOUS BIOFUELS

Gaseous fuels such as biogas are obtained by anaerobically (in an air free environment) digesting organic material to produce a combustible gas known as methane. Animal waste and municipal waste are two common feedstocks for anaerobic digestion. Gaseous bio-fuels obtained from biomass decomposition contain primarily hydrogen, methane, carbon monoxide, ammonia and other gases depending upon the organic nature of biomass and the process condition.

Traditional use of biomass is more than its use in modern application. In the developed world biomass is again becoming important for applications such as combined heat and power generation. In addition, biomass energy is gaining significance as a source of clean heat for domestic heating and community heating applications. In fact in countries like Finland, USA and Sweden the per capita biomass energy used is higher than it is in India, China or in Asia.

Biomass fuels used in India account for about one third of the total fuel used in the country, being the most important fuel used in over 90% of the rural households and about 15% of the urban households.

Instead of burning the loose biomass fuel directly, it is more practical to compress it into briquettes (compressing them through a process to form blocks of different shapes) and thereby improve its utility and convenience of use. Such biomass in the dense briquetted form can either be used directly as fuel instead of coal in the traditional chulhas and furnaces or in the gasifier. Gasifier converts solid fuel into a more convenient-to-use gaseous form of fuel called producer gas.

Scientists are trying to explore the advantages of biomass energy as an alternative energy source as it is renewable and free from net CO2 (carbon dioxide) emissions, and is abundantly available on earth in the form of agricultural residue, city garbage, cattle dung, firewood, etc. Bio-energy, in the form of biogas, which is derived from biomass, is expected to become one of the key energy resources for global sustainable development.

At present, biogas technology provides an alternative source of energy in rural India for cooking. It is particularly useful for village households that have their own cattle. Through a simple process cattle dung is used to produce a gas, which serves as fuel for cooking. The residual dung is used as manure.

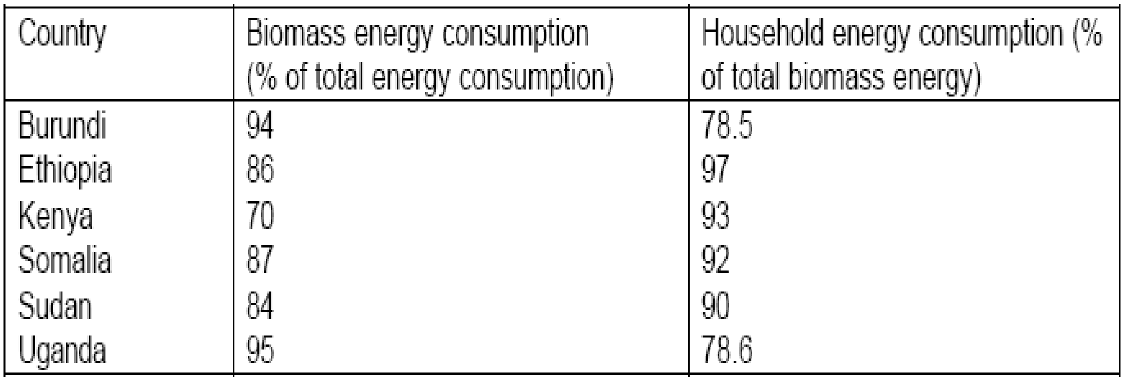
Biogas plants have been set up in many areas and are becoming very popular. Using local resources, namely cattle waste and other organic wastes, energy and manure are derived.

Indian sugar mills are rapidly turning to bagasse, the leftover of cane after it is crushed and its juice extracted, to generate electricity. This is mainly being done to clean up the environment, cut down power costs and earn additional revenue. According to current estimates, about 3500 MW of power can be generated from bagasse in the existing 430 sugar mills in the country. Around 270 MW of power has already been commissioned and more is under construction.

Moreover a lot of chemicals are obtained from various biomasses. These include many pharmaceuticals and medicines, acetic acid, rayon, cellophane, various plastics, paints and resigns, turpentine, food additives, citric acid, vitamins such as riboflavin etc.

2.3 BIOMASS USE IN THE DEVELOPING WORLD

More than two million people in the developing world use biomass for the majority of their household energy needs. It is used mainly for cooking, heating water and domestic space heating. Table 1 below shows household energy consumption as a percentage of total biomass consumption in a number of selected countries in Africa. Biomass is also used widely for non-domestic applications.



Country	Biomass energy consumption (% of total energy consumption)	Household energy consumption (% of total biomass energy)
Burundi	94	78.5
Ethiopia	86	97
Kenya	70	93
Somalia	87	92
Sudan	84	90
Uganda	95	78.6

Table 1: Household energy consumption as a percentage of total biomass consumption in a number of selected African countries

2.4 BIOMASS RESOURCES

As mentioned earlier, natural biomass resources vary in type and content, depending on geographical location. For convenience sake, we can split the world's biomass producing areas into three distinct geographical regions:

TEMPERATE REGIONS -These provide wood, crop residues, such as straw and vegetable leaves, and human and animal wastes. In Europe short rotation coppicing (SRC) has become popular as a means for supplying wood fuel for energy production on a sustainable basis.

Fast growing wood species, such as willow are cut every two to three years and the wood chipped to provide a boiler fuel. In the UK there is a functioning 12.6 Megawatt power plant which burns poultry litter (which has relatively low moisture content) as fuel and others which burn wheat straw. There are also many non-woody crops which can be grown for production of biofuels and biogas, and investigation of energy crops for direct combustion is underway. In western countries, where large quantities of municipal waste are generated, this is often processed to provide useful energy either from incineration or through recovery of methane gas from landfill sites.

ARID AND SEMI-ARID REGIONS

These produce very little excess vegetation for fuel. People living in these areas are often the most affected by desertification and often have difficulty finding sufficient wood as fuel.

HUMID TROPICAL REGIONS

These produce abundant wood supplies, crop residues, animal and human waste, commercial, industrial and agro- and food-processing residues. Rice husks, cotton husks and groundnut shells are all widely used to provide process heat for power generation, particularly. Sugarcane bagasse is processed to provide ethanol as well as being burned directly; and many plants, such as sunflower and oil-palm are processed to provide oil for combustion. Many of the world's poorer countries are found in these regions and hence there is a high incidence of domestic biomass use. Tropical areas are currently the most seriously affected by deforestation, logging and land clearance for agriculture.

2.5 BIOFUELS

The fuels obtained from biomass are called biofuels .Two major biofuels are Bioethanol and Biodiesel. These fuels are being commercially produced in large scales mainly as an alternative for conventional fuels used for transportation needs.

Bioethanol mainly contains ethanol similar to the ethanol used in beverages. It is made by fermenting any biomass reach in carbohydrates (starch, cellulose or sugar) through a process similar to that of the brewing of beer. Bioethanol is mainly used as a fuel additive to cut down vehicle's carbon monoxide and other smog causing emissions. Now a day flexible – fuel vehicles are available which use up to 85% bioethanol.Generally bioethanol is obtained from bagasse.

Biodiesel is made combining alcohol (usually methanol) with vegetable oil, animal fat or recycled cooking greases. It can be used as an additive to reduce vehicle emissions (typically 20%) or in its pure form as renewable alternate fuel for diesel engines.

Other biofuels include methanol and reformulated gasoline components. Methanol, commonly known as wood alcohol is currently produced from natural gas but can also be produced from biomass mainly agricultural wastes. There are a number of ways to produce methanol from biomass but most likely approach is gasification.

Most reformulated gasoline components produced from biomass are pollution –reducing fuel additives, such as methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE).

2.6 WHY BIOFUELS HAVE AN EDGE OVER FOSSIL FUELS

It can be said that carbons obtained from biofuels are better than those emitted by that of fossil fuels because it does not lead to a net increase in atmospheric carbon concentrations. The carbon released by biofuels to the atmosphere was originally derived through photosynthesis by plants that used CO2 from the atmosphere's carbon sink.

Photosynthesis:-

$6CO_2 + 6O_2 + \text{Solar Energy} = C_6H_{12}O_6 + 6O_2$

Fossil fuels on the other hand increase atmospheric CO_2 because the carbon is from the prehistoric carbon that over time and under pressure accumulated in the form of coal, petroleum and natural gas. It can be said that the carbon of fossil fuels comes from a separate, older sink than the terrestrial and atmospheric sinks and therefore leads to net increase in carbon and carbon dioxide levels in the atmospheric sinks.

Carbon obtained from biomass is naturally converted back to CO_2 through respiration and degradation.

Respiration:-

$C_6H_{12}O_6 + 6O_2 = 6H_2O + 6CO_2 + \text{energy}$

Through other means biomass can be converted to CO_2 while providing energy for human usage. Thus one can say that biofuels are forms of renewable sources of energy and alternatives to fossil fuels. Biomass, like coal can be burned to produce steam, heat and electricity, or it can be converted to a liquid fuel such as bioethanol.

2.7 BIOMASS INTO BIOFUELS

Biomass can be converted into biofuels by three main processes:-

1. PHYSICAL PROCESS
2. BIOLOGICAL PROCESS
3. THERMO-CHEMICAL PROCESS

PHYSICAL PROCESS

In this process, the biomasses used are oil rich seeds. Oils are extracted from oilseeds and the extracted oil is refined by esterification with alcohol to reduce viscosity and improve the quality of biofuels.

BIOLOGICAL PROCESS

In biological process, wet biomass is used as raw materials. The wet biomass is treated with micro-organisms in the presence or absence of oxygen for a longer time. The main products obtained in this process are Bioethanol and Bio-Gas. Biological processes are of two types:-

- Fermentation
- Anaerobic Digestion

FERMENTATION:-

Bio-ethanol is generally produced by fermentation of sugar components of biomass. Feedstocks for the process are sugar cane and sugar beets which store the energy as simple sugars, baggase, other plants which store the energy as more complex sugars like starch, cellulosic biomass that is made of very complex sugar polymers, etc. Complex polysaccharides are converted to simple sugars by hydrolysis. During hydrolysis, acids and catalysts are used to catalyze the reaction. Then sugars are converted to ethanol by the fermentation process using yeast or bacteria as catalyst.

ANAEROBIC DIGESTION:-

In this process, the biomass is treated with micro-organisms like yeast in absence of oxygen to produce biogases, the main product being Methane. Depending upon the solid content in biomass, the anaerobic digestion process is classified into two categories:-

- Dry Digestion
- Wet Digestion

In dry digestion process, solid content is 25-30% while in wet digestion the solid content should be less than 15%. Solid content of biomass play an important in designing the reactor and the economy of the process.

THERMO-CHEMICAL PROCESS

In these processes, the feedstock is heated in the presence (or absence) of oxygen or water for a considerable amount of time. The products thus obtained are fuel gases and bio-oils, which can used as fuels directly or are blended with other fuels to increase the efficiency or can be treated by various processes to produce a myriad of energy rich and useful chemicals of various proportions. The different thermo-chemical processes are:-

- COMBUSTION
- GASIFICATION
- PYROLYSIS
- HYDROTHERMAL LIQUIFICATION

COMBUSTION

It involves complete oxidation of carbon to CO_2 accompanied by release of substantial amount of energy which is used up as soon as possible. It includes direct burning of wood, bark of wood, burning of bagasse in boilers, cow dung cakes and detritus of other animals which results in release of energy. This is a very common method of obtaining energy and this practice has been followed by humans for centuries and it is still being followed up. But the thermal efficiency of this process is very low and it is behest with emission related problems.

GASIFICATION:-

Biomass can be converted into Synthesis Gas consisting mainly of Carbon monoxide, Carbon Dioxide and Hydrogen by a high temperature heating process. In this process, the temperature range is high and so is the residence time and the products is mainly gaseous in nature. Normally the gases produced using gasification processes are either used in boilers or for the production of valuable chemicals.

2.8 PYROLYSIS:-

Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam. In some cases catalysts are used to enhance the efficiency. The temperature ranges from around 350^{o} C to 700^{o} C and the products are vapours, char and bio-oil which can further decompose into tar. It is a thermally initiated depolymerization process also known as "**Thermolysis**", which doesn't involve any oxidizing agent. Sometimes with limited supply of oxidizing agent and controlling the reaction leads to partial gasification.Pyrolysis products basically consist of gases like CH_4, CO_2, and NH_3.and liquids like acetone, acetic acid etc. and solid char.

With increasing research in this field, it is believed by various research personnel that pyrolysis (to be specific fast pyrolysis) is one of major areas of development and with slight modification in the process or the process condition, it might act as a proper methodology for the conversion of biomass into biofuels in order to make up the shortcomings, arising due to the depletion of fossil fuels.

DIRECT HYDROTHERMAL LIQUEFACTION

Direct hydrothermal liquefaction involves converting biomass to an oily liquid by contacting the biomass with water at elevated temperatures (300-350°C) with sufficient pressure to maintain the water primarily in the liquid phase (12-20 MPa) for residence times up to 30 minutes. Alkali may be added to promote organic conversion. The primary product is an organic liquid with reduced oxygen content (about 10%) and the primary byproduct is water containing soluble organic compounds.

Table-2.2 Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood

Mode	Conditions	Liquid	Char	Gas
Fast pyrolysis	moderate temperature, short residence time particularly vapour	75%	12%	13%
Carbonisation	low temperature, very long residence time	30%	35%	35%
Gasification	high temperature, long residence times	5%	10%	85%

2.9 LITERATURE OF GASIFICATION AND PYROLYSIS

BIOMASS GASIFICATION

When biomass is heated with no oxygen or only about one-third the oxygen needed for efficient combustion (amount of oxygen and other conditions determine if biomass gasifies or pyrolyzes), it gasifies to a mixture of carbon monoxide and hydrogen—synthesis gas or syngas.

Combustion is a function of the mixture of oxygen with the hydrocarbon fuel. Gaseous fuels mix with oxygen more easily than liquid fuels, which in turn mix more easily than solid fuels. Syngas therefore inherently burns more efficiently and cleanly than the solid biomass from which it was made. Biomass gasification can thus improve the efficiency of large-scale biomass power facilities such as those for forest industry residues and specialized facilities such as black liquor recovery boilers of the pulp and paper industry—both major sources of biomass power. Like natural gas, syngas can also be burned in gas turbines, a more efficient electrical generation technology than steam boilers to which solid biomass and fossil fuels are limited.

Most electrical generation systems are relatively inefficient, losing half to two-thirds of the energy as waste heat. If that heat can be used for an industrial process, space heating, or another purpose, efficiency can be greatly increased. Small modular biopower systems are more easily used for such "cogeneration" than most large-scale electrical generation.

Just as syngas mixes more readily with oxygen for combustion, it also mixes more readily with chemical catalysts than solid fuels do, greatly enhancing its ability to be converted to other valuable fuels, chemicals and materials. The Fischer-Tropsch process converts syngas to liquid fuels needed for transportation. The water-gas shift process converts syngas to more concentrated hydrogen for fuel cells. A variety of other catalytic processes can turn syngas into a myriad of chemicals or other potential fuels or products.

PYROLYSIS

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Lower process temperature and longer vapour residence times favour the production of charcoal. High temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapour residence time are optimum for producing liquids.

Fast pyrolysis for liquids production is of particular interest currently as the liquids are transportable and storage. Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles and a short hot vapor residence time in the reaction zone. Several

reactor configurations have been set up to assure this condition and to achieve yields of liquid product as high as 75% based on the starting dry biomass weight. They include bubbling fluid beds, circulating and transported beds, cyclonic reactors, and ablative reactors.

Fast pyrolysis occurs in a time of few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. The critical issue is to bring the reacting biomass particle to the optimum process temperature and minimize its exposure to the intermediate (lower) temperatures that favour formation of charcoal. One way this objective can be achieved is by using small particles, for example in the fluidised bed processes. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source, which is applied in ablative processes.

In fast pyrolysis biomass decomposes to generate mostly vapours and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yields of liquid.

The essential features of a fast pyrolysis process for producing liquids are:

- Very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed.
- Carefully controlled pyrolysis reaction temperature of around 500ºC and vapour phase temperature of 400-450ºC.
- short vapour residence times of typically less than 2 seconds
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

2.10 CHEMISTRY

In the fast pyrolysis process, biomass is rapidly heated to a temperature of 450-600 ^{o}C. Due to heavy vibrations at this temperature the atoms vibrate apart at random positions. The figure given below shows that fragmentation of a complex structure like wood at random positions results in a wide variety of products.

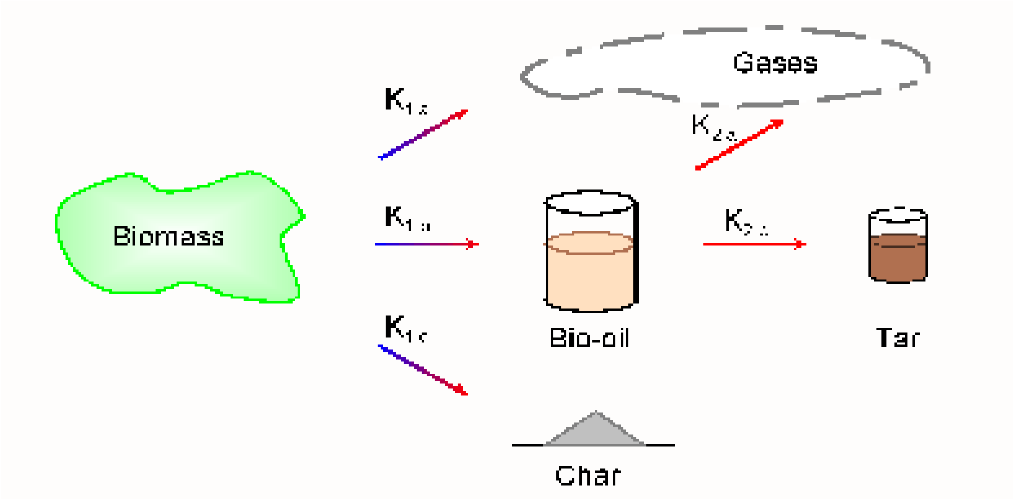


fig 2.1.chemistry of pyrolysis of Biomass

When biomass decomposes at elevated temperatures, three primary products are formed: gas, bio-oil and char. At high temperatures the bio-oil vapours are decomposed in secondary products like gas and polymeric tar.

2.11PYROLYSIS MECHANISM

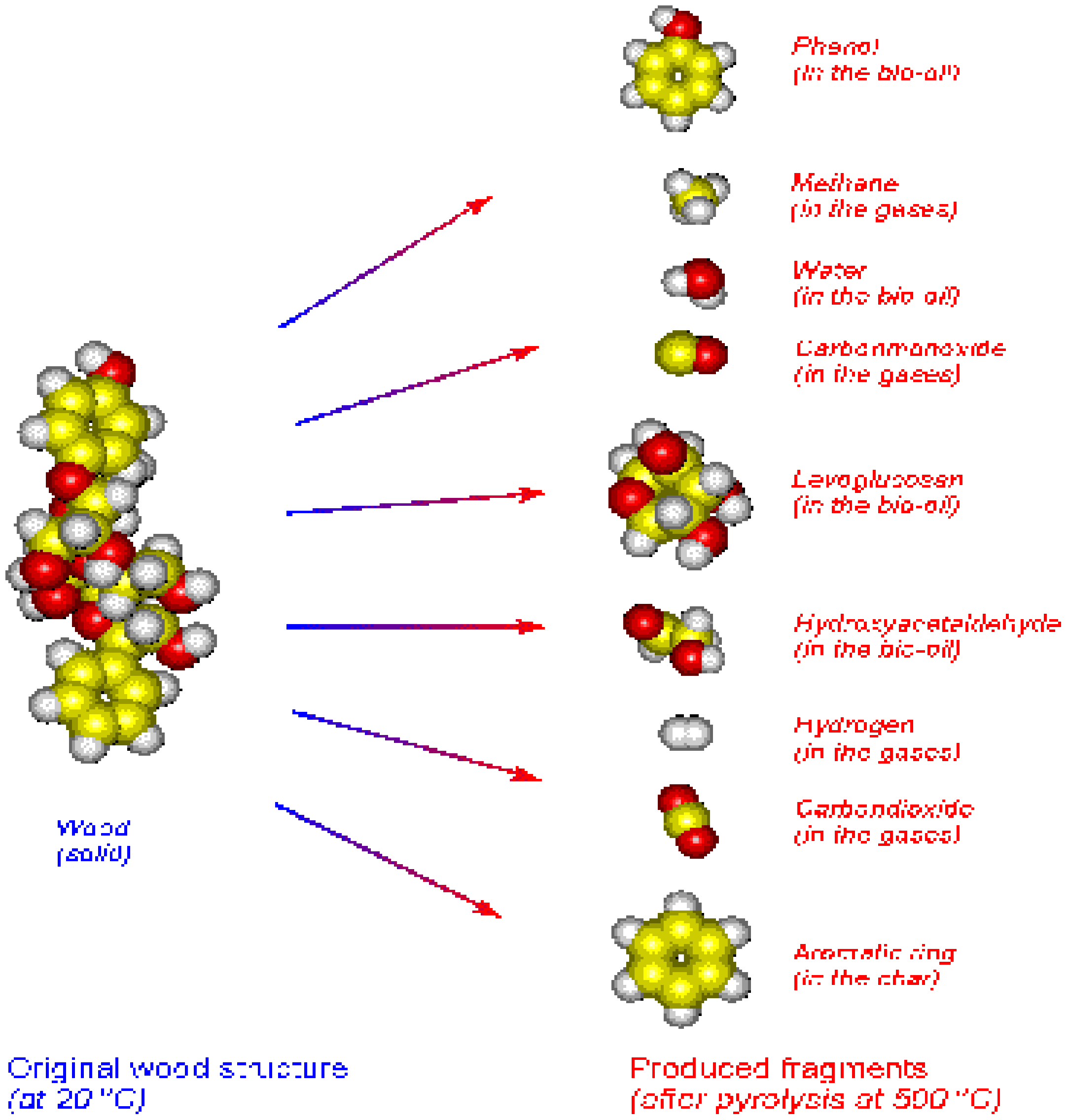


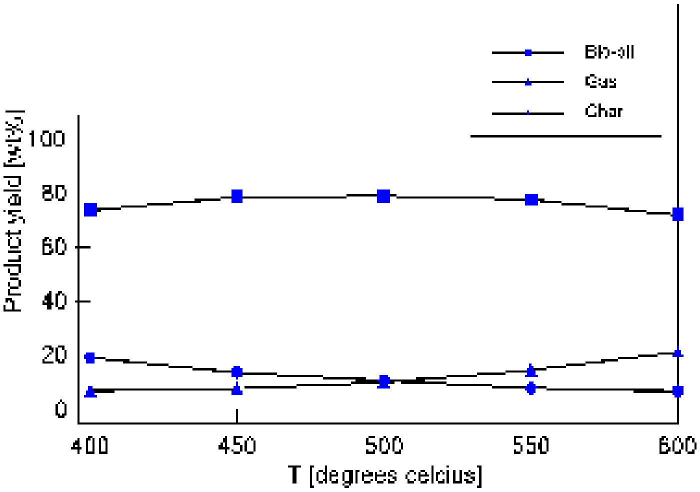
fig.2.2 Pyrolysis Mechanism

The conversion processes of biomass usually involve a reduction of the water content of the material, resulting in the simultaneous increase in its thermal value and preservation potential, and in an improving the handling characteristics of the biomass, for example turning it into a fluid, which may be either gas o liquid? Oxygen removal from the biomass in the form of carbon dioxide (and carbon monoxide) will result in products with high hydrogen to carbon (H/C) ratio.

The time and temperature profile between formation of pyrolysis vapours and their quenching influences the composition and quality of the liquid product. High temperatures will continue to crack the vapours and the longer the vapours are at higher temperatures, the greater the extent of cracking. Vapour residence times of a few hundred milliseconds are necessary for optimum yields of chemicals and food additives, while fuels can tolerate vapour residence times of up to around 2 s. The oils produced by pyrolytic techniques have a relatively higher oxygen content and lower stability than those produced by hydrothermal liquefaction.

The pyrolysis is a fast reaction at temperatures above 300°C. Pyrolysis of cellulose proceeds through two types of reactions: a gradual degradation, decomposition and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures. The initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration and decarboxylation. The high char yield obtained at low heating rate and low temperature can be explained by a predominance of the dehydration reactions. At temperatures below 300°C the dominating reaction of cellulose is dehydration. The gaseous products are carbon dioxide, water and carbon monoxide, while the cellulose is converted to more stable anhydrocellulose. The anhydrocellulose is more stable than cellulose, which results in a high char production. At temperatures above 300°C cellulose depolymerizes producing mainly levoglucosan. High heating rates provide shorter time for the dehydration to take place, which results in a more unstable material left for depolymerization to primary volatiles and therefore lower final char yields.

Yields of the primary pyrolysis products are temperature dependent. It can be observed that a maximum oil yield of 79 wt.% is obtained at 500 °C. For the temperature range studied, the char yield decreases and the gas yield increases with temperature.



graph 2.1.product yield vs temperature

The main product, bio-oil, is obtained in yields of up to 75% wt on dry feed basis, together with by-product char and gas which are used within the process to provide the process heat requirements so there are no waste streams other than flue gas and ash.

A fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimise the water in the product liquid oil (although up to 15% can be acceptable), grinding the feed (to around 2 mm in the case of fluid bed reactors) to give sufficiently small particles to ensure rapid reaction, pyrolysis reaction, separation of solids (char), quenching and collection of the liquid product (bio-oil).

Virtually any form of biomass can be considered for fast pyrolysis. While most work has been carried out on wood due to its consistency, and comparability between tests, nearly

100 different biomass types have been tested by many laboratories ranging from agricultural wastes such as straw, olive pits and nut shells to energy
crops such as miscanthus and sorghum, forestry wastes such as bark and solid wastes such as sewage sludge and leather wastes.

At the heart of a fast pyrolysis process is the reactor. Although it probably represents at most only about 10-15% of the total capital cost of an integrated system, most research and development has focused on the reactor, although increasing attention is now being paid to control and improvement of liquid quality including improvement of collection systems. The rest of the process consists of biomass reception, storage and handling, biomass drying and grinding, product collection, storage and, when relevant, upgrading.

2.12 GENERAL SET UP FOR PYROLYSIS

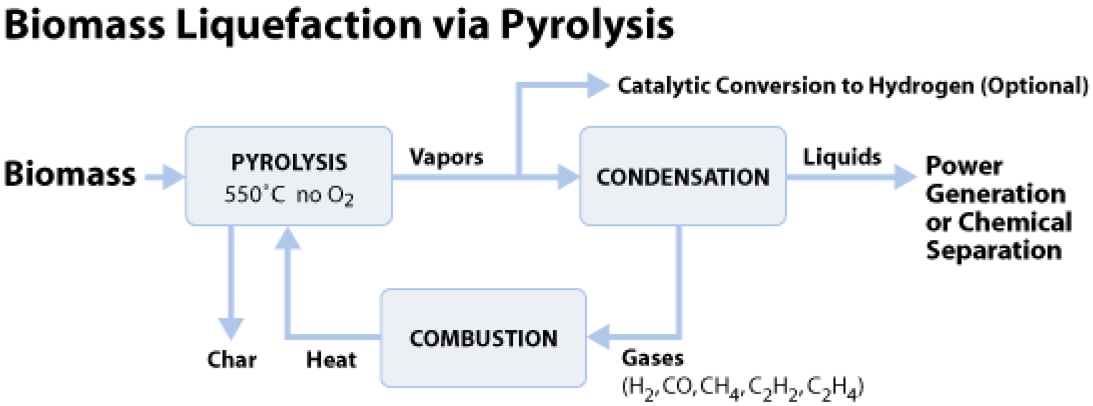


fig.2.3 General set up for Pyrolysis process

2.13 VARIOUS SET-UPS FOR PRODUCTION OF BIO-OIL BY PYROLYSIS:

1) A process flow diagram of BTG's fast pyrolysis process is given below

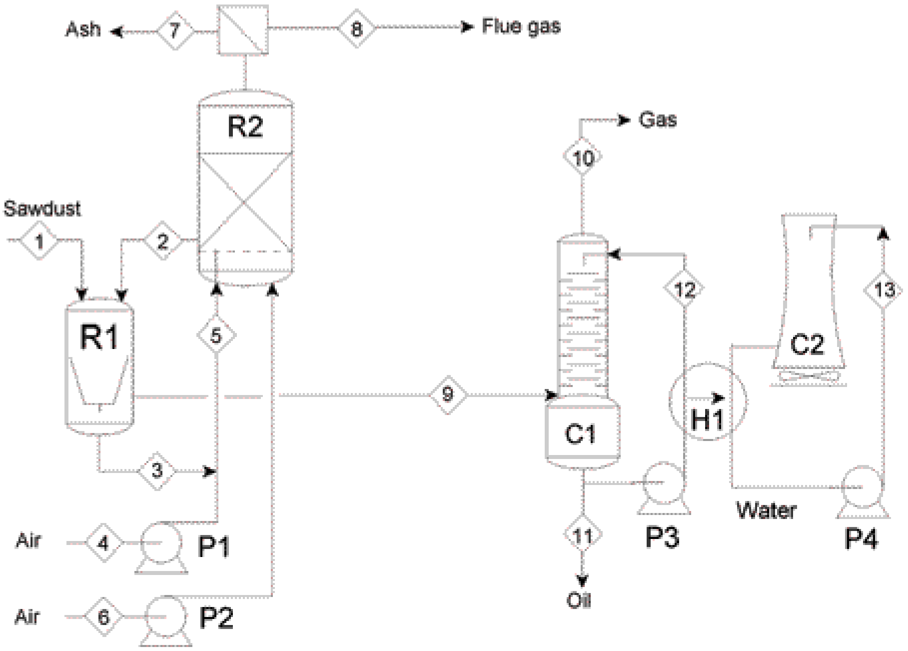


fig2.4 BTG’s fast pyrolysis setup

PROCESS DESCRIPTION:-

Biomass particles are fed near the bottom of the pyrolysis reactor together with an excess flow of hot heat carrier material such as sand, where it is being pyrolysed. The produced vapours pass through several cyclones (not shown) before entering the condenser, in which the vapours are quenched by re-circulated oil. The pyrolysis reactor is integrated in a circulating sand system composed of a riser, a fluidized bed char combustor, the pyrolysis reactor, and a down-comer. In this concept, char is burned with air to provide the heat required for the pyrolysis process. In this case the plant is self sustaining. Oil is the main product; non-condensable pyrolysis gases are currently flared-off, but application in a gas engine is foreseen. Excess heat can be used for drying the feedstock.

2) Dynamotive Biotherm Bio-oil pilot plant

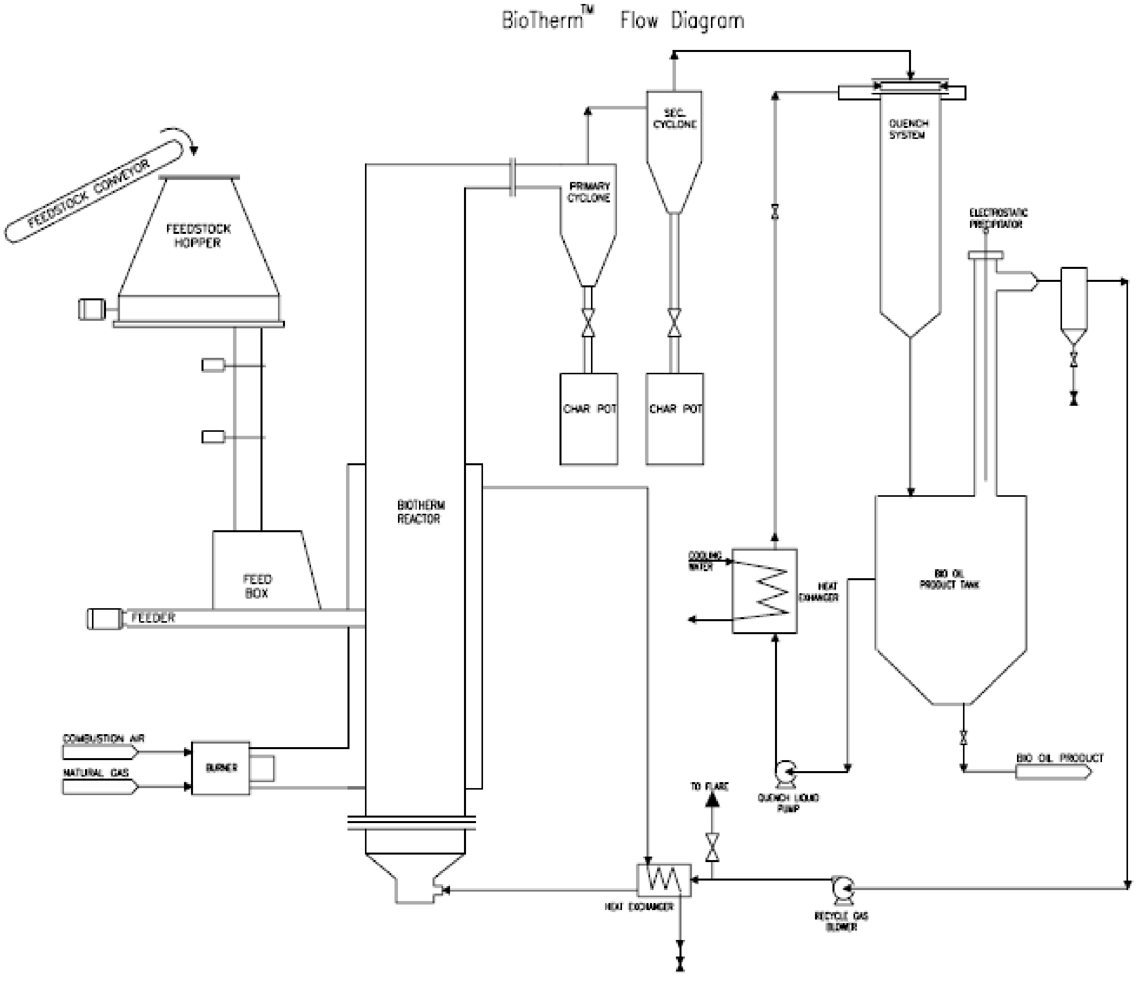


fig.2.5 Dynamotive Biotherm Bio-oil pilot plant set up

PROCESS DESCRIPTION:-

Prepared feedstock is conveyed by an auger to a storage hopper located above the metering feedbox. A screw feeder located under the storage hopper supplies feedstock to a lock hopper, comprising a series of two knife-gate valves which, in turn, supplies the feed to a metering box. This metering box, equipped with a live bottom, feeds a controlled amount of feedstock to the reactor through a constant speed injector screw.

A natural gas burner provides heat to an external jacket surrounding the reactor shell in order to indirectly heat the fluidized sand. The exhaust from the jacket passes through a gas to gas heat exchanger where the recycled pyrolysis gas is preheated before re-entering the reactor. In the BioTherm reactor, feedstock is rapidly heated to temperatures above 450 ^{o}C by fluidized sand, in the absence of oxygen. The biomass decomposes into a combination of solid char, gas, vapors and aerosols. The recycled pyrolysis gases that are used for fluidizing remove the newly formed pyrolysis products from the reactor.

After exiting the reactor, these products pass through two mechanical cyclones arranged in series. These cyclones remove most of the entrained solid char particles. The char is collected in separate char pots located under the cyclones.

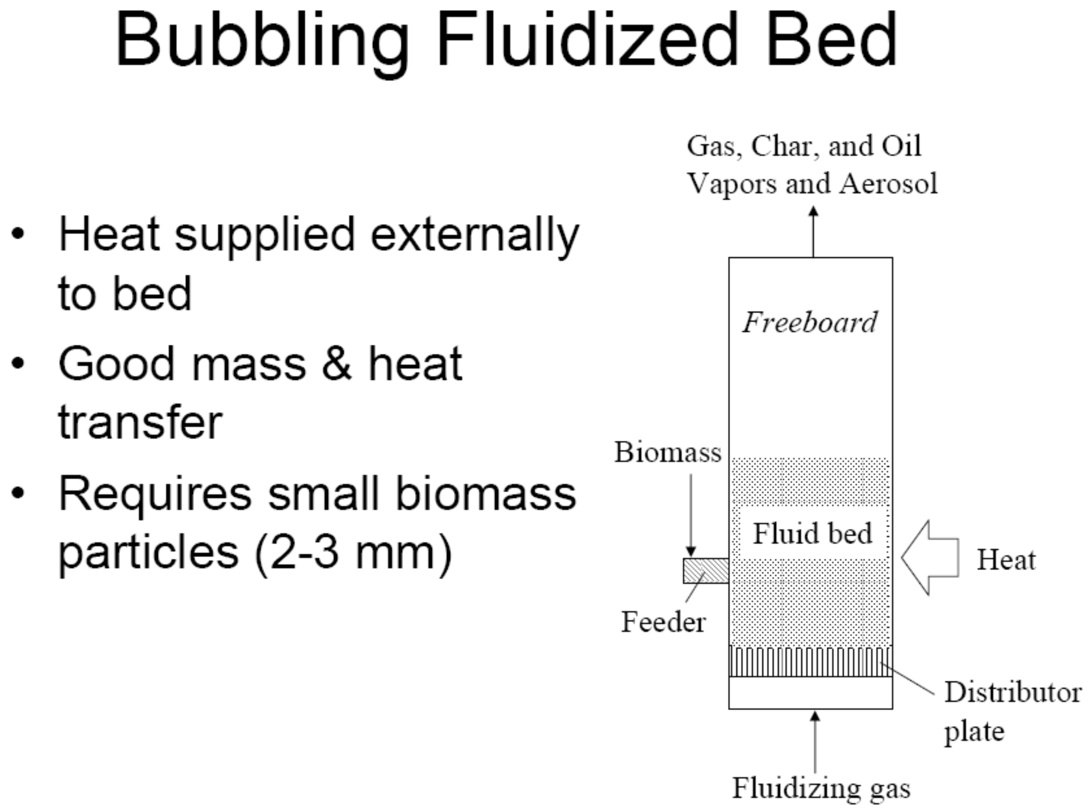
The scrubbed gases, vapors and aerosols then enter a direct quenching system where they are rapidly cooled to below 50□C with a liquid, immiscible in bio-Oil. The Bio-Oil portion of the gases is condensed and collected in a product tank. Quench liquid recovered from this tank is cooled in a heat exchanger then recycled to the recovery system.

The non-condensable gas and any residual bio-Oil aerosol droplets then enter a precipitator which electro statically cleans the gas of all these particulates and aerosols. The clean, inert gas is then recycled back to the bubbling fluid bed reactor. The excess noncondensable gas is vented from the system. This medium calorific gas can be combusted to provide heat to the reactor sand.

Liquid Bio-Oil separates from the quench liquid and is then transferred to shipping containers. The quench liquid is decanted from the tank and recycled to the Bio-Oil recovery system.

2.14 SEVERAL KINDS OF FAST PYROLYSIS REACTORS:

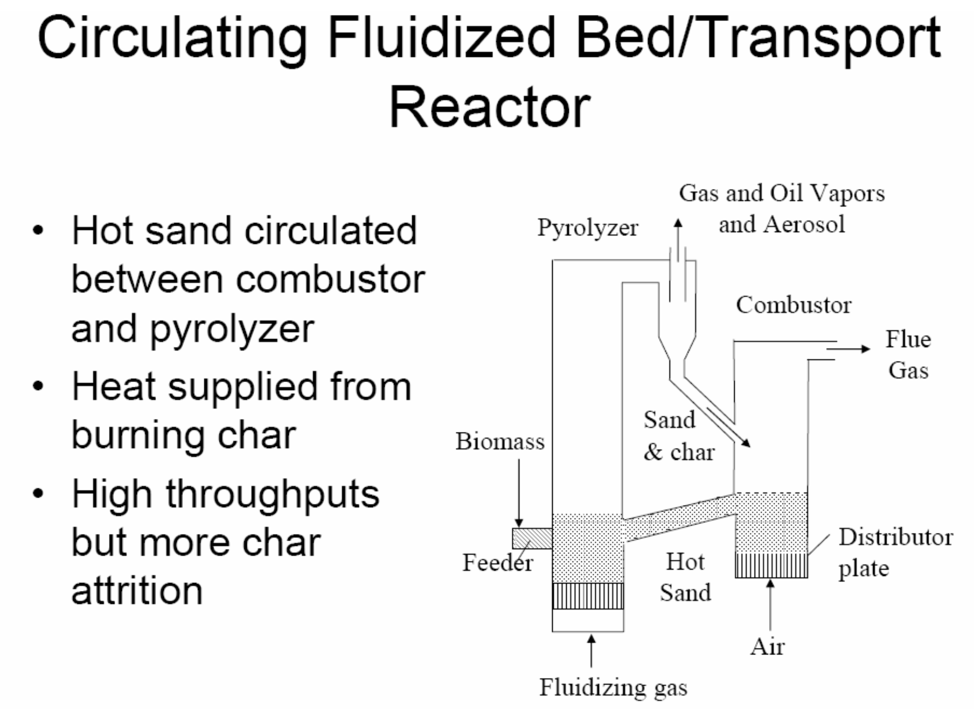
- Bubbling fluidized bed
- Circulating fluidized beds/transport reactor
- Rotating cone pyrolyzer
- Ablative pyrolyzer
- Vacuum pyrolysis
- Auger reactor



Bubbling Fluidized Bed

- Heat supplied externally to bed
- Good mass & heat transfer
- Requires small biomass particles (2-3 mm)

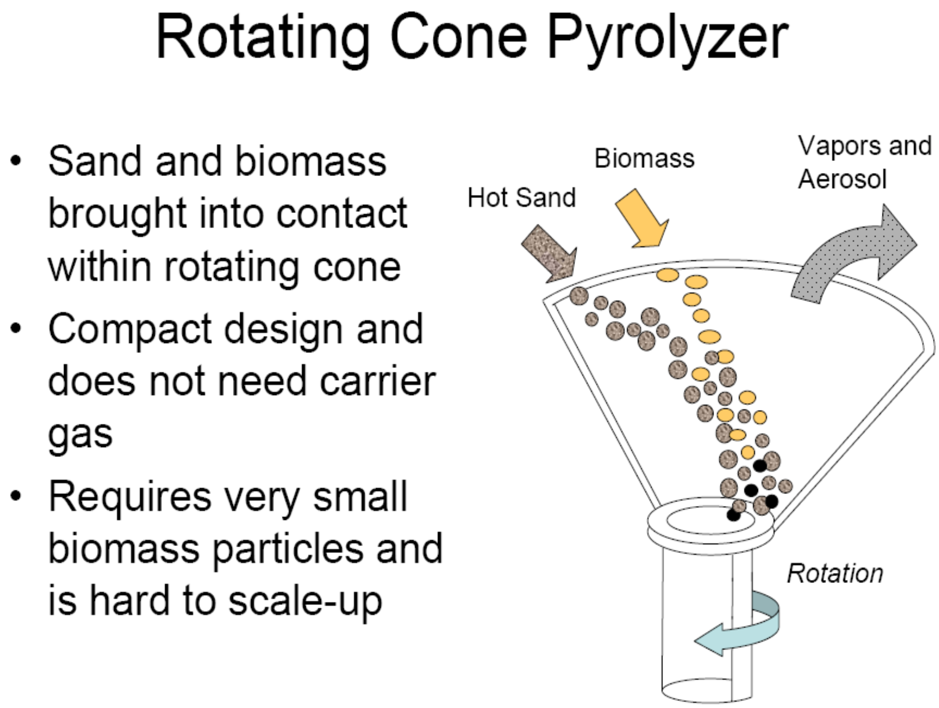
fig.2.6 Bubbling Fluidized Bed



Circulating Fluidized Bed/Transport Reactor

- Hot sand circulated between combustor and pyrolyzer
- Heat supplied from burning char
- High throughputs but more char attrition

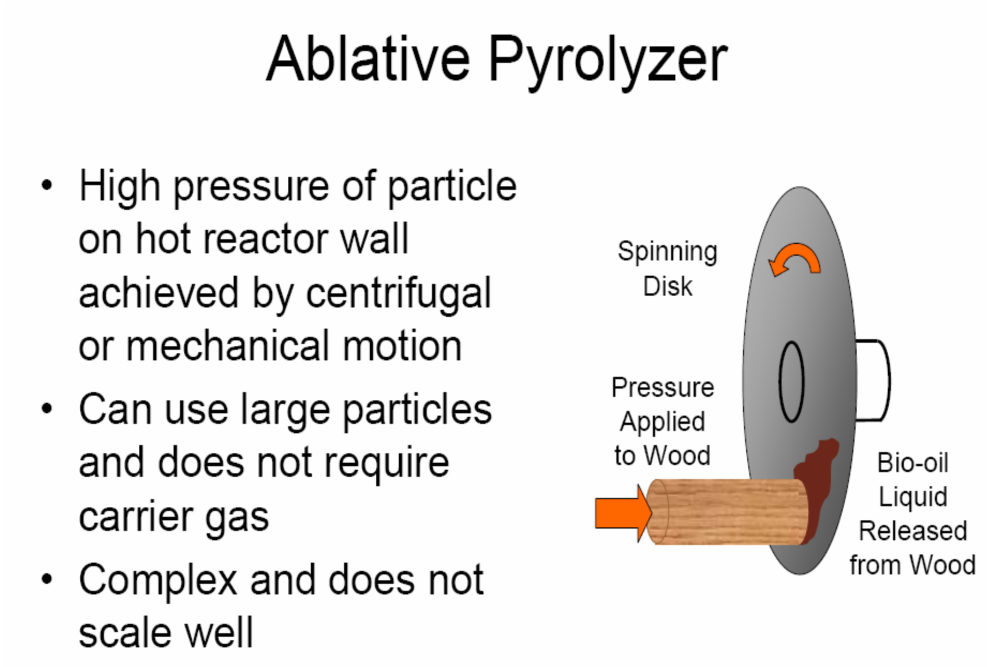
Fig.2.7 Circulating fluidized Bed/Transport Reactor



Rotating Cone Pyrolyzer

- Sand and biomass brought into contact within rotating cone
- Compact design and does not need carrier gas
- Requires very small biomass particles and is hard to scale-up

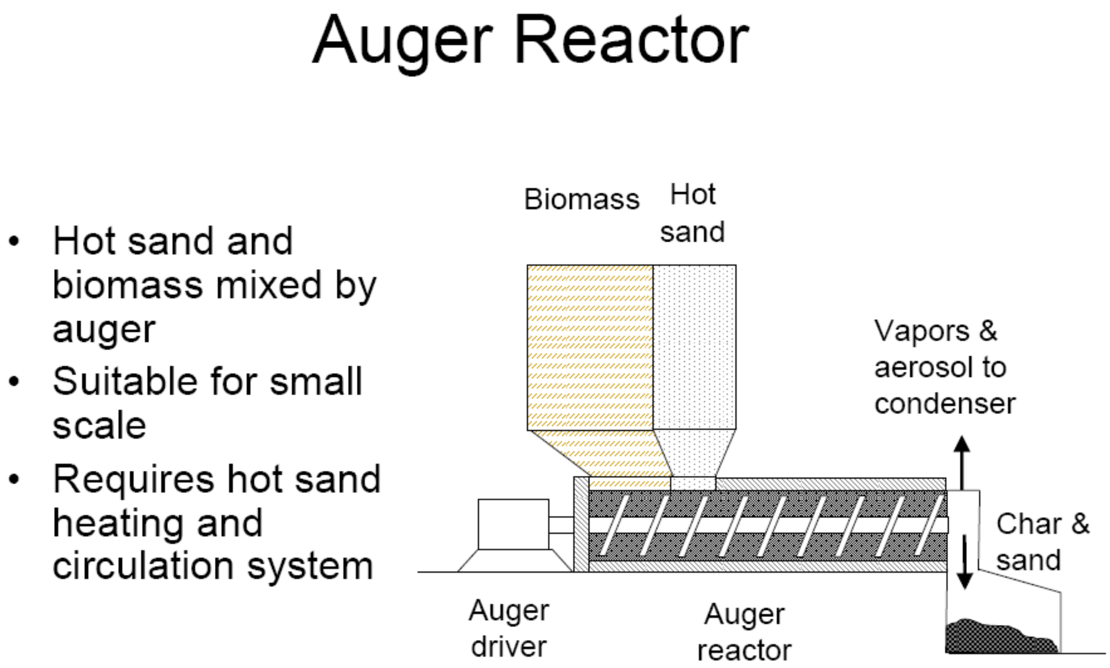
fig2.8 Rotating Cone Pyrolyser



Ablative Pyrolyzer

- High pressure of particle on hot reactor wall achieved by centrifugal or mechanical motion
- Can use large particles and does not require carrier gas
- Complex and does not scale well

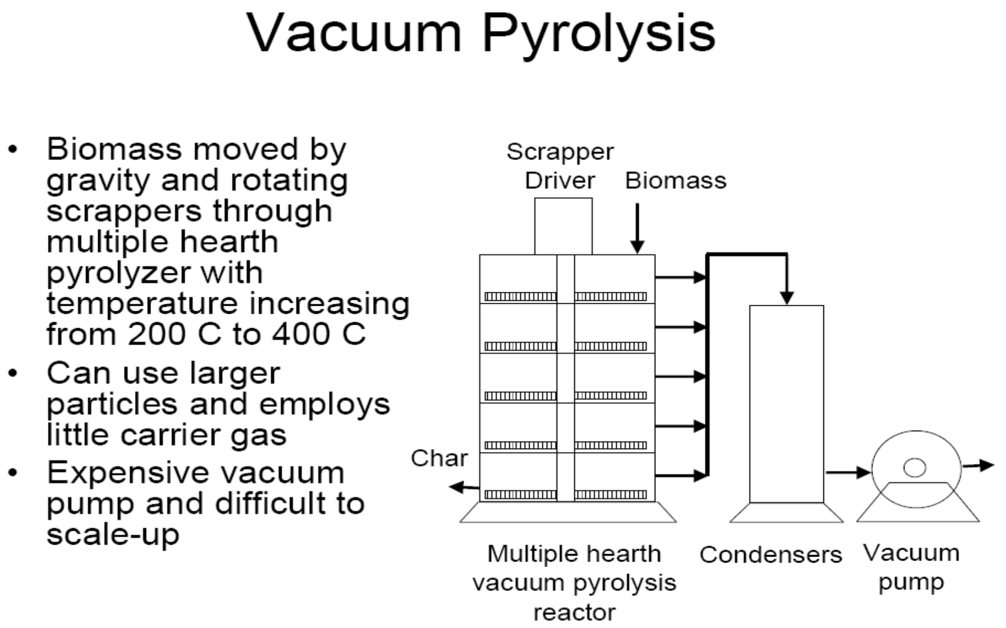
fig2.9 Ablative Pyrolyser



Auger Reactor

- Hot sand and biomass mixed by auger
- Suitable for small scale
- Requires hot sand heating and circulation system

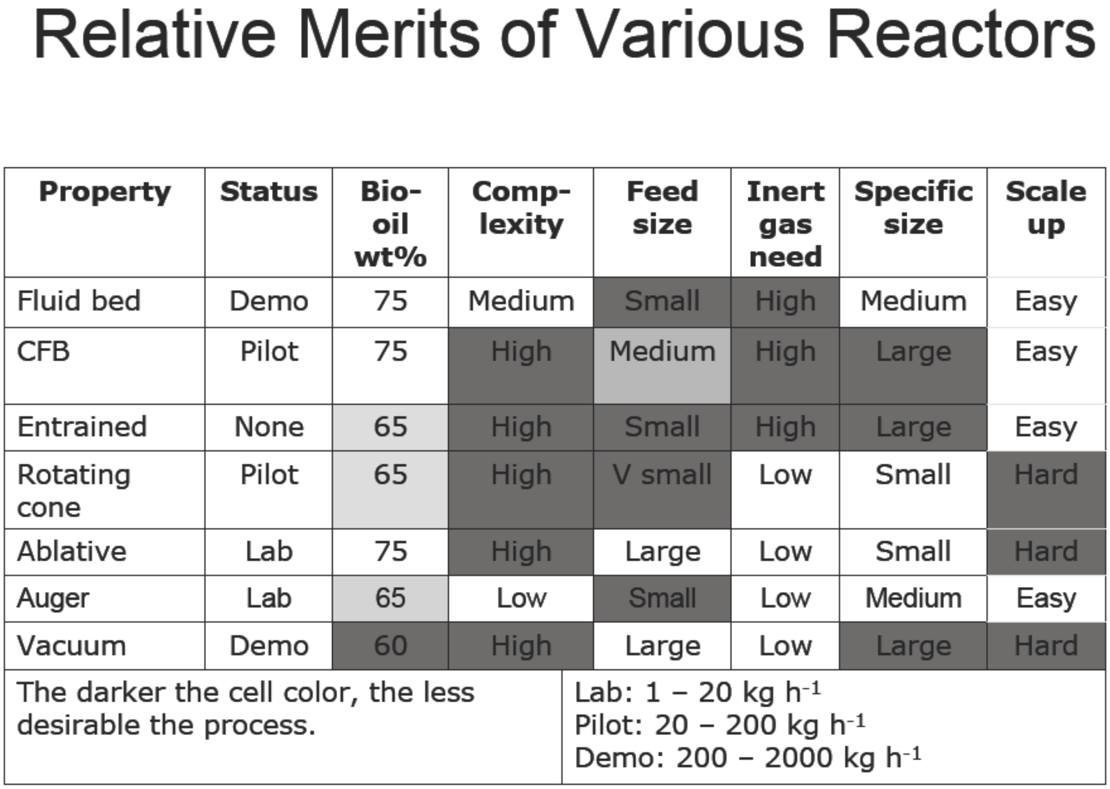
fig2.10 Auger Reactor



Vacuum Pyrolysis

- Biomass moved by gravity and rotating scrappers through multiple hearth pyrolyzer with temperature increasing from 200 C to 400 C
- Can use larger particles and employs little carrier gas
- Expensive vacuum pump and difficult to scale-up

fig2.11 Vaccum Pyrolyser



Relative Merits of Various Reactors

Property	Status	Bio-oil wt%	Comp-lexity	Feed size	Inert gas need	Specific size	Scale up
Fluid bed	Demo	75	Medium	Small	High	Medium	Easy
CFB	Pilot	75	High	Medium	High	Large	Easy
Entrained	None	65	High	Small	High	Large	Easy
Rotating cone	Pilot	65	High	V small	Low	Small	Hard
Ablative	Lab	75	High	Large	Low	Small	Hard
Auger	Lab	65	Low	Small	Low	Medium	Easy
Vacuum	Demo	60	High	Large	Low	Large	Hard

The darker the cell color, the less desirable the process.

Lab: 1 – 20 kg h^{-1}
Pilot: 20 – 200 kg h^{-1}
Demo: 200 – 2000 kg h^{-1}

Table 2.3 Relative comparision between various reactor

2.15 DIFFERENT METHODS FOR BIO-OIL ANALYSIS

The bio-oil thus obtained by the above process has to be subjected to the following analysis methods for determining its characteristics.

These methods include:-

- Fourier Transform Infrared Spectroscopy (FTIR)
- Mass Spectroscopy(MS)
- Nuclear Magnetic Resonance Spectroscopy(NMR)
- Gas Liquid Chromatography(GLC)

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of various infrared light wavelengths by the material of interest. These infrared absorption bands identify specific molecular components and structures.

Absorption bands in the range of 4000 - 1500 wave numbers are typically due to functional groups (e.g. -OH, C=O, N-H, CH3, etc.). The region between 1500 - 400 wave numbers is referred to as the fingerprint region. Absorption bands in this region are generally due to intra-molecular phenomena, and are highly specific for each material. The specificity of these bands allow computerized data searches to be performed against reference libraries to identify a material.

MASS SPECTROSCOPY

Mass spectrometry helps in determining the molecular weight of the sample and hence constituent elements. It is based on slightly different principles to the other spectroscopic methods. The physics behind mass spectrometry is that a charged particle passing through a magnetic field is deflected along a circular path on a radius that is proportional to the mass to charge ratio, m/e. In an electron impact mass spectrometer, a high energy beam of electrons is used to displace an electron from the organic molecule to form a radical cat ion known as the molecular ion**.** If the molecular ion is too unstable then it can fragment to give other smaller ions. The collection of ions is then focused into a beam and accelerated into the magnetic field and deflected along circular paths according to the masses of the ions. By adjusting the magnetic field, the ions can be focused on the detector and recorded.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

Nuclear Magnetic Resonance Spectroscopy most commonly known as NMR Spectroscopy is the name given to the technique which exploits the magnetic properties of nuclei. This phenomenon and its origins are detailed in a separate section on Nuclear magnetic resonance or NMR. Two very important techniques are proton NMR and carbon-13 NMR, although some other nuclei can be measured as well.

Many areas of information can be obtained from this single phenomenon. In its simplest form NMR allows identification of individual atoms in a pure molecule. Analysis of a 1D NMR spectrum tells us what atom environments (like a methyl proton), and in some cases how many atoms of each type, exist within the sample. NMR is based in quantum mechanical properties of nuclei, and as such is very reliable, predictable and reproducible. Since its advent, it has become the most important analytical tool available for organic chemists; it yields far more information than for example infrared spectroscopy.

The impact of NMR Spectroscopy on the natural sciences is substantial. It can be used to study mixtures of analytes; to understand dynamic effects such as change in temperature and reaction mechanisms; it can be used in the solution and solid state; and critically it is an invaluable tool in understanding protein and nucleic acid structure and function.

GAS LIQUID CHROMATOGRAPHY (GLC)

Gas chromatography - specifically gas-liquid chromatography - involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid. Gas chromatography helps in the determination of a variety of substances. By using various types of detectors in the process, one can detect most of the organic compounds, halides, nitrates, nitriles, sulphur, phosphorus, organometallics, aliphatics, aromatics, esters, heterocyclics, organosulphur etc. It is used extensively in the analysis of petroleum and aviation fuels and other oils.

2.16 BIO-OIL :- PYROLYSIS LIQUID

Crude pyrolysis liquid or bio-oil is dark brown and approximates to biomass in elemental composition. It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product. Solid char may also be present.

The liquid is formed by rapidly quenching and thus ‘freezing’ the intermediate products of flash degradation of hemi cellulose, cellulose and lignin. The liquid thus contains many reactive species, which contribute to its unusual attributes. Bio-oil can be considered a micro-emulsion in which the continuous phase is an aqueous solution of holocellulose decomposition products, which stabilizes the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding. Aging or instability is believed to result from a breakdown in this emulsion. In some ways it is analogous to asphaltenes found in petroleum.

Fast pyrolysis liquid has a higher heating value of about 17 $MJkg^{-1}$ as produced with about 25% wt. water that cannot readily be separated. While the liquid is referred to as ‘bio-oil’, it will not mix with any hydrocarbon liquids. It is composed of a complex mixture of oxygenated compounds that provide both the potential and challenge for utilisation. There are some important characteristics of this liquid that are summarised in the table below.

The liquid has a distinctive odour - an acrid smoky smell, which can irritate the eyes if exposed for a prolonged period to the liquids. The cause of this smell is due to the low molecular weight aldehydes and acids. The liquid contains several hundred different chemicals in widely varying proportions, ranging from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides.

The liquid contains varying quantities of water, which forms a stable single phase mixture, ranging from about 15 wt% to an upper limit of about 30-50wt% water, depending on how it was produced and subsequently collected. Pyrolysis liquids can tolerate the addition of some water, but there is a limit to the amount of water, which can be added to the liquid before phase separation occurs, in other words the liquid cannot be dissolved in water. It is miscible with polar solvents such as methanol, acetone, etc. but totally immiscible with petroleum-derived fuels.

The density of the liquid is very high at around 1.2 kg/litre compared to light fuel oil at around 0.85 kg/litre. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications on the design and specification of equipment such as pumps and atomisers in boilers and engines.

The viscosity of the bio-oil as produced can vary from as low as 25 cSt to as high as 1000 cSt (measured at 40°C) or more depending on the feedstock, the water content of the oil, the amount of light ends that have been collected and the extent to which the oil has aged. Viscosity is important in many fuel applications.

Pyrolysis liquids cannot be completely vaporised once they have been recovered from the vapour phase. If the liquid is heated to 100ºC or more to try to remove water or distil off lighter fractions, it rapidly reacts and eventually produces a solid residue of around

50wt% of the original liquid and some distillate containing volatile organic compounds and water. While bio-oil has been successfully stored for several years in normal storage conditions in steel and plastic drums without any deterioration that would prevent its use in any of the applications tested to date, it does change slowly with time; most noticeably there is a gradual increase in viscosity. Recent samples that have been distributed for testing have shown substantial improvements in consistency and stability.

Table 2.4.Typical properties of wood derived crude bio-oil

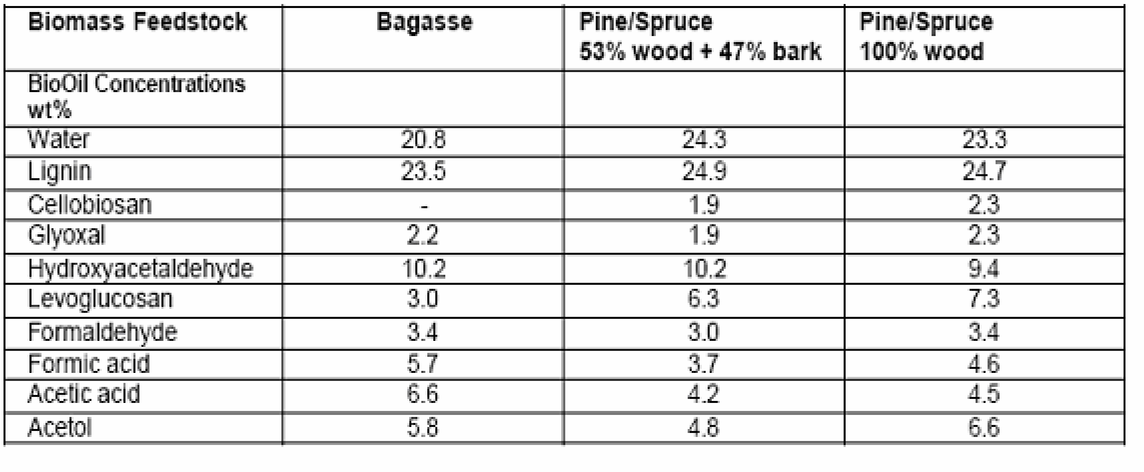
Physical property	Typical value	Characteristics
Moisture content	20-30%	· Liquid fuel
pH	2.5	
Specific gravity	1.20	· Ready substitution for conventional fuels in many stationary applications such as boilers, engines, turbines
Elemental analysis		
C	55-58%	
H	5.5-7.0%	· Heating value of 17 MJ/kg at 25% wt. water, is about 40% that of fuel oil / diesel
O	35-40%	
N	0-0.2%	
Ash	0-0.2%	
HHV as produced	16-19 MJ/kg	· Does not mix with hydrocarbon fuels
Viscosity (40C and 25% water)	40-100 cp	· Not as stable as fossil fuels
Solids (char)	0.1 – 0.5%	· Quality needs definition for each application,
Vacuum distillation residue	up to 50%	

2.17 COMPARISON OF BIO-OIL CHARACTERISTICS OBTAINED FROM VARIOUS BIOMASS

In general the density of BioOil is high, approximately 1.2 kg/liter. On a volumetric basis BioOil has 55% of the energy content of diesel oil and 40% on a weight basis. The solids entrained in the BioOil principally contain fine char particles that are not removed by the cyclones. As can be seen, the solids in the BioOil have been reduced significantly to levels of approximately 0.1% by weight. The ash content in these solids ranges from 2% to 20%, depending on the ash content in the feedstock. BioOil is miscible with alcohols such as ethanol and methanol but is immiscible with hydrocarbons.

The chemical composition of bio-oil obtained from various biomass types has been listed in the table below:-

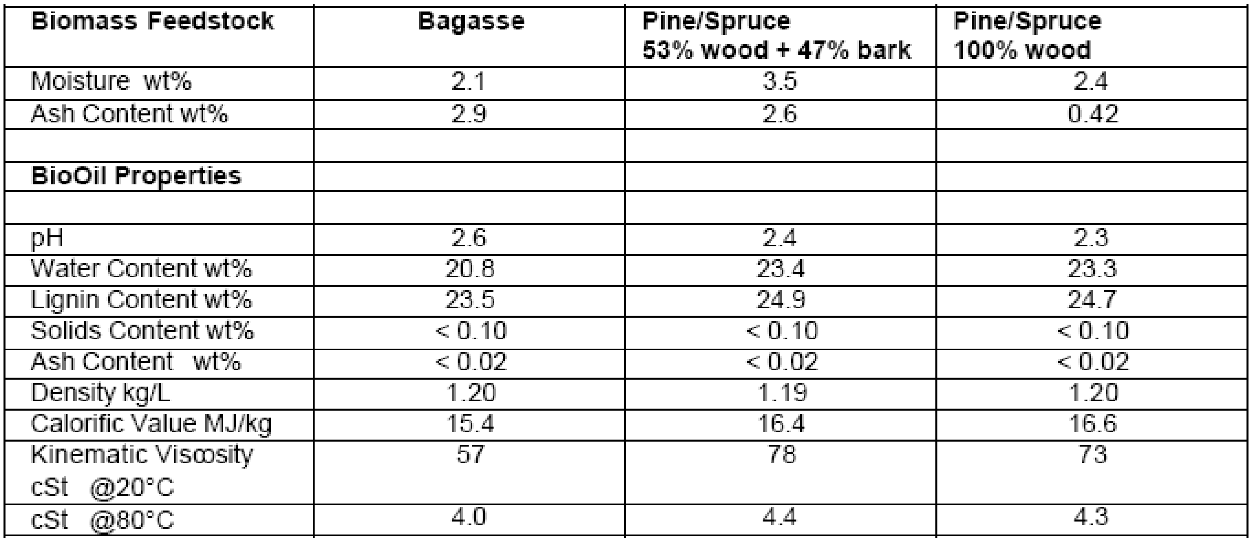
Table 2.5.Chemical composition of bio-oil



Biomass Feedstock	**Bagasse**	**Pine/Spruce 53% wood + 47% bark**	**Pine/Spruce 100% wood**
BioOil Concentrations wt%			
Water	20.8	24.3	23.3
Lignin	23.5	24.9	24.7
Cellobiosan	-	1.9	2.3
Glyoxal	2.2	1.9	2.3
Hydroxyacetaldehyde	10.2	10.2	9.4
Levoglucosan	3.0	6.3	7.3
Formaldehyde	3.4	3.0	3.4
Formic acid	5.7	3.7	4.6
Acetic acid	6.6	4.2	4.5
Acetol	5.8	4.8	6.6

The table below gives the characteristics of bio-oil derived from various biomass sources.

Table 2.6 characteristics of bio-oil



Biomass Feedstock	**Bagasse**	**Pine/Spruce 53% wood + 47% bark**	**Pine/Spruce 100% wood**
Moisture wt%	2.1	3.5	2.4
Ash Content wt%	2.9	2.6	0.42
BioOil Properties			
pH	2.6	2.4	2.3
Water Content wt%	20.8	23.4	23.3
Lignin Content wt%	23.5	24.9	24.7
Solids Content wt%	< 0.10	< 0.10	< 0.10
Ash Content wt%	< 0.02	< 0.02	< 0.02
Density kg/L	1.20	1.19	1.20
Calorific Value MJ/kg	15.4	16.4	16.6
Kinematic Viscosity cSt @20°C	57	78	73
cSt @80°C	4.0	4.4	4.3

CHAPTER 3

EXPERIMENTAL WORK

3.1 OUR PROPOSED EXPERIMENTAL SET UP

Usually a typical pyrolysis set up consists of a reactor maintained in an inert atmosphere, a condenser, a heat exchanger and a bio-oil storage tank. The process is quite similar to the above mentioned procedures. Our setup is similar though with some modifications.

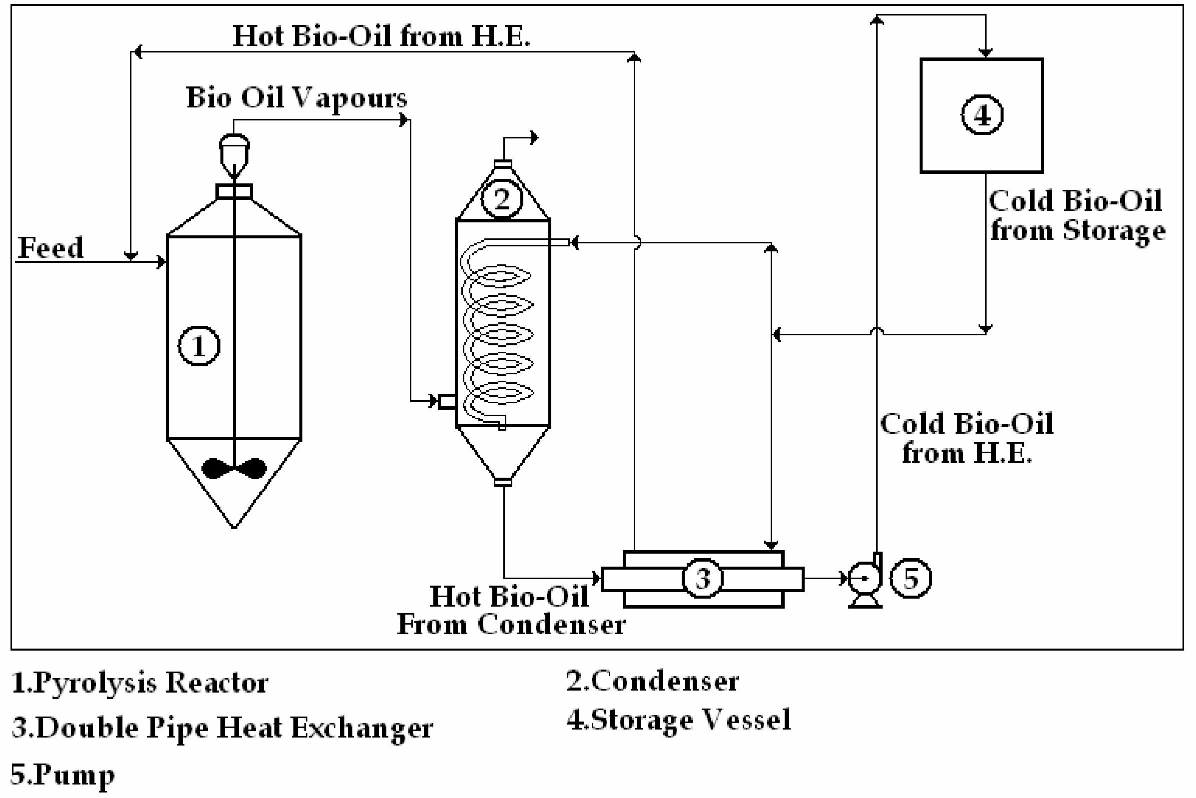


Fig 3.1

In our setup feed along with bio-oil is fed to the reactor. The feed can be wood, wood chips saw dust etc. For the first run, bio-oil with somewhat similar composition as that of the feed biomass has to be taken. It provides the inert atmosphere as it cuts off the contact of the biomass with air as the biomass gets drenched in the bio-oil. The reactor is a vessel of 10L capacity. It is provided with electrical arcs for high temperature heating and in it temperature up to 1000 ^{o}C can be attained. The reactor is provided with an agitator. It is equipped with two thermocouples for constantly measuring and monitoring the temperature of the vessel. In the reactor, temperature can range from around 350 ^{o}C to around 650 ^{o}C for achieving the best efficiency out of the pyrolysis process. The vapours produced after the pyrolysis process would be fed at the bottom of a condenser. The condenser consists of spiral tubes in which cold bio-oil would be circulated. When the vapours would come in contact with the cold bio-oil liquid, condensation would take place resulting in hot bio-oil liquid which would be then taken out of the condenser from the bottom and allowed to pass through a Shell and Tube heat exchanger. In the exchanger, cold bio-oil liquid would be passed in counter– current direction with respect to the hot bio-oil produced. As a result, the cold bio-oil liquid would be heated and this heated liquid would be fed to the main reactor along with the biomass feed. The hot bio-oil liquid that would have cooled to normal temperature would be then sent to the bio-oil storage using a pump.

3.2 RAW MATERIALS USED:-

1) Rice Husk
2) Saw Dust
3) Coconut Coir/Husk

RICE HUSK

RICE husk is the outer covering of paddy and accounts for 20–25% of its weight. It is removed during rice milling and is used mainly as fuel for heating in Indian homes and industries. Its heating value of 13–15 MJ/kg, is lower than most woody biomass fuels. However, it is extensively used in rural India because of its widespread availability and relatively low cost. The annual generation of rice husk in India is 18–22 million tons and this corresponds to a power generation potential of 1200 MW. A few rice husk-based power plants with capacities between 1 and 10 MW are already in operation and these are based either on direct combustion or through fluidized bed combustion. Both these routes are beset with technical problems because of the chemical composition of rice husk and its combustion characteristics.

Rice husk is characterized by low bulk density and high ash content (18–22% by weight). The large amount of ash generated during combustion has to be continuously removed for a smooth operation of the system. Rice husk is a very important raw material for the gasification process as it yields considerable amount of gases like CH_4, CO, CO_2 etc when operated at higher temperatures(>600^0c). At temperatures around 450^0c to 500^0c, the yield of liquid is in substantial amounts and the liquid/oil obtained in this process is further processed to obtain sores of other important chemicals. Normally fluidized reactors are used for the pyrolysis process, though the rotating cone method may be applied in case when there is considerable amount of dust and impurities (like sand) associated with the rice husk. For quite a long time, gasification has been the process associated with rice husk, but in the recent past a lot of focus is being concentrated on the pyrolysis method.

SAW DUST:-

It is the dust obtained during the processing of wood for various purposes. During the processing of wood for making different kinds of furniture, a lot of saw dust is produced which is actually a mixture of wood dust of the various types of wood used in the process. The amount of saw dust produced is quite high and thus its disposal is a serious menace with respect to waste management. Moreover in industries using wood such as sports equipments industries, matchbox industries, packaging industries etc., and a great deal of this waste is produced. Though there are a few methods for its waste disposal, on a large scale it causes enormous problems. It is biodegradable in nature but stacking of large amounts of the dust is a problem as it consumes a lot of space and valuable labour is wasted for its handling.

As a result of the burgeoning amounts of saw dust being produced day to day, and the problems it carries along with it, there has been a cry to look for profitable methods of waste disposal which would be cost effective. Moreover a lot of efforts are being made to drive mileage out of this waste i.e. efforts are being made to derive profitable and useful products from this waste.

And in this regard, subjecting the waste to pyrolysis process to obtain oil/liquid and char is one such widely researched field. In this process the saw dust is feed in the reactors and subjected to high temperatures of around 400^0c to 500^0c. The products are mostly the liquid/oil and char though some amount of off gases are also released. Saw dust is seldom subjected to gasification or carbonization process as the liquid produced in the pyrolysis process acts as a good kind of bio-oil and also various valuable chemicals are processed from it.

COCONUT HUSK:-

In the past, driving around the countryside of the Asian-Pacific region, one could see many coconut husks simply scattered around. This was because of the wrong notion that a coconut husk was nothing but waste material. But now, realizing its true value, resulting from its fibrous structure and resilience, people are able to find many uses and applications for coconut husks. Coconut coir dust is mostly composed of middle lamella and is separated from coir fiber, which is composed of secondary walls. These were supported by lignin content, and structural characteristics of wall polysaccharides and lignin Its coir fibers are extensively used as raw materials for making mattresses, rugs, doormats, and ropes.

Coconut husk is also a good potential energy source because of the high heating values of its three main components :-

1.Lignin
2.Cellulose
3.Hemicellulose

It is better used as a fuel in indirectly-fired kilns than in directly-fired kilns, for it produces quite a large amount of smoke.

Research is also directed towards making coconut husk briquettes or charcoal briquettes, as well as the production of pyrolytic oil from the coconut husk. There is also an interest in the high lignin content of the husk for the manufacture of plastic sheets and the production of metalloligno- sulfonates, which have possible uses as adhesives and emulsifiers.

3.3 PROCEDURE AND PRODUCTS:-

Coconut coir/husk is a very good source for obtaining charcoal..Charcoal can be produced from coconut shell/husk/coir when it is subjected to high temperature pyrolysis process or gasification process. Carbonization or pyrolysis of the shell to produce charcoal is usually conducted in the absence of air and at a temperature of around 500-600^0 C. Normally it has been found out that liquid yilelds of pyrolysis using coconut coir/husk isn't that encouraging. In this process very little amount of liquid products are obtained in comparison to that of the gases formed or the charcoal produced. Hence this is a potential source for the production of charcoal. It has been inferred from data obtained from various tests and experiments that subjecting the raw material to carbonization/gasification process yields more amount of charcoal than the pyrolysis method.

After this carbonization process, the residual charcoal is further processed to decrease the ash content. Charcoal making is principally a small-scale industry. In rural communities, pits are dug from the earth and often lined with bricks to serve as charcoal pyrolyzers. A fire is lit at the bottom of the pit, which is then filled with coconut shells. The recovery of the charcoal from coconut shell is about 20-25%. Due to the large transportation costs and problems brought about by the bulky nature of the coco- nut shell, large-scale production of coconut shell charcoal is uneconomical.

3.4 ACTIVATED CARBON FROM COCONUT SHELLS/HUSK:-

An important application of coconut-shell charcoal would be the manufacture of activated carbon from it. Further processing of charcoal in the presence of oxidizing agents, such as steam and carbon dioxide, will yield a product known as activated carbon.

This product has a high adsorptive capacity due primarily to the large surface area available for adsorption - around 500 to 1500 square meters per gram of activated carbon. This results from the large number of internal pores produced during processing.

Activated carbon from coconut shells is currently being produced in the U.S.A., Europe, Japan, Sri Lanka and the Philippines. Malaysia also manufactures activated carbon, but the raw material being used is palm kernel and wood charcoal from rubber trees.

THE MANUFACTURE OF ACTIVATED CARBON:-

As in most industrial operations, the first step in the manufacture of activated carbon involves preparing raw materials. Screening is employed to remove the powder and other foreign matter so as to improve charcoal quality. After all the impurities are removed then only can the raw material subjected to treatment .The charcoal then goes through the heart of the manufacturing process, the activation. This is done in a rotary kiln.

One type of activation involves the use of steam as an oxidizing agent at a temperature of around 1000^0 C. Under this operating condition, the oxidizing action of steam selectively erodes the surface to increase the surface area, develop greater porosity, and leave the remaining atoms arranged in configurations with specific affinities. The steam is made to flow co current with the flow of the carbon. Thus the gaseous byproducts join the flue gas in leaving the system. The activated carbon is then recovered and further crushed and screened to the desired size, dictated by the market specifications. In certain applications, the product is washed and then dried in a rotary drier, after which it is again screened through a rotary sifter, and then packaged. All this occurs in a continuous operation. In other processes, carbon dioxide can be used instead of steam; at activating temperature of 800-900 C. Alternative equipment to rotary kilns is available for activation purposes. The Herreschoff furnace, for example, is a multiple-hearth furnace equipped with stirrers to constantly change the carbon particles on the surface exposed to the activating gases. These stirrers also lead the carbon particles the next chamber until the activation process has been completed.

Another method makes use of a fluidized bed whereby the activating gases are passed upward through the bed of carbon particles at a sufficient velocity that these particles are kept in a suspended state. In this way, the temperature distribution is uniform and all particles are in contact with the gas stream. The gases obtained during the gasification process are passed through the bed .It has been seen that as a result of this passing of gases, productivity or efficiency in the activated charcoal formation enhances. In some set ups, the gases from gasification/pyrolysis of coconut coir/husk is passed through the beds and act as the fluidizing medium as well. Thus maximum utilization of the byproducts can be made. Product recovery for operations using the fluidized bed also makes use of a different scheme. As carbon particles become activated and reach a certain lower density that corresponds to the desired activity, the activated carbon is carried away by the effluent gases into collectors for separation purposes.

3.5 THE LABORATORY SETUP:-

Introduction:-

As shown below in the diagram, this is a very simple and rudimentary setup. It has been designed keeping in mind that it –

a) The design should be as simple as possible.
b) It could be assembled without much fuss even in small workshops.
c) It should be as economical as possible.
d) It should be convenient to operate.
e) It should be safe enough so as to minimize any health hazards.

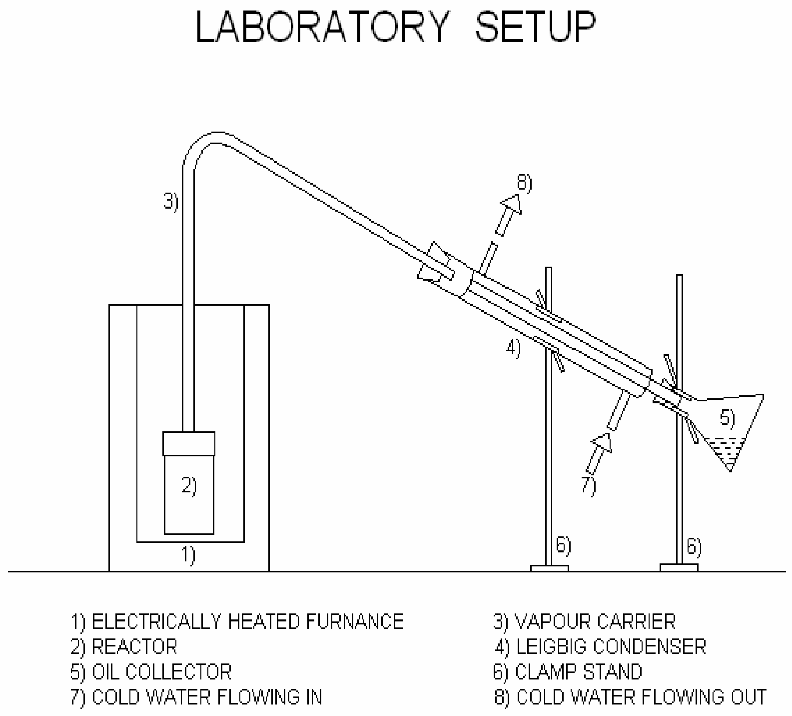


Fig.3.2 laboratory setup

DESCRIPTION:-

It basically consists of a furnace, a condensing system and vessel for storage. The heart of the setup is the electrically heated furnace. In this furnace, one can attain as high as temperatures of 1000^{o}c. Electrical coils are placed inside the furnace and a high voltage thermostat is used to regulate the supply of electric current which in turn is converted into energy in the form of heat. The walls of the furnace are made of highly heat resistant ceramic titles and the outer covering is made up of iron and its alloys. The inside lining of ceramic tiles is highly essential as it not only acts as a high heat resistant material, but also it is necessary for concentrating the released heat and effectively heating the feed in the reactor.

The reactor is a vessel made of mild steel (MS). It is a cylindrical vessel with outside diameter of 3 inches and the height of the reactor is around 6 inches. The thickness of the vessel is around 3 mm. It has its base completely sealed using a 2mm mild steel (MS) plate joined to the parent body using arc welding technique. The top of the vessel is a threaded cap of similar thickness and again it has a similar sealed top but has a opening for letting out a seamless pipe with a 10mm outer diameter.

The condensing system comprises of a transparent glass Leigbig Condenser supported on a long stand. The condensing system is based on a counter-current method of cooling using water as the cooling fluid. Cold water enters the bottom of the condenser, whereas heated water moves out from the top. As a result, the oil flowing inside the condenser is cooled.

Finally there is a provision for oil collection. It consists of a glass flask mounted on a long stand in which the product/liquid condensed is collected and finally taken for storage in glass containers.

Initially feed is taken in the reactor. The stuffing of feed into the reactor should be in such a manner that air content is as minimum as possible. This is because pyrolysis occurs in absence of air or the presence of very minimal amount of air. A suitable temperature is set which would be attained inside the furnace. The reactor is placed inside the electrical furnace and the furnace is switched on. Slowly but steadily, as the coils are heated, temperature increases and as a result, the feed stock gets heated up. After certain amount of time, during which proper heating of the feed has been done, vapours get evolved from the reactor and move up the seamless pipe into the condenser. Here vapours are condensed using the cold water system and as a result liquid droplets are formed. Finally, the liquid droplets formed are collected in the flask and then taken out for storage.

3.6 ARGUMENTS IN FAVOUR FOR SELECTING THE PARTICULAR DESIGN:-

Normally the reactors used in various commercial pyrolysis setups are either fluidized bed reactors or agitating type reactors. No doubt, they yield products with very good efficiency but these are very expensive. Our setup has been designed keeping in mind this factor. Our endeavor is to study what differences will occur if no fluidizing or agitating mechanism is used. Here we have selected a very easy to assemble design and which is quite economical. The results obtained using this process would be compared with the theoretical and existing procedures and then conclusions regarding efficiency, cost effectiveness and ease of handling can be drawn out.

CHAPTER 4

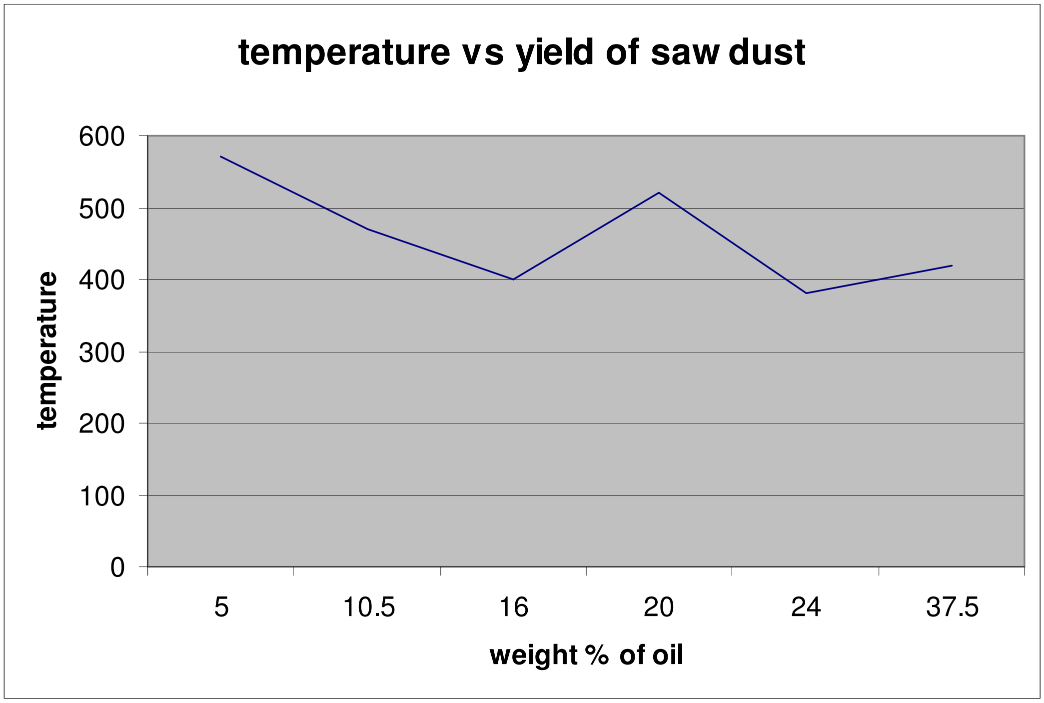
OBSERVATION AND RESULTS

OBSERVATIONS AND INFERENCES:-

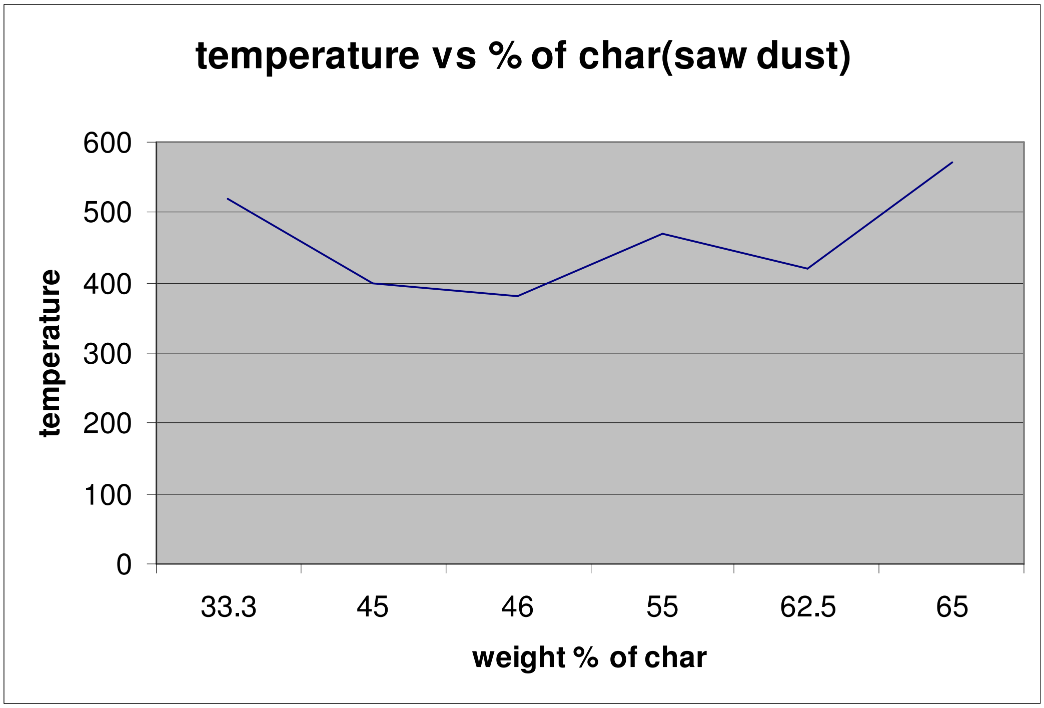
4.1 OBSERVATIONS FOR SAW DUST

S.L.N.O	Temperature (in ^{0} c)	Weight of Feed (in gms)	Weight of Oil (in gms)	Weight of Char (in gms)	Amount of Oil (in wt %)	Amount of Char (in wt %)
1.	380	50	12	23	24	46
2.	400	60	10	27	16.67	45
3.	420	40	15	24	37.5	60
4.	470	38	04	21	10.53	55.26
5.	520	30	06	10	20	33.33
6.	570	40	02	26	05	65

Table 4.1. Observations for Saw Dust



Graph 4.1.temperature vs yield for saw dust



Graph 4.2 .temperature vs % char for saw dust

INFERENCES:-

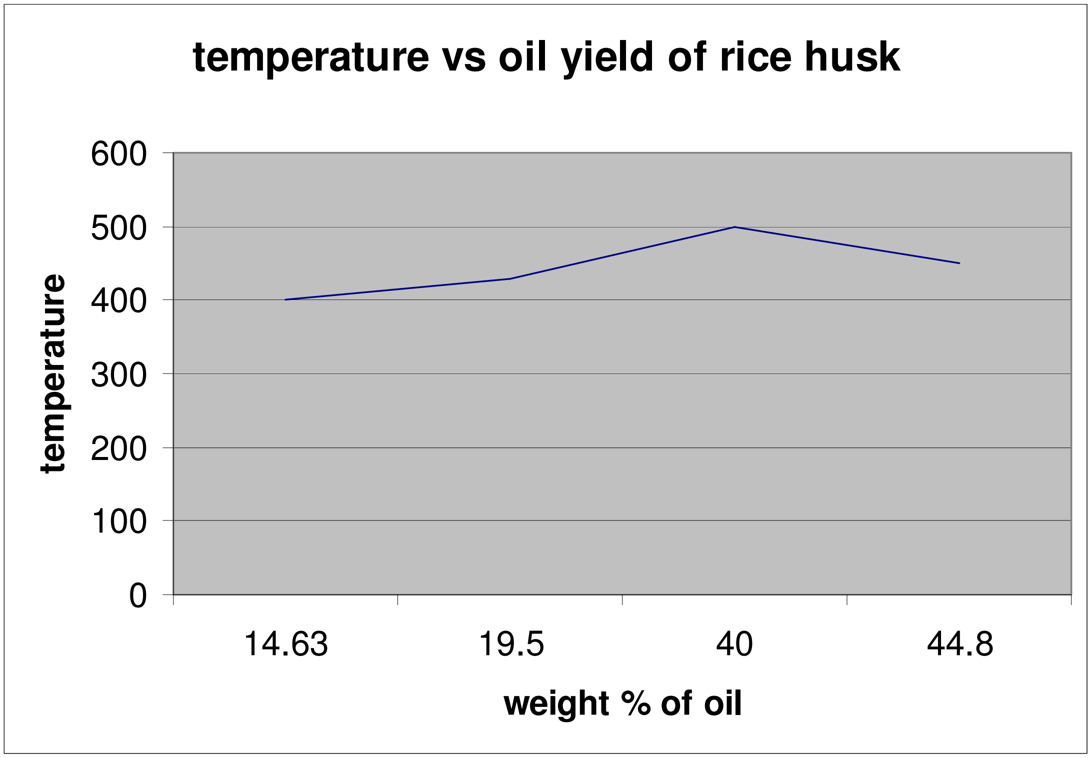
Initially saw dust was taken as the feed in the reactor and it was subjected to pyrolysis under test conditions. The experiments were carried out under a wide range of temperatures varying from around 380^0c to 570^0c. But all the tests were carried out under atmospheric pressure.

It was observed that highest (% by weight) of the liquid/oil was 37.5 at 420^0c and lowest was 5 at 570^0c. In the case of char, the highest (% by weight) was 65 at 570^0c and lowest was around 33.33 at 520^0c. Both from the graph and the data from the table, it can be concluded that maximum degree of pyrolysis (with respect to amount of liquid/oil formed) occurred at around 420^0c. As the temperature was increased beyond 500^0c, dominant reaction was of the carbonization nature as indicated by the high char yield. The irregularities can be best explained as the outcome of leakage of vapours which couldn't be avoided.

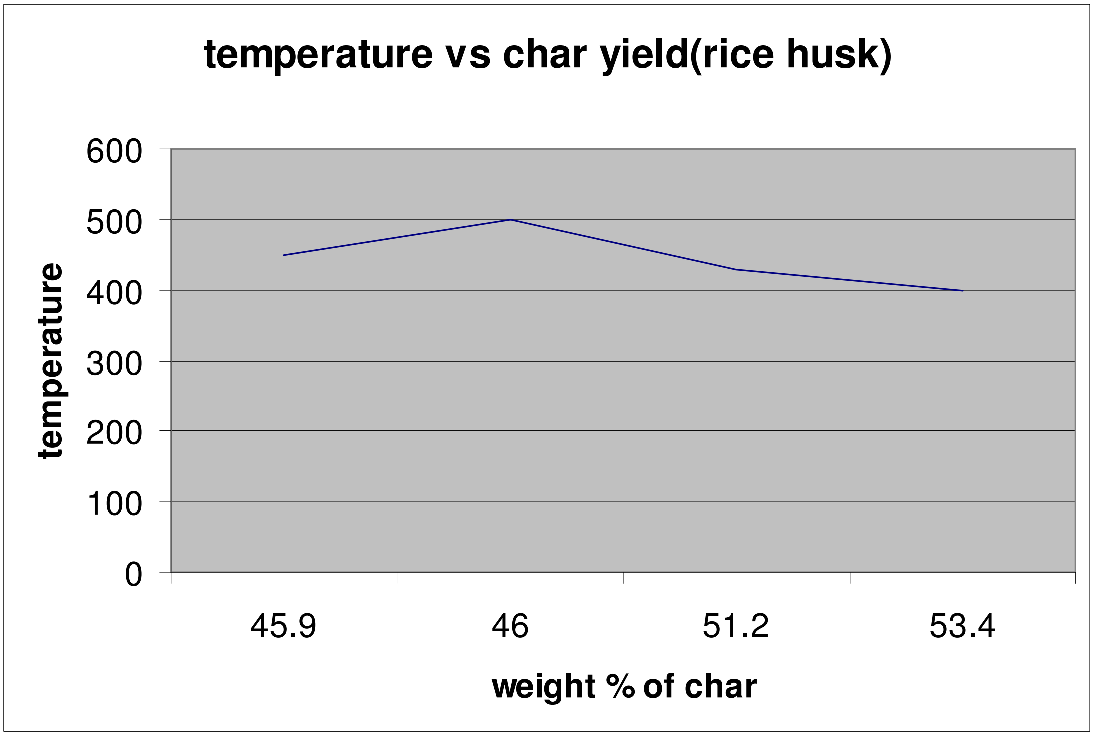
4.2. OBSERVATIONS FOR RICE HUSK:-

S.L.N.O	Temperature (in ^{0} c)	Weight of Feed (in gms)	Weight of Oil (in gms)	Weight of Char (in gms)	Amount of Oil (in wt %)	Amount of Char (in wt %)
1.	400	82	12	44	14.63	53.4
2.	430	82	16	42	19.5	51.2
3.	450	87	39	40	44.8	45.9
4.	500	100	40	46	40	46.0

Table 4.2. Observations for Rice Husk



Graph.4.3 temperature vs yield for rice husk



Graph 4.4 temperature vs char yield (rice husk)

INFERENCES:-

Initially rice husk was taken as the feed in the reactor and it was subjected to pyrolysis under test conditions. The experiments were carried out under a wide range of temperatures varying from around 400^0c to 500^0c. But all the tests were carried out under atmospheric pressure.

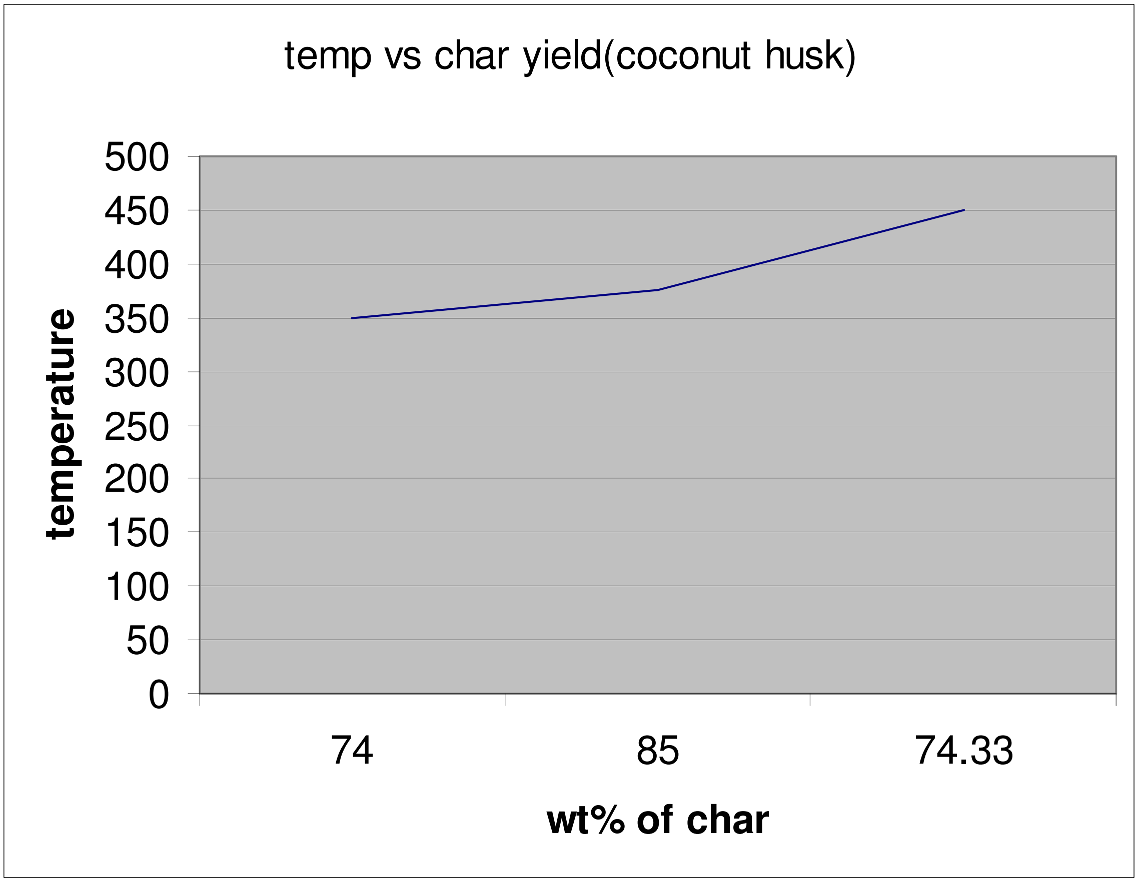
It was observed that highest (% by weight) of the liquid/oil which was around 40-44.8 at temperatures around 450^0c to 500^0c and lowest was around 14.63 at 400^0c. In the case of char, the highest (% by weight) was 53.4 at 400^0c and lowest was around 45.9 at 450^0c. Both from the graph and the data from the table, it can be concluded that maximum degree of pyrolysis (with respect to amount of liquid/oil formed) occurred at around 450^0c to 500^0c. The amount of liquid/oil obtained from rice husk was substantially higher than that obtained from saw dust. It can be pointed out that rice husk pyrolysis yields the best efficiency when operated around 450-500^{0}c but in case of saw dust it was around 380^{0}c to 420^{0}c.

As temperature was increased above 420^{0}c, the yield of char increased in case of saw dust while in case of rice husk, it showed a declining trend. Thus rice husk pyrolysis temperature should be around 450^{0}c to 500^{0}c for obtaining the highest efficiency. Moreover if the irregularities due to vapour leakages in case of some tests are ignored, it can be noted that incase of saw dust, the average amount of char formation (>53%) was quite higher than that of rice husk (<47%). The irregularities can be best explained as the outcome of leakage of vapours which couldn't be avoided.

4.3 OBSERVATIONS FOR COCONUT COIR/HUSK:-

S.L.N.O	Temperature (in ^{0} c)	Weight of Feed (in gms)	Weight of Oil (in gms)	Weight of Char (in gms)	Amount of Oil (in wt %)	Amount of Char (in wt %)
1.	350	50	4	37	8	74
2.	375	20	--	17	--	85
3.	450	60	6	44	10	73.33

Table 4.3 Observation for coconut coir



Graph 4.5 .temperature vs % char for coconut coir

INFERENCES:-

Initially coconut coir was taken as the feed in the reactor and it was subjected to pyrolysis under test conditions. The experiments were carried out under a wide range of temperatures varying from around 350^0c to 450^0c. But all the tests were carried out under atmospheric pressure.

It was found out that yield of oil / liquid from coconut coir/husk was very less or negligible. Actually the weight % of liquid was found out to be around 4-6% which is indeed too less to be carried out commercially. But it can be considered a very useful raw material for char formation as it gives very high yields of char at normal pyrolysis conditions. In fact the highest yield of char was around 85% (wt basis) at 375^0c. The average char yield was around 78% with temperatures varying from 350^0c to 450^0c. At still higher temperatures i.e. around 550^0c or even more, the predominant reaction is gasification with lower yields of liquid and char but quite substantial amount of gases. Hence it can act as an excellent raw material for production of both char and gases like CO_2, CO, CH_4 etc. If temperature is around 450^0c-500^0c, it can be used for obtaining char while at high temperatures(>600^0c), it produces a lot of gases.

CHAPTER 5

ADVANTAGES AND USES

5.1 COMPETITIVE ADVANTAGES:--

As a clean fuel, Bio-Oil has a number of competitive advantages over petroleum based fuels:

• **No SOx Emissions** – Bio-Oil produces virtually no heavily regulated SOx emissions and would not be subjected to SOx taxes.

• **Low NOx** – Bio-Oil fuels generate 50% lower NOx emissions than light fuel oil in gas turbines and diesel fuel in stationary diesel engines.

• **CO2 Neutral** – Because Bio-Oil is manufactured from organic waste, it is considered greenhouse gas neutral and can generate carbon dioxide credits.

• **Renewable and Locally Produced** – Bio-Oil can be produced in countries where there are large volumes of organic waste such as sugar cane bagasse. Therefore, it can help non-oil producing nations reduce reliance on imported fossil fuel.

• **Storage and handling**:-Compared to other biomass fuels, Bio-Oil can be stored, pumped and transported in a manner similar to petroleum based products to equalize energy demand and distribution. This can make Bio-Oil more economical to use because transportation and storage of -liquid fuels are much less expensive than for competing fuels such as wood, straw and peat.

5.2 USES OF BIO-OIL:-

Bio-oil produced using the pyrolysis process can be used for number of purposes. It finds use in a lot of filelds. Some of the uses are listed below:-

1) Bio-oil is used commercially as a fuel in gasifiers, boilers etc. Moreover its blends are used for fuel purposes in a lot of cases.

2) It is being used as a bio-efficient fuel in transportation systems thereby helping in decreasing pollution.
3) It finds extensive use as preservative, food additives and as resign precursors.
4) It is seen as a source for the manufacturing of Hydrogen by the reforming process.
5) Activated Carbon can be obtained as a byproduct of this process.
6) Some important chemicals like Acetic acid, Levoglucosan, Formaldehyde, Hydroxyactaldehyde etc. are commercially obtained from bio-oil.
7) It can be used as binders and elasticizers and also as a source of various polymers.

CHAPTER 6

CONCLUSIONS

CONCLUSIONS:-

As discussed earlier, there is a need to find alternative fuels for eradicating the deadly menaces affecting our energy security. Bio-fuels derived from biomass can be one such alternative. Further bio-oil derived from biomass using the pyroysis technique is a concept which can be and is being commercially developed to be an answer to our ever increasing energy needs as well as taking care of the pollution factor.

During the course of our study involving biomass to produce bio-oils, we have come across certain facts and finding which we would like to list and conclude in the following way:-

1) Even without agitation or fluidized beds reactors, pyrolysis can be conducted out and substantial amount of bio-oil can be obtained. On an experimental basis, it has been found out that, yields of bio-oil using agitating/fluidizing techniques are on a average around 30-33% .The efficiency of yield using our design was around 20-25% which is quite satisfactory considering the facts that there were vapour losses which could have been prevented using better apparatus.

2) The thought to be biomass wastes like saw dust, rice husk, coconut coir etc. are infact potential sources of energy which has been validated by the quite substantial amounts of bio-oil obtained using these as raw materials.

CHAPTER 7

SCOPE FOR FUTURE WORK

SCOPE FOR FUTURE WORK:-

This is a burgeoning field in which a lot of research is going on. Liquefaction using pyrolysis techniques to produce bio-fuels is a major area to be studied, developed and commercially exploited. In our case, a lot of further work is possible. Here we have used a design which is very simple and cost effective and doesn't involve any agitation process. Some modifications should be incorporated to minimize the vapour losses. The economics part should also be dealt with to decide whether this can be converted into an economically viable process.

We have also given another design in which we had suggested a continuous process in which the bio-oil produced is used to provide inert atmosphere and thereby increasing the efficiency. We suggest that future work should be done using that setup also and comparisons and analysis should be carried ot to ascertain the effectiveness of the process both on economical and product basis

Moreover the char obtained can be used for the manufacturing of activated carbon. We have found during our study that coconut coir/husk yielded substantial amounts. A method should be devised to use the gases formed during the pyrolysis process and these should be passed to increase the efficiency. We suggest that some work should be carried out in this field which we believe could be commercially developed.

A field which can be looked upon is the steam reforming process. The term “reforming” was originally used to describe the thermal conversion of petroleum fractions to more volatile products of higher octane number and represented the total effect of many simultaneous reactions, such as cracking, dehydrogenation and isomerization. Reforming also refers to the conversion of hydrocarbon gases and vaporized organic compounds to hydrogen containing gases such as synthesis gas, a mixture of carbon monoxide and hydrogen. Production of H_2 by catalytic steam reforming of compounds of biomass fast pyrolysis oil should be investigated. Further the effect of shifting reactions like water gas shift reactions to upgrade the bio-oil can also be carried out.

Moreover work can be carried out for producing various types of blends. The effect of blending on bio-oil can be studied to produce blends of bio-oil and diesel, engine oils, fuel oils etc.

CHAPTER 8

REFERENCES

REFERENCES

BOOKS:_

1. Badger.C Phillips, A New Vision For Value Added Forestry.

2. Semida Silveira , Bioenergy - Realizing the Potential, July 2005

3. John R. Fanchi , Energy Technology and Directions for the Future, February 2004

4. AV Bridgwater , Fast Pyrolysis of Biomass: A Handbook Volume 2, CPL Press 2002

5. Aldo da Rosa , Fundamentals of Renewable Energy Processes

6. A V Bridgwater , Pyrolysis and Gasification of Biomass and Waste

7. C.G Ruban and B.G. Prakash, Biofuel production & Meeting Challenges, Chemical Engineering World, May 2001.

JOURNALS:-

1. Engin Ozcivici, High temperatures pyrolysis, Journal of the American Ceramic Society, VOL 84 Issue 10

ONLINE RESOURCES:-

1. Development of advanced fast pyrolysis processes for power and heat, 1998-2001, Project partners: Aston University (UK), BHF-IWCT (GE), Wellman (UK), KARA (NL), Ormrod Diesels (UK), EC Joule JOR3-CT-97-0197

2. BTG, Biomass Technology Group BV 2002-2003 pyrolysis technology leaflet.

3. The rotating cone flash pyrolysis pilot, 1994-1995, Project partner: Royal Schelde, Supported by FAO, project DP/CPR/88053-001/AGO-1

4. United States Patent No. 5,728,271 Energy Efficient Liquefaction of Biomaterials byThermolysis. Piskorz et al.

5. International Energy Agency statistics on world CO2 emissions,
http://www.iea.org/stats/files/keystats/stats_98.htm, 1996.
6. Bio-oil from pyrolysis , UOP-A Honeywell company, DG-E3726tr

URLs:

1 http://www.pyne.co.uk/

2, http://www.undp.org/gef/new/ccinfo.htm

3. http:// www.dynamotive.com

4. http://www.ensyn.com/

5. http://www.btgworld.com/