MAIN CHAPTERS
CHAPTER –I
INTRODUCTION

1. INTRODUCTION

The growth of economic and social development may be ensured by meeting the energy demand at affordable cost in all sectors of economy. Energy intensity of the nations clearly shows demarcation between developed and developing countries. Fossil fuels are meeting the demand of all the countries at present. The gap between supply and demand would be larger in future due to the limited reserves of fossil fuels. Solid, liquid and gaseous fossil fuels have their different properties and characteristics and make them most suitable for the specific task or application.

Liquid and gaseous Petroleum fuels are predominantly used by the industrial, transport and commercial sectors. However the transport sector is one of the largest consumers of Petroleum fuels especially liquid fuels. The present and future supply-demand scenario of these fuels seems to be problematic as pointed out below.

1. The 70% of the petroleum reserves are concentrated only in 13 OPEC countries in Gulf. Therefore, Price and supply may be unpredictable depending on reserves stock, political decisions, wars, relations and other so many factors. Consequently, the import of petroleum products would create the problem of balance payments especially in the case of developing countries. The situations during oil crises in 1973 and Iraq war were very well realized and an evidence for the unpredictable and unstable oil market.

2. The accelerated economic growth was derived from the excessive consumption of the fossil fuels by all developed countries. Consequently, the huge amounts of solid, liquid and gaseous pollutants were loaded more than the sink capacity of the environment. The land, air, soil, water and upper atmosphere were critically degraded. The environmental effects are seen as global warming, climate change, acid rains etc. Ultimately, all living and non-living bodies starts getting affected on the globe.
In view of the above problems, one has to look for sustainable and alternative options to meet the demands of grown or growing economies of different nations. In this direction, biomass can play a very important role, as it is easily available, eco-friendly in nature and helpful in sustainable development. Biomass may be an attractive and cost effective resource to produce the bio-oils through pyrolysis process. Biomass is popularly considered to be a major potential biofuel and a renewable energy resource for the future. Over the last three decades, special attention has been given to the conversion of residual biomass and renewable materials into bio-fuels (Perez et al., 2002). Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resource (Ozcimen et al., 2004, M.Jefferson et al., 2006). It appears to be an attractive feedstock for three main reasons. First, of all it is a renewable resource that could be sustainably developed in future. Secondly, it appears to have decisive positive environmental properties, thus resulting in no net releases of carbon dioxide and very low sulfur content. Third, it seems to have significant economic potential provided the fossil fuel prices increase in future. Biomass is clean as it has negligible content of sulfur, nitrogen and ash, which emit low values of SOx, NOx and soot than the conventional fossil fuels. Zero net emission of CO2 can be achieved because CO2 released from biomass will be recycled into the plants by photosynthesis quantitatively (Bridgwater et al., 2000, Czernik et al., 2004, Zhang et al., 2007). The most important benefits of using biofuels are its renewability, better quality exhaust gas emissions, its biodegradability as it does not contribute to a net rise in the level of CO2 in the atmosphere and consequently to the green house effect. Biomass can be converted into useful forms of energy using a number of different processes. Factors that influence the choice of conversion process are the type and quantity of biomass feedstock; the desired form of the energy, i.e. end-use requirements; environmental standards; economic conditions and project specific factors. In many situations it is the form in which the energy is required that determines the process route, followed by the available types and quantities of biomass. Conversion of biomass to energy is undertaken using two main process technologies: thermo-chemical conversion and biochemical / biological. Mechanical extraction (with esterification) is the third technology for producing energy from biomass (Alcantra et al., 2000, Demirbas et al., 2000, Zanzi et al., 2002). Thermo-chemical conversion process has four processes involved combustion, gasification,
pyrolysis and liquefaction. Bio-chemical conversion encompasses two process options: digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol (Mckendry et al., 2002).

Above all it does not generate any toxic emission after combustion and through thermo-chemical conversion method. Biomass can be converted into liquid bio-oil. Among all the processes pyrolysis is one of the good options for bio-oil production to meet the energy demand, partially or fully. In pyrolysis process, biomass decomposes at a higher temperature in absence of oxygen and the emitted vapors get converted into bio-oil via rapid condensation process. Bio-oil has low calorific value, acidic in nature, smoky smell and dark brown in colour. It has a complex mixture of hydrocarbons like alcohols, aldehydes, phenol, benzene, cyclohexane, etc.

Liquids from biomass obtained through thermo-chemical conversion processes are expected to play an important role in the future as high value energy carriers and value-added chemicals. These products may offer many advantages over raw solid biomass as an energy source. Furthermore, the energy density of liquids is higher than that of raw biomass because of their chemical and physical characteristics. The bulk density of solid biomass is much less than that of liquids, since plant structures have high porosity besides, there is ease of transportation in the case of liquids (Bridgwater et al., 1991, Encinar et al., 1998, Chen et al., 2003, Demirbas et al., 2005). The thermo-chemical processes of pyrolysis are available for converting the biomass to a more useful energy. Pyrolysis process is the heart of all thermo-chemical fuel conversion processes and is assumed to become an avenue to petroleum type products from renewable biomass (Antal et al., 1982, Putun et al. 1996). The broad aim of this study is to focus on development of slow pyrolysis an efficient process, characterization of products, cost effectiveness and uses of the pyrolytic oil (bio-oil).
1.1 THERMO-CHEMICAL CONVERSION OF BIOMASS

The thermo-chemical conversion of biomass can be classified into four processes namely, pyrolysis, liquefaction, combustion and gasification. Each method gives different range of products, employs different equipment configuration and operates in different modes.

![Thermo-chemical Conversion of biomass and their products](image)

Figure 1.1: Thermo-chemical Conversion of biomass and their products
Different conversion technologies along with their primary product and applications are shown in Table 1.1. The primary products being converted into secondary products using an intermediate processing technology are also shown in Figure 1 (Bridgwater et al., 1994, Demirbas et al., 2005).

Table 1.1: Thermo-chemical conversion technologies, primary products and applications

<table>
<thead>
<tr>
<th>Technology</th>
<th>Primary product</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast or Flash pyrolysis</td>
<td>Liquid</td>
<td>Liquid fuel substitution, chemicals</td>
</tr>
<tr>
<td>Slow pyrolysis</td>
<td>Liquid tar</td>
<td>Liquid fuel substitution, chemicals</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>Fuel gas</td>
</tr>
<tr>
<td></td>
<td>Solid char</td>
<td>Solid fuel or slurry fuel</td>
</tr>
<tr>
<td>Liquefaction</td>
<td>Liquid</td>
<td>Oil or liquid fuel substitution</td>
</tr>
<tr>
<td>Gasification</td>
<td>Gas</td>
<td>Synthesis gas or fuel gas</td>
</tr>
<tr>
<td>Combustion</td>
<td>Heat</td>
<td>Heating</td>
</tr>
<tr>
<td>Carbonization</td>
<td>Charcoal</td>
<td>Solid fuel or slurry fuel</td>
</tr>
</tbody>
</table>

Source: Bridgwater et al., 1994
1.1.1 Combustion

Combustion involves direct burning of biomass to get heat. This is a process in which the biomass is degraded at higher temperature to char and volatiles, which in turn are oxidized with the excess oxygen provided. A large amount of heat due to reaction is released along with the formation of carbon dioxide and water as gaseous emittants. With the present state of various technologies and with the present scale of biomass power generation being 5-20 MW, biomass combustion based steam power plants is still the most economical option in comparison to present conventional technologies. Environmental and economic concerns of reducing greenhouse gas CO\textsubscript{2} emissions and increasing fuel flexibility have been motivating to use biomass fuels and substitute fossil fuels for heat and electricity generation. Among the various conversion technologies, combustion is the most common and developed way of converting biomass fuels to energy (Alcantra et al. 2000, Demirbas et al., 2000). Direct combustion process is not very efficient and systems having the problems in heterogeneous characteristics of biomass materials.

1.1.2 Gasification

Gasification is carried out in sub-stoichiometric oxygen atmosphere at temperatures ranging from 700 °C to 1200 °C. The final product, called as the “producer gas”, is a low to medium calorific value fuel gas, depending on the medium of gasification. Air gasification, that leads to a lower calorific value producer gas, is however most common, particularly in scales of economic operation. Failures of systems were often reported (Raveendran et al., 2005) due to the high temperature combustion zones.

In gasification the reactions are as follows-

\[
C + \frac{1}{2}O_2 \rightarrow CO
\]

...........................................(1)

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2
\]

...........................................(2)

\[
CO_2 + C \rightarrow 2CO
\]

...........................................(3)

\[
CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O
\]

...........................................(4)
1.1.3 Liquefaction

Direct liquefaction of biomass involves application of high pressures in reduced atmosphere of hydrogen in the presence of a catalyst. The conditions mentioned indicate the non-viability of the process economically, as of now, for the scales of the operations possible. Pyrolysis, gasification and combustion are thermo-chemical decomposition processes, the major difference being the amount of oxygen used for the process. Teed et al. (1985) defined pyrolysis, gasification and combustion based on the amount of air supplied:

Pyrolysis - when air supplied is less than 1 kg/kg of biomass,
Gasification - when it is between 1 and 1.5 kg/kg of biomass; and
Combustion - when it is above 1.5 kg /kg of biomass.

Thermo-chemical processes are thought to have great promise as a means for converting biomass into higher value fuels (Elliott et al., 1989).

1.1.4 Pyrolysis

It is a thermal conversion processes, one of the convenient technique is to produce bio-oil for energy purposes. Pyrolysis is the thermal decomposition of organic material in the absence of oxygen. Pyrolysis, as well as other forms of biomass conversions, are well known processes which can be directed to the preferential production of one of its three main products, charcoal, liquid fraction and gas (Maschio et al., 1992). There is need to develop the efficient process with viable and feasible cost economics.

1.1.4.1 Slow Pyrolysis

In slow pyrolysis the measured impact is dependent on the heating rate. For slow pyrolysis the heating rate is 4- 8 °C/min. All the researchers have used different temperatures and heating rates to produce bio-oil through slow pyrolysis. In slow pyrolysis the output products are bio-oil, gaseous product and char. In this process the quantity of bio-oil production is less as compared to char and gaseous product, but simple and easy in handling of the systems.

1.1.4.2 Fast Pyrolysis

In fast pyrolysis process the heating rate is 5-10 °C/s. The biomass material inside the reactor during this process decomposes quickly. The reactions get completed inside the reactor in short intervals of time. The output results in larger amount of bio-oil, less char and gaseous products. The temperature range used for
fast Pyrolysis process is 500-1000 °C. Researchers have used various types of reactors for the generation of bio-oil. Some of them are entrained flow reactor, rotating reactor, circulating fluidized bed reactor, vacuum reactor, vortex reactor, vacuum furnace reactor etc.

1.1.4.3 Types of Fast Pyrolysis

Fast Pyrolysis are of three types –

- Flash Pyrolysis,
- Vacuum Pyrolysis
- Ablative Pyrolysis.

1.1.4.3.1 Ablative Pyrolysis

Ablative pyrolysis is one type of fast pyrolysis process. In this process the biomass particle size used can be larger than that employed in other fast pyrolysis processes. This process is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing biomass. Much of the pioneering works on ablative pyrolysis reactor have been carried out by NREL in their vortex reactor and by CNRS at Nancy. Recently lot of developmental work has been carried out at Aston University. The fast pyrolysis process offers a more intensive and potentially compact reaction system. During the process of fast pyrolysis, the material is kept in an inert environment such as nitrogen and then the required temperatures as well as heating rate are provided to maximize the liquid fraction as a fuel from organic material.

When the biomass is rapidly heated in the absence of oxygen, it decomposes to generate mostly vapors, 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 process for making charcoal, fast pyrolysis is an advanced process that has to be carefully controlled to get high yields of liquid.

1.1.4.3.2 Flash Fast Pyrolysis Process

In the case of flash fast pyrolysis process the heating rate is very high likely in the range of 10-15 °C/s and in this condition the biomass residence time in the reactor is very low. The output yields are bio-oil, gaseous product and char but the quantity of bio-oil produced is very large in quantity. Entrained flow reactor and fluidized bed reactors are used for the flash fast pyrolysis process. In the case of flash fast pyrolysis, the biomass particle size used should be small and the reactors
heating rate should be kept high. There are two types of Flash fast pyrolysis processes:

1.1.4.3.3 Flash hydro-pyrolysis

This process is carried out in an atmosphere of hydrogen with pressures up to 20 Mpa.

1.1.4.3.4 Rapid thermal process

This is a heat transfer process with a very short heat residence time (between 20-30 ms and 1.5 s) and with temperatures between 350 - 900°C, rapid depolymerization and cracking of feedstock takes place. Through the rapid thermal process pyrolysis removes most of the side reactions and yields oil, which has a viscosity comparable with that of diesel fuel.

1.1.4.3.5 Solar Flash Pyrolysis

Solar flash pyrolysis is possible through concentrated solar radiation. The biomass materials are placed on the sample holder, which in turn is placed on the solar furnace. The heat is concentrated on the sample holder with the help of solar sources such as solar towers, dish connectors, etc.

1.1.4.3.6 Vacuum Flash Pyrolysis

In this process biomass can be degraded in vacuum, which converts biomass into a form of bio-oil. In this process biomass can be converted into larger quantities of bio-oil and less of charcoal.

1.1.4.3.7 Catalytic biomass pyrolysis

The bio-oil produced through slow pyrolysis, fast pyrolysis and flash pyrolysis cannot be used directly as a fuel for transportation purposes. This oil requires some chemical treatment to remove the high oxygen content and water content. Bio-oil is not stable and it is less miscible in conventional fuels. Through catalytic biomass pyrolysis its quality can be improved. This technique is economical, as it does not require any costly pre-upgradation involving condensation and evaporation. Zeolite (HZSM-5) and ZnO₂ are the catalysts, which have been used by various researchers.

1.3 FACTORS AFFECTING THE PROCESS

Pyrolysis process can be affected by the following parameters – (1) Pyrolytic fuel oil (bio-oil) production depends on the temperature and heating rate of reactor.
(2) Pyrolytic fuel oil (bio-oil) production also depends on the sweep gas (N\textsubscript{2} gas) flow rate.

(3) Oil production also depends on the particle size of the biomass; small particle size increases the production rate of pyrolytic fuel oil and decreases the rate of charcoal production.

1.4 OBJECTIVES

The whole research work has been analyzed through the objectives given below.

Figure 1.3: Objectives pathway of the thesis
(1) Study the physio-chemical characterization, suitability and availability of five biomass materials (soya husk, rice husk, cotton stalk, bagasse and wood saw dust) to assess their bio-oil potential.

(2) Design and development of a laboratory scale reactor for the production of bio-oil from different materials.

(3) Study and development of the process (pyrolysis) for maximum production of bio-oils (pyrolysis oils) from different biomass feeds (agriculture residues).

(4) Study the effect of different biomass feeds and process conditions on the rate and kinetics of chemical reactions during pyrolysis.

(5) Study the effect of physiochemical parameters on the generation rate of bio-oils.

(6) Study the physio-chemical characterization of generated bio-oils.

(7) Performance evaluation of bio-oil as a fuel and secondary treatment by mixing it with some additives.

(8) Evaluation of the techno economical feasibility for the production of bio-oil as a fuel.
1.5 REFERENCES


