PRODUCTION AND CHARACTERIZATION OF BIO OIL FROM WOOD SAWDUST VIA FAST PYROLYSIS

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Thesis submitted in fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering in Gas Technology

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DECEMBER 2010

ABSTRACT

In this study, the production and characterization of bio oil from wood sawdust via fast pyrolysis was investigated. In fast pyrolysis of wood sawdust, the yields of the products were studied to elucidate the effect of the process parameters such as pyrolysis temperatures, nitrogen (N_2) gas flow rate and pyrolysis holding time. This research was carried out in a design electric furnace reactor and heated externally. The yields product from this experiment were collected and analyzed. The experiments were conducted at a temperature range of 450-550 ^oC. The holding time was varied in the range 1-5 minutes, and the nitrogen (N_2) gas flow rate was varied in the range of 1-3 liter/min. The general characteristic of the product was investigated by the determination of the functional groups present in the bio oil using Fourier Transform Spectroscopy (FTIR). The best conditions to produce bio oil from various parameters that give the highest product yield were at temperature 500 ^oC, 1 minute of holding time and 3 liter/min of nitrogen (N_2) gas flow rate. The maximum yield of bio oil produced from these conditions was 44.6%. From the analysis, it was shown that the pyrolysis oils contain complex compounds mostly functional groups of phenol, alcohols, ketones, aldehydes and carboxylic acids aromatic and also carbonyl structures.

ABSTRAK

Dalam kajian ini, penghasilan dan ciri-ciri yang minyak bio dari serbuk kayu melalui pirolisis pantas diselidiki. Dalam pirolisis pantas dari serbuk gergaji kayu, hasil dari produk tersebut dikaji untuk menjelaskan pengaruh parameter proses seperti suhu pirolisis, (N_2) laju alir gas nitrogen dan masa pegangan. Kajian ini telah dijalankan menggunakan reaktor tiub yang direka dan dipanaskan menggunakan elektrik dari luar. Produk hasil dari percubaan ini dikumpul dan dianalisa. Percubaan dilakukan pada suhu di antara 450-550 ^{o} C. Masa pegangan divariasikan dalam julat 1-5 minit, dan laju alir gas nirogen (N_2) yang berbeza-beza di antara 1-3 liter/minit. Ciri-ciri umum produk ini digunakan untuk menentukan kumpulan berfungsi yang hadir dalam minyak bio dengan menggunakan Fourier Transformasi Spektroskopi (FTIR). Keadaan terbaik untuk menghasilkan minyak bio dari berbagai parameter yang memberikan hasil produk yang tertinggi ialah pada pada suhu 500 ^{o} C, 1 minit masa pegangan dan 3 liter/minit laju aliran gas nitrogen (N_2). Keputusan maksimum minyak bio yang dihasilkan dari keadaan ini adalah sebanyak 44.6%. Dari analisis, di dapati bahawa minyak pirolisis mengandungi sebatian kompleks yang sebahagian besarnya terdiri dari kumpulan berfungsi fenol, alkohol, keton, aldehid dan asid karboksilik aromatik dan juga struktur karbonil.

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LIST OF ABBREVIATIONS

BCO	bio-crude oil
C_2H_4	ethylene
C_2H_6	ethane
$C_5H_8O_4$	xylem
$C_6H_{10}O_3.OCH_3$	hemicelluloses
$C_6H_{10}O_5$	cellulose
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
cP	centipoise
FTIR	fourier transform infra ied
GC	gas chromatography
H_2	hydrogen
H_2O	water
HCl	hydrochloric acid
IGCC	integrated gasification combined cycle
IR	infra red
LPM	litre per minute
mPa.s	milipascal-second
MW	megawatt
N_2	nitrogen
N_2O	nitrous oxide
NMR	nuclear magnetic resonance
NO_x	nitrogen oxide
NREL	National Renewable Energy Laboratory
O_2	oxygen

PAHs	polycyclic aromatic hydrocarbon
PID	proportional–integral–derivative
SO_2	sulphur dioxide
SO_x	sulphur oxide
UMP	University Malaysia Pahang
UV	ultraviolet

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

Energy comes in a variety of renewable forms; wood, biomass, wind, sunlight. It also comes in the nonrenewable form of fossil fuels- oil and coal and their use is a major source of pollution of land, sea and above all the air we breathe. Two centuries of unprecedented industrialization, driven mainly by fossil fuels, have changed the face of this planet. The present civilization cannot survive without motor cars and electricity. The increasing rate at which the changes in human lives are occurring has important consequences for the environment and carrying capacity of earth. The industrial revolution has brought greatly increased wealth to one quarter of the population and severe inequalities. Pollution and accelerating energy consumption has already affected equilibrium of earth land masses, oceans and atmosphere. Particularly, important is the loss of biodiversity. Fortunately, the last 25 years has seen growing awareness of some of these consequences.

Renewable energy is of increasing consequence in satisfying environmental concerns over fossil fuel usage. It also considered as a very vital contributors to the energy supply in global as they contribute to energy supply security, reducing dependency on fossil fuel resources, and also provides an opportunities for mitigating greenhouse gases. This energy can be generated from natural resources such as sunlight, wind, rain, and geothermal heat, which are renewable. Basically this energy is used to generate electricity or produce heat in much application, especially in industrial area.

Modern agriculture is an extremely energy intensive process. However high agricultural productivities and subsequently the growth of green revolution has been made possible only by large amount of energy inputs (Leach, 1976). With recent price rise and scarcity of these fuels there has been a trend towards use of alternative energy sources like solar, wind, geothermal etc (Rajvanshi, 1978). However these energy resources have not been able to provide an economically viable solution for agricultural applications (Dutta, 1981).

Since the energy crisis in 1970s, the energy utilization from biomass resources (called biomass energy) has received much attention. The energy obtained from agricultural wastes or agricultural residues is a form of renewable energy and, in principle, utilizing this energy does not add carbon dioxide (CO_2), which is a greenhouse gas, to the atmospheric environmental pollution and health risk than fossil fuel combustion (McKendry, 2002).

As we can see, nowadays, biomasses becomes the world’s primary renewable and source of energy replacing fossil fuels such as oil, natural gas and coal which had been our foremost energy demand for a long time ago. This highest potential biomass is considered the renewable energy source that contributed to the energy desires of modern society for both the developed and developing economies global. Biomass is a major source of energy for mankind and is presently estimated to contribute of the order of 10%-14% of the world's power supply. Its typically possesses higher hydrogen content and a larger volatile component and produces a more reactive char after devolatilization or pyrolysis. It contains lower ash and sulfur contents (Guo, 2004).

Biomass may vary in its physical and chemical properties due to its diverse origin and species. However, biomass is structurally composed of cellulose, hemicellulose, lignin, extractives and inorganics. From the chemistry point of view, biomass is composed of series of long chain hydrocarbons with functional groups such as hydroxyls and carboxyls (Sukiran, 2008)

The main advantages of using this biofuel are its renewability, as it gives a better quality exhaust gas emission, its biodegradability and, it does not contribute to a net rise in the level of CO_2 in the atmosphere, and consequently to the green house effect (Sensoz et al., 2006)

Additionally, biomass, when grown and converted in a closed-loop feedstock production scheme, generates no net CO_2 emissions, thereby claiming a neutral position in the build-up of atmospheric greenhouse gases. Also, biomasses offer the only source of renewable liquid, gaseous and solid fuels. The fuels and residues that come from the biomass can be converted to energy through several processes which are thermal, biological and physical processes (Guo, 2004).

1.2 Problem Statement

In this century, it is believed that the crude oil and petroleum products will become very scarce and costly. Day to day, fuel economy of engine is getting improved and will continue to improve. However, enormous increases in number of vehicles have started dictating the demand for fuel. Gasoline and diesel will become scarce and most costly in the near future. With increased use and the depletion of fossil fuels, alternative fuel technology will become more common in the coming decades (Behera, 2010).

The scientific consensus on global warming is clear. If atmospheric concentrations of greenhouse gases continue to rise in this century the way they did during the twentieth century, global ecosystems will be disrupted in ways that will alter the environmental conditions in which human civilizations have developed and thrived (Morris et al., 2001). Also, concerning the depletion of fossil fuels worldwide and the increasing environmental pollution, numerous endeavors have been attempted to find other renewable and environmental friendly energy sources and to advance the technologies (Guo, 2004).

Malaysia is blessed with natural resources, particularly crude oil and natural gas, which are the main sources of energy. However, these are depleting energy resources and increasing demand has made it necessary for the Government to embark on alternative energy sources. Rising crude oil prices have led to higher government expenditures on subsidies to keep retail fuel prices at relatively low levels (Economic Report 2006/2007, 2007).

The rapid climate change and the need to manage diminishing fossil fuel reserves are the latest biggest challenges facing by our planet. In order to secure the future for ourselves and generations to follow, we must take a drastic act now in order to reduce energy consumption and substantially cut greenhouse gases problem, such as the emission and high CO_2 content in the atmosphere. This environmental strain caused by fossil fuel make an effort from many industries to find an alternative fuel that focused on sources of raw material based on renewable resources.

Towards this direction, the oil obtained by using a method of pyrolysis of renewable biomass was seen as an attractive substitute for the limited supply fossil fuels and possibly to be use an alternative sources. Wood sawdust is one of the biomass wastes that come from agriculture activities which composed of fine particles of wood and it can be used for renewable energy or fuel feedstock production. This kind of material is a byproduct from cutting woods from the furniture factory as an example. There are several uses come from this material such as mulch, an option to clay cat litter, for manufacture of particle board or as a fuel. So, the explorations of the uses of wood sawdust as a main raw material in producing bio-oil were investigated.

1.3 Objectives of Study

In the course of completing this project, there are few objectives to be fulfilled as follows:

1. To produce bio oil from wood sawdust via fast pyrolysis.
2. To investigate the effect of various pyrolysis parameters on product yields.
3. To analyze the characteristics of bio oil from wood sawdust.

1.4 Scope of Study

The main idea behind this project would be:

- The production of bio oil from biomass. The formulation of bio-oil is obtaining from a biological waste such wood sawdust via fast pyrolysis.
- Parameters that have been evaluated in this study were temperature (450-550 °C), nitrogen (N_2) / sweeping gas flow rate (1-3 litre/min) and holding time (1-5 minute) to find the best operating.
- Characterizations of bio-oil produced from wood sawdust were then analyzed using Fourier Transform Infra Red (FTIR).

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass

Concerning the depletion of fossil fuels worldwide and the increasing environmental pollution, numerous actions have been attempted to find other renewable and environmental friendly energy sources and to advance the technologies. As to the power generation, biomass fuels technology becomes one of the most promising technologies in the last two decades.

Biomass, the name given to the plant matter which is created by photosynthesis, includes firewood plantations, forestry residues, animal waste, agricultural residues, etc. The supply of energy from biomass plays an increasing role in the debate on renewable energies. The relative large amount of biomass has already used for energy generation that reflects mainly the use of wood and traditional fuels in the developing countries. Nevertheless, the use of biomass in industrialized countries is also significative (Zanzi, 2001 and Gercel, 2002).

The biomass resource also can be considered as organic matter, in which the energy of sunlight is stored in chemical bonds. When the bonds between adjacent carbon, hydrogen (H_2) and oxygen (O_2) molecules are broken by digestion, combustion, or decomposition, these substances release their stored, chemical energy. Biomass has always been a major source of energy for mankind and is presently estimated to contribute of the order 10– 14% of the world's energy supply (Guo, 2004).

Biomass is derived from the reaction between carbon CO_2 in the air, water (H_2O) and sunlight, via photosynthesis, to produce carbohydrates that form the building blocks from biomass. Typically photosynthesis converts less than 1% of the available sunlight to stored, chemical energy. The solar energy driving photosynthesis is stored in the chemical bonds of the structural components of biomass. If biomass is processed efficiently, either chemically or biologically, by extracting the energy stored in the chemical bonds and the subsequent ‘energy’ product combined with O_2, the carbon is oxidized to produce CO_2 and H_2O. The process is cyclical, as the CO_2 is then available to produce new biomass (McKendry, 2002).

The energetic and industrial usage of biomass is becoming more and more technologically and economically attractive. The use of biomass offers the advantages of benefits, such as biomass is available in every country in various forms. Thus, assures a secure supply of raw material to the energy system. Maintaining biomass as a significant contributor to the national energy supply is for many countries, the best way of ensuring greater autonomy and cheap energy for the industry. From environmental benefits, the consumption of biomass for energy is an option for decreasing current environment problems such an increase of CO_2 in the atmosphere caused by the use of fossil fuels. Furthermore, biofuels from biomass contain minimal sulphur, thus avoiding sulphur dioxide (SO_2) emissions. To be successful, alternative fuels is needed to give low emission and rival gasoline and diesel in terms of cost, supply, and distribution, delivery to vehicles, on-board storage and power density (Zanzi, 2001).

2.2 Biofuel and Impact to Environment

At this time, biofuels are the most important type of renewable energy in road transportation, but the argument over their environmental impact is continuing. Some argue that when farming or in the process of growing plants, including deforestation and soil acidification, is taken into account, biofuels consume more energy than they produce.

Biofuels, resulting from programs launched in the late 1970s to reduce oil dependence, have been in industrial development for more than twenty years. Today, there is strong renewed interest in biofuels: in the transport sector, they could lead to a reduction in oil consumption and greenhouse gas emissions (Prieur et al., 2006)

Atmospheric gases such as CO_2, nitrous oxide (N_2O) and methane (CH_4) can regulate temperature of the earth. These greenhouse gases particularly CO_2 allow energy from the sun to penetrate to the earth, but trap the heat radiated from the earth's surface. Researchers, scientists and others are concerned about those gases being emitted to atmosphere by human activities which will increase the global warming at a rate extraordinary in human history. The CO_2 emission from the usage of fossil fuels that provide about 85% of the total world demand for primary energy, cause an increase of the CO_2 concentration in the atmosphere (Zanzi, 2001 and Gerkova et al., 1992). Another acidic gaseous pollutant is hydrochloric acid (HCl) gas, produced from chlorine and mainly associated with combustion of municipal wastes. HCl also plays an important role for dioxin formation during combustion.

The use of biomass fuels in a closed carbon cycle as a substitute for fossil fuels, is one of the most promising ways for tentative the increase of the CO_2 concentration. Biomass fuels make no net contribution to atmospheric CO_2 if used sustainable to allow regrowth (Onay et al., 2001). Biomass plays a significant role in reducing CO_2 by acting both as a reservoir of carbon, absorbing CO_2 from the atmosphere during growth and as direct substitute for fossil fuels. Furthermore, reforestations and introduction of alternative crops are needed to stop and revert phenomena like erosion and desertification (Zanzi, 2001 and Gercel 2002).

Special attention is being paid to the N_2O emission from combustion of nitrogen-containing fuels such as biomass, coal, peat or municipal waste. The N_2O emission from combustion of a nitrogen-containing fuel comes from two sources, thermal N_2O and fuel N_2O. The formed from the nitrogen in the combustion air and its formation is more or less dependent on the temperature and pressure in the combustor. The latter comes from the oxidation of N_2 in the fuel and is not particularly temperature sensitive. All the oxides of N_2 also enhance the greenhouse effect (Zanzi, 2001).

2.3 Wood Sources

Wood is a ready source of fuel ever known to man. Its uses in both industry and domestic purposes cannot be over emphasized. In most developing countries wood and charcoal are the predominant fuels for preparation of food as well as serving as fuel for small and medium scale industries (Zerbe, 2004 and Bhattacharya et al., 1999). Wood is said to be the major renewable source of energy at present and the fourth largest source of energy, for example rated after petroleum, coal and natural gas in that order, all of which are non-renewable energy sources. In recent years, however, the high cost of oil and gas has again induced people to burn more wood.

2.3.1 Wood Sawdust

Sawdust is the powdery wood waste produced by cutting wood with a saw. The size of the sawdust particles depends on the kind of wood from which the sawdust is obtained and also on the size of the teeth of the saw (Afuwape, 1983). In wood industries such as the furniture industry or paper industry, a great amount of wood flakes and wood flours in the form of sawdust are always found as wastes. These unused materials are usually applied as a fuel source or for the manufacture of plywood.

Malaysia contributes more than 50% of the world palm oil production. Palm tree based plywood's are increasingly used due to its environmental friendliness. Nearly 100,000 hectares of replanting is carried out every year. Several saw mills ranging from small scale to large scale engaged in plywood production resulting generation of large amount of saw dust. The saw dust generated during plywood processing finds extensive applications in compressed powder boards, fuel pellets, mosquito coils, incense sticks, activated carbon etc. Furthermore, large scale sawmills can utilize the sawdust for cogeneration facility utilizing Integrated Gasification Combined Cycle (IGCC) technology (Kannan, 2008).

2.3.2 Wood Sawdust Properties

The chemical composition of wood is an important parameter in determining the energy value of wood materials. Wood is a composite of three basic polymers, namely cellulose ($C_6H_{10}O_5$), lignin ($C_6H_{10}O_3$) (OCH_3) and hemicelluloses such as xylem ($C_5H_8O_4$) (Tillman, 1978). Hard woods are deciduous trees or wide leafed trees, while soft woods are coniferous trees which are cone-bearing evergreens. Hard wood generally contains more energy than softwood on a dry weight basis due to higher lignin content plus the presence of more resins in the extraction (Brown et al., 1952).

Specific heat capacity is the amount of heat energy required to raise the temperature of a unit mass of a substance by one degree centigrade. Specific heat capacity differs from one species of wood to another. Thermal conductivity is the measure of the rate at which heat is conducted through the material; conductivity increases with the wood density. Wood thermal conductivity is found to increase with higher moisture content (Panskin et al., 1962).

2.4 Technology Description

Biomass can be converted to biofuels which is a liquid and gaseous fuel such as ethanol, methanol, gasoline, diesel fuel and methane.

Biomass fuels and residues can be converted to energy via thermal, biological and physical processes. Each process area is described with the greatest highlighting on the technologies that are attracting the most interest in the research and demonstration arenas. In the thermochemical conversion technologies, biomass gasification has fascinated the highest interest as it offers higher efficiencies compared to combustion and fast pyrolysis, but it is still at a relatively early stage of development.

The energy potential from the biomass can be recovered either by direct use in combustion systems or by improvement into a more valuable and utilizable fuel or gas or higher-value products for the different industries. But the combustion of biomasses is not such economical option. So the improvement by pyrolysis, liquefaction, or gasification becomes more eye-catching and interesting. Biomass pyrolysis has been practiced for centuries in the manufacture of charcoal, but only in the last time the physical and chemical processes during pyrolysis were investigated (Gheorghe et al., 2009).

2.5 Thermal Conversion Processes

Thermochemical process is thought to have a great promise as a means for efficiency and economically converting biomass into advanced value fuels. Biomass fuels and residues can be converted to energy via thermal, biological and physical processes. There are three main thermal processes available for converting biomass to a more useful energy form which is combustion, gasification and pyrolysis. This thermochemical conversion of biomass (pyrolysis, gasification, combustion) is one of the most promising non-nuclear forms of future energy. It is renewable form with many ecological advantages (Koufopanos et al., 1989). Each process gives their different range of products.

In thermal conversion, combustion is already widely practiced. Gasification attracts a high level of interest as it offers higher efficiencies compared to combustion. While fast pyrolysis is interesting as a liquid is produced that offers advantages in storage and transport and versatility in applications. The products and applications of these thermal conversion processes are summarized in Figure 2.1.

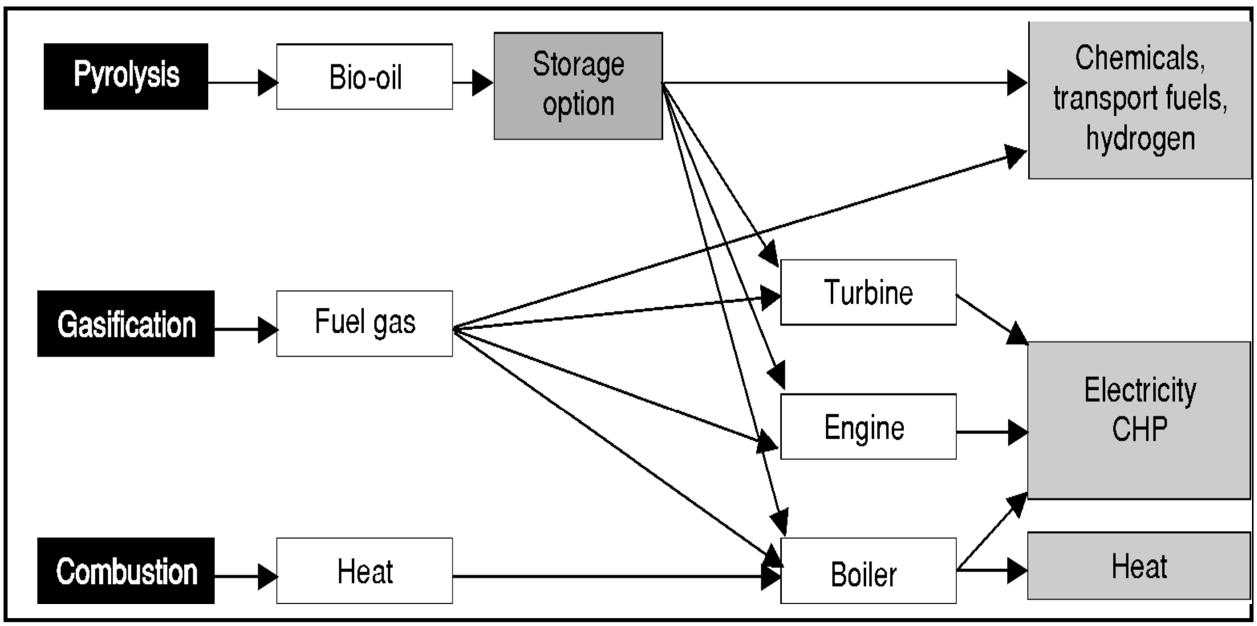

Figure 2.1: Products from thermal bio mass conversion (Bridgwater, 2004)

The biodegradable fractions in wastes such as paper, wood, and food residue are important sources of biomass for renewable-energy production through thermal or biological conversion. While direct combustion is the dominant method applied to mixed wastes, specific streams of industrial wastes with high energy content could be converted into fuel feedstock using advanced techniques, such as pyrolysis and gasification. One example of such materials is waste furniture, of which over 2.4 million tons were generated in Korea in the past 3 years (Yoo, 2008).

Although the wood in waste furniture could have been treated with paint, surface coating, or pesticides, unlike fresh wood or forestry residues, it usually contains less moisture and is available for pyrolysis and gasification after size reduction.

2.5.1 Combustion

Combustion of biomass and related materials is widely trained commercially and economically justified to provide heat and power. The productions only satisfy the heat market directly or power production via a Rankine cycle or similar (Bridgwater, 2004). Efficiencies are low at small capacities and fouling and emissions are problematic in many applications. The technology is commercially available and presents minimum risk to investors. The product is heat, which must be used immediately for heat and/or power generation as storage is not a viable option. Combustion of biomass processes heat the biomass in the presence of unlimited O_2. The products of the reaction are basically additional heat, ash, and smoke.

2.5.2 Gasification

Gasification offers higher efficiencies at all scales of operation, and while on the verge of being fully commercial still requires demonstration at commercially attractive scales of operation (Bridgwater, 2004). Gasification heats the biomass to higher temperatures (about 600-700 ^{0}C) in an environment of limited O_2. The biomass begins to char and gives off a gaseous product that is a mixture of carbon monoxide (CO), H_2, and CH_4.

2.5.3 Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of O_2. 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 vapor residence times favor the production of charcoal. High temperature and longer residence time increase the bio mass conversion to gas and moderate temperature and short vapor residence time are optimum for producing liquids.

Pyrolysis lies at the heart of all thermochemical fuel conversion processes. It is eye-catching because solid biomass and wastes, which are difficult and costly to manage, can be readily converted to liquid products. Pyrolysis heats the biomass to temperatures (around 300-500 ^{0}C) in the nonexistence of air. The biomass "melts" and vaporizes, producing petroleum-like oil called "bio-oil." This bio-oil can be transformed to gasoline or other chemicals or materials.

These liquids have advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. Pyrolysis also gives gas and solid (char) products, the relative proportions of which depend very much on the pyrolysis method and process condition (Putun et al., 2002). As usual, the pyrolysis processes under development are based on two different concepts: slow pyrolysis and fast or flash pyrolysis. These differ from each other in terms of chemistry, overall yields and quality of products.

2.6 Pyrolysis Process Types

2.6.1 Slow Pyrolysis

Slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. In slow pyrolysis, biomass typically was heated to 500 ºC. The vapor residence time varies from 5 to 30 minute (Mohan et al., 2006).

Putun et al. (2001) had conducted fixed bed pyrolysis of Euphorbia rigida, sunflower presses bagasse and hazelnut shell, at different temperatures and heating rate of 7 K/min. Product yield was found to increase in all the three cases when the pyrolysis temperature was increased from 673 to 973 K. Their findings are as shown in Table 2.1 for increasing of N_2 flow rate.

Table 2.1: Percent yields of products (approx.) from various biomasses at different temperatures (Putun et al., 2001).

Temp. (K)	Product Yield (%)		
	Char	Oil	Water
Euohorbia rigida			
673	44	24	13
773	28	32	17
973	21	26	13
Sunflower			
673	35	36	12
773	27	44	12
973	26	38	12
Hazelnut shell			
673	47	20	14
773	41	23	14
973	36	21	14

Slow pyrolysis of cottonseed cake at heating rates of 7 ºC/min in a tubular reactor was reported by Ozbay et al. (2001). Pyrolysis works were conducted in two reactors, Heinz retort and a well-swept tubular reactor. From results shown in Table 2.2, it was seen that with the increase in the temperature the oil yield increased up to 600 ºC but decreased at around 750 ºC. Char yield showed continuous decrease. Oil yield was maximum at N_2 flow rate of 100 cm^3/min.