

Doctoral Thesis

Production of biofuels and chemicals from
pyrolysis of biomass solid wastes

(熱処理による固形有機廃棄物からの
バイオ燃料および化学物質の生成)

September, 2016

Momtaz Parveen

Production of biofuels and chemicals from pyrolysis of biomass solid wastes

A dissertation
presented to the Graduate Course of Manufacturing Engineering of
Kitami Institute of Technology, Japan, in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

By
Momtaz Parveen

September, 2016

ABSTRACT

Biofuels can help in solving some of the global energy related problems. Therefore, how to derive biofuels from various resources has earned a great deal of attention. In this respect, thermochemical decomposition technology called pyrolysis can be used. This study, in particular, addresses the derivation of biofuels and other chemical substances from the selected biomass solid wastes: jute stick, tamarind seed, and cedar wood using a fixed-bed pyrolysis unit. Note that jute stick is available in India, Bangladesh, and China, whereas tamarind seed is available in tropical countries located in South East and South Asia, and cedar wood is available in Japan.

The selected biomass solid wastes have been characterized by using the proximate, ultimate, gross calorific value, and thermo-gravimetric analyses. The analyses help determine whether the selected biomasses are suitable for pyrolysis (i.e., a thermal decomposition in partially/completely absence of oxygen). Thermal gravimetric (TG) and differential thermal gravimetric (DTG) behavior of selected three biomass have been investigated under nitrogen atmosphere at heating rates 10 and 60°C/min over temperature range 30-600°C. The percentage weight loss was higher for Japanese cedar wood and lower for tamarind seed for both heating rates. Using the results of these analyses, the kinematic models have been developed for the respective solid wastes for predicting TG and DTG data. The models are based on the Arrhenius Law, and exhibit a good correlation with the experimental results.

In the next phase of this study, the particles of the selected biomass solid wastes (hereinafter referred to as feedstock) have been processed using pyrolysis. A fixed-bed pyrolysis unit has been used to obtain the biofuels and other chemical substances from the feedstock. The pyrolysis performance of the respective solid wastes (i.e., liquid yields) have been determined varying such conditions as fixed-bed reactor temperature, feedstock size, nitrogen gas flow rate, and running time. The maximum liquid yields are about 50%, 45%, and 48% (in terms of weight fraction) for the feedstock of jute stick, tamarind seed, and cedar wood at the fixed-bed reactor temperature equal to 425°C, 400°C, and 450°C, respectively. The other conditions corresponding to maximum liquid yields for all three types of feedstock are as follows: nitrogen gas flow rate is equal to 6 l/min, feedstock size is in the range of 1180 μm to 1700 μm , and running time is 30 min.

Liquid products obtained at these conditions were characterized by physical properties, chemical analysis and GC-MS techniques. The results show that it is possible to obtain liquid products that are comparable to petroleum fuels and valuable chemical feedstock from the selected three biomass if the pyrolysis conditions are chosen accordingly.

CONTENTS

	Page No.:
ABSTRACT	i
CONTENTS	ii
NOMENCLATURE	vi
LIST OF FIGURES	vii
LIST OF TABLES	ix

Chapter 1

Introduction

1.1 Biomass as renewable source of energy	1
1.2 Available biomass conversion process	5
1.3 Thermochemical conversion process	6
1.3.1 Pyrolysis	6
1.3.2 Biomass Gasification	7
1.3.3 Direct Combustion	7
1.3.4 Liquefaction	7
1.4 Pyrolysis principles	7
1.5 Pyrolysis conversion of biomass solid wastes	8
1.6 Availability of the three selected biomass	9
1.6.1 Tamarind seed	9
1.6.2 Jute stick	10
1.6.3 Japanese cedar wood	11
1.7 Objectives of the study	12

Chapter 2

Characterization and pyrolysis kinetics behavior of biomass solid wastes

2.1	Characterization studies	13
2.1.1	Proximate analysis	14
2.1.2	Ultimate Analysis	15
2.1.3	Gross calorific value	15
2.2	Pyrolysis kinetics behavior	16
2.2.1	Apparatus and experimental conditions	16
2.2.2	Theoretical	16
2.2.3	Thermo-gravimetric and differential thermo-gravimetric analysis	19
2.2.4	Pyrolysis rate equation	26
2.2.4.1	Rate equations for heating rate of 10°C/min	27
2.2.4.2	Rate equations for heating rate of 60°C/min	28
2.3	Conclusions	30

Chapter 3

Experimental set-up and procedure

3.1	The Fixed bed pyrolysis set up	31
3.2	Process flow chart	33
3.3	Experimental procedure	34
3.4	Description of experimental set-up	35

Chapter 4

Pyrolysis of selected biomass solid wastes

4.1 Feed material preparation	38
4.2 Pyrolysis of three selected biomass	38
4.3 Results and discussion	38
4.3.1 Effect of reaction conditions on product yields of tamarind seed	39
4.3.1.1 Effect of reactor temperature	39
4.3.1.2 Effect of feed size	40
4.3.1.3 Effect of N ₂ gas flow rate	42
4.3.1.4 Effect of running time	44
4.3.2 Effect of reaction conditions on product yields of jute stick	45
4.3.2.1 Effect of reaction temperature	45
4.3.2.2 Effect of feed particle size	47
4.3.2.3 Effect of N ₂ gas flow rate	48
4.3.2.4 Effect of running time	50
4.3.3 Effect of reaction conditions on product yields of Japanese cedar wood.	51
4.3.3.1 Effect of reactor temperature	51
4.3.3.2 Effect of feed particle size	53
4.3.3.3 Effect of N ₂ gas flow rate	54
4.3.3.4 Effect of running time	55
4.4 Conclusions	56

Chapter 5

Physical and chemical properties of pyrolysis oils

5.1 Physical properties	57
5.1.1 Kinematic viscosity	57
5.1.2 Density	57
5.1.3 Ash content	57
5.1.4 Flash point	58
5.1.5 Pour point	58
5.1.6 Gross calorific value	58
5.1.7 pH Value	58
5.2 Fuel properties of the pyrolytic liquids	59
5.3 Chemical properties analysis	61
5.4 Classification identified compounds present in selected biomass derived pyrolysis oils	73
5.5 Conclusions	80

Chapter 6

Recommendations

6.1 Recommendations	81
6.1.1 On the current experimental set-up	81
6.1.2 On the future work	82
References	83
Acknowledgements	90
Appendix	91

NOMENCLATURE

%	-	Percent
°C	-	Degree Celsius
T	-	Temperature
kJ/kg	-	kilo joule per kilogram
GCV	-	Gross calorific value
cSt	-	centistoke
kJ/kg	-	kilojoule per kilogram
wt%	-	weight percent
A	-	Frequency factor (1/min)
dX/dt	-	Normalized weight loss rate
TGA	-	thermo-gravimetric analysis
DTG	-	Differential thermogravimetric analysis
E	-	Activation energy (kJ/mol)
t	-	Reaction time
β	-	Heating rate
μm	-	micrometer
l/min	-	liter per minute

LIST OF FIGURES

Figure No.:		Page No.:
Fig. 1.1:	The main process of energy conversion from organic solid waste	5
Fig. 1.2:	Representation of the reaction paths for biomass pyrolysis	8
Fig. 1.3:	Tamarind fruit	9
Fig. 1.4:	Tamarind seed	9
Fig. 1.5:	Jute plant	10
Fig. 1.6:	Jute sticks	10
Fig. 1.7:	Japanese cedar tree	11
Fig. 2.1:	Thermal decomposition scheme for solid biomass	17
Fig. 2.2 :	TG and DTG plots for tamarind seed at heating rates of 10 and 60°C/min	19
Fig. 2.3:	TG and DTG plots for jute stick at heating rates of 10 and 60°C/min	20
Fig. 2.4:	TG and DTG plots for cedar wood at heating rates of 10 and 60°C/min	20
Fig. 2.5:	TG plots for jute stick, cedar wood and tamarind seed at heating rate of 10°C/min	21
Fig. 2.6:	TG plots for jute stick, cedar wood and tamarind seed at heating rate of 60°C/min	21
Fig. 2.7:	DTG plots for jute stick, Japanese cedar wood and tamarind seed at heating rate of 10°C/min	22
Fig. 2.8:	DTG plots for jute stick, Japanese cedar wood and tamarind seed at heating rate of 60°C/min	22
Fig. 2.9:	Comparison of TG data and computed values from numerical integration of rate equation	27
Fig. 2.10:	Arrhenius plots of Japanese cedar wood, tamarind seed, Jute stick in nitrogen at heating rate of 10°C/min	28
Fig. 2.11:	Arrhenius plots of Japanese cedar wood, tamarind seed, Jute stick in nitrogen at heating rate of 60°C/min	29

Figure No.:	PageNo.:
Fig. 3.1: Process flow chart for fixed bed pyrolysis	33
Fig. 3.2: Sketchmatic diagram of the fixed bed pyrolysis system	36
Fig. 3.3: Photograph of the fixed-bed pyrolysis system	37
Fig. 4.1: Effect of temperature on product yields of tamarind seed pyrolysis at N ₂ gas flow rate 6 l/min with feed particle size 1180-1700 μm	39
Fig. 4.2: Effect of feed size on product yields for temperature 400°C and N ₂ gas flow rate 6 l/min with feed particle 1180-1700 μm	41
Fig. 4.3: Effect of N ₂ gas flow rate on product yields for temperature 400°C and feed size 1180-1700 μm	42
Fig. 4.4: Effect of running time on product yields for N ₂ gas flow rate 6 l/min and temperature 400°C with feed particle size 1180-1700 μm	44
Fig. 4.5: Effect of reaction temperature on product yields of pyrolysis of jute stick for particle size 1180-1700 μm and N ₂ gas flow rate 6 l/min	45
Fig. 4.6: Effect of feed particle size on product yields from pyrolysis of jute stick at reactor temperature 425 with N ₂ gas flow rate 6 l/min	47
Fig. 4.7: Effect of N ₂ gas flow rate on product yields from pyrolysis of jute stick at reactor temperature 425 for particle size 1180-1700 μm	48
Fig. 4.8: Effect of running time on product yields at temperature 425°C for particle size 1180-1700 μm with N ₂ gas flow rate 6 l/min	50
Fig. 4.9: Effect of reaction temperature on product yields from pyrolysis of cedar wood for particle size 1180-1700 μm and N ₂ gas flow rate 6 l/min	51
Fig. 4.10: Effect of feed particle size on product yields from pyrolysis of cedar wood at reactor temperature 450 at N ₂ gas flow rate 6 l/min	53
Fig. 4.11: Effect of N ₂ gas flow rate on product yields from pyrolysis of cedar wood at reactor temperature 450 for particle size 1180-1700 μm	54
Fig. 4.12: Effect of running time on product yields at temperature 400°C for particle size 1180-1700 μm with N ₂ gas flow rate 6 l/min	55

LIST OF TABLES

Tables No.:		Page No.:
Table 1.1:	Thermochemical conversion technologies, products and application	06
Table 2.1:	Proximate analysis of selected biomass	14
Table 2.2:	Ultimate analysis of selected biomass	15
Table 2.3:	Gross calorific value of selected biomass	15
Table. 2.4:	Reaction characteristics of the selected biomass	23
Table 2.5:	Comparisons of kinetic parameters of selected biomass	24
Table 5.1:	Comparison of tamarind seed, jute stick and cedar wood pyrolysis oil with petroleum fuels	60
Table 5.3.1:	Possible identified compounds in jute stick pyrolysis oil by GC/MS analysis with their structural formula and applications	62
Table 5.3.2:	Possible identified compounds in jute stick pyrolysis gas by GC/MS analysis with their structural formula and applications	65
Table 5.3.3:	Possible identified compounds in tamarind seed pyrolysis oil by GC/MS analysis with their structural formula and applications	66
Table 5.3.4:	Possible identified compounds in tamarind seed pyrolysis gas by GC/MS analysis with their structural formula and applications	68
Table 5.3.5:	Possible identified compounds in Japanese cedar wood pyrolysis oil by GC/MS analysis with their structural formula and applications	69
Table 5.3.6:	Possible identified compounds in Japanese cedar wood pyrolysis gas by GC/MS analysis with their structural formula and applications	72

Chapter 1

Introduction

1.1 Biomass as renewable source of energy

Energy is a strategic input for socio-economic development. It helps meet the basic human needs. In fact, energy propels the society. The standard of living is correlated with per capita energy consumption. The sources of energy are categorized as renewable and non-renewable. The fascination of renewable energy is that it is not dwindling, rather non-depleting and that it does not damage environment, rather it contributes towards a hazard-free safe environment. Renewable energy sources have proven their reliability in comparison with conventional source of energy. It is reported by Sayigh [1] that in the United States alone, at present, the annual turnover of the renewable industry is more than 2 billion dollars. Gassi [2] mentions that renewable energy sources are capable of providing a significant fraction of Europe's energy needs as equivalent to 2 million barrels of oil per day. The important forms of renewable energy are: biomass and biogas application; solar water heating; photovoltaic (PV) applications; and wind and hydro-energy applications. Amongst these biomass is the most popular form of renewable energy and covers a wide range from wood burning to land fill gas, bio-digesters, alcohol production.

The energy crisis and environmental degradation are the main problems mankind is facing today. These problems owe their origin to a growing population, rapid industrialization and huge quantities of solid refuse, which are generated daily. By the year 2100, the world population is expected to be in excess of 12 billion and it is estimated that the demand for energy will be increased by five times from what it is now. Also it is estimated that petroleum reserve of the world will be nearly exhausted by (2040) recent future [3]. To alleviate part of our energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for the

possible recovery of resources from non-conventional sources. The problems related to the disposal of organic wastes available from urban, agro-industries or agricultural farms, etc. using biotechnology have already been addressed by several researchers [4, 5]. The disposal of solid wastes from human activity is a growing environmental problem for modern society, especially in developing countries [6].

Biomass has been recognized as a major renewable energy source to supplement declining fossil fuel sources of energy. It is the most popular form of renewable energy and currently biofuel production is becoming very much promising. Biomass is potentially the most attractive renewable energy resource available because it is widely dispersed and could contribute zero net carbon dioxide emission to the atmosphere. Biomass is already the fourth largest source of energy in the world supplying about 14% of primary energy [7]. It is considered the renewable energy source with the highest potential to meet the energy demand of modern society for both the developed and developing economies worldwide [7-8]. Biomass has three components about half celluloses, a quarter hemicelluloses and extractives, and quarter lignin for a typical woody biomass and possess a high energy content [9-10]. The cellulose fibers containing 49 wt% oxygen are held together in a matrix of lignin containing 12 to 29 wt% oxygen and hemicelluloses containing 54 wt% oxygen, similar in concept to fiber glass fibers in polyester resins. The overall range for the oxygen content of woody and herbaceous biomass is 40 to 45 wt% on moisture and ash free basis [11]. Lukas et. al. [12] found that in biomass decomposition processes proceed in three main stages: water evaporation, active and passive pyrolysis. The decomposition of hemicellulose and cellulose takes places in temperature ranges of 200- 380°C and 250-380°C, while lignin decomposition seems to be ranging from 180°C up to 900°C. Disposing of waste has huge environmental impacts and can cause serious problems. In the world much of wastes is buried in landfill sites, holes in the ground, sometimes old quarries, sometimes specially dug. Some waste will eventually rot, but not all, and in the process it may smell or generate methane gas, which is explosive and contributes to the greenhouse effect. Biomass produced as waste

decomposes may cause pollution. Badly managed landfill sites may attract vermin or cause litter [13].

Bangladesh is an agriculture-based country. Some of the major agricultural residues or by-products in Bangladesh along with some other countries are tamarind seed and jute-stick. Besides a lot of soft woods like eucalyptus and cedar grow major part of the world in forests, road side etc. The conventional uses of these biomass solid wastes are as fuel for cooking, raw material for paper and pulp industries and a huge amount is unused and wasted that creates disposal problem. These carbonaceous solid wastes are renewable energy source and therefore, the potential of converting them into useful energy such as liquid fuel should be seriously considered. In this way, the wastes would be more readily usable and environmentally more acceptable [14-15].

Transformation of energy into useful and sustainable forms that can fulfill and suit the needs and requirements of human beings in the best possible way is the common concern of the scientists, engineers and technologists. From the view point of energy transformation, pyrolysis is more attractive among various thermochemical conversion processes because of its simplicity and higher conversion capability of biomass and its solid wastes into liquid product [16-19]. Thermal decomposition is not only a part of the pyrolysis process, it is also a first step in gasification and combustion process. The rate of heat supply, total energy and operation time are the important design parameters for a pyrolysis system [20]. These parameters can be determined by thermal decomposition behavior studies of the biomass under pyrolysis. The technique of thermo-gravimetric analysis (TGA) has been extensively used to determine complex solid state reactions of materials in the thermal decomposition process. Therefore, the knowledge of pyrolysis characteristics of a particular biomass waste is necessary.

Pyrolysis is a thermal decomposition technology which could convert biomass and its wastes into energy in absence of oxygen. Pyrolysis of biomass solid wastes is considered as an emerging potential technology for liquid oil production. Three products are typically obtained from pyrolysis of the biomass: liquids, char and gases. The pyrolysis of

solid biomass waste has received increasing attention because the process conditions may be optimized to produce high energy density liquids, char and gases [21-23].

Biomass pyrolysis liquids have been found to have a moderate calorific value of around 17 to 23 MJ/kg which would encourage their use as replacements for conventional liquid fuels. Pyrolytic char may be used as a solid fuel or as a precursor for activated carbon manufacture. The gas has also calorific value, sufficient to be used for the total energy requirements of the pyrolysis plant [24-25]. By deriving more energy from renewable feed stocks, the United States and other countries might be able to significantly decrease their reliance on foreign petroleum. For this reason, efforts have been made to develop new processes for converting renewable biomass to energy [26]. Moreover the pyrolytic breakdown of biomass produces a large number of chemical substances [27-30].

Hundreds of chemical compounds are usually found in different bio-mass oil such as 3-decyn-2-ol, 2, 6-dimethoxy phenol, 2-cyclohexen-1-one, 2-propenyl ester, acetic acid, crotonic acid, phenol, 2-methoxy (guaiacol), furans 1, 4 benzene diol (hydroquinone), oleic acid, n-propyl acetate, pentacosane, hexacosane, p-xylene, 2-furan carboxaldehyde etc [17]. The chemical compounds which are usually found in different bio-mass pyrolysis gases are 1-propane allyene, L-alanine etc.

The chemical compounds found in biomass pyrolysis oil may be used in perfume, flavors, soap, synthetic projects, safety, and labeler flavors in food, vegetable oil for cooking and industrial activities, irrigation, fertilizers, water spray, chemical foam and research, eye irritation test, preparing reagent, evaporative light-scattering detection, bactericide in water treatment, skin cream, stencil paper, paints, liquid soaps oxidizing agent, solvents column chromatography, solvent in manufacture, water fog, regular foam etc. The chemical compounds of non-condensable gases may be used in fuel, manufacture of iron, steel, rayon, film, fertilizers and dye, petroleum refining water spray, dye-sensitized solar cells, paint coating, pharmaceuticals, polymers, plastics, thermoplastics polyethylene recreational purposes, fragrance, biological, research, glassware material safety etc.

1.2 Available biomass conversion processes

The energy in Biomass solid waste may be upgraded either by a direct combustion or through upgrading process to produce more valuable and useable product such as gaseous, liquid or solid fuel. This upgrading may physical, biological or thermo-chemical methods. The available process for the energy conversion from biomass solid wastes and the main products are summarized in Fig. 1.1.

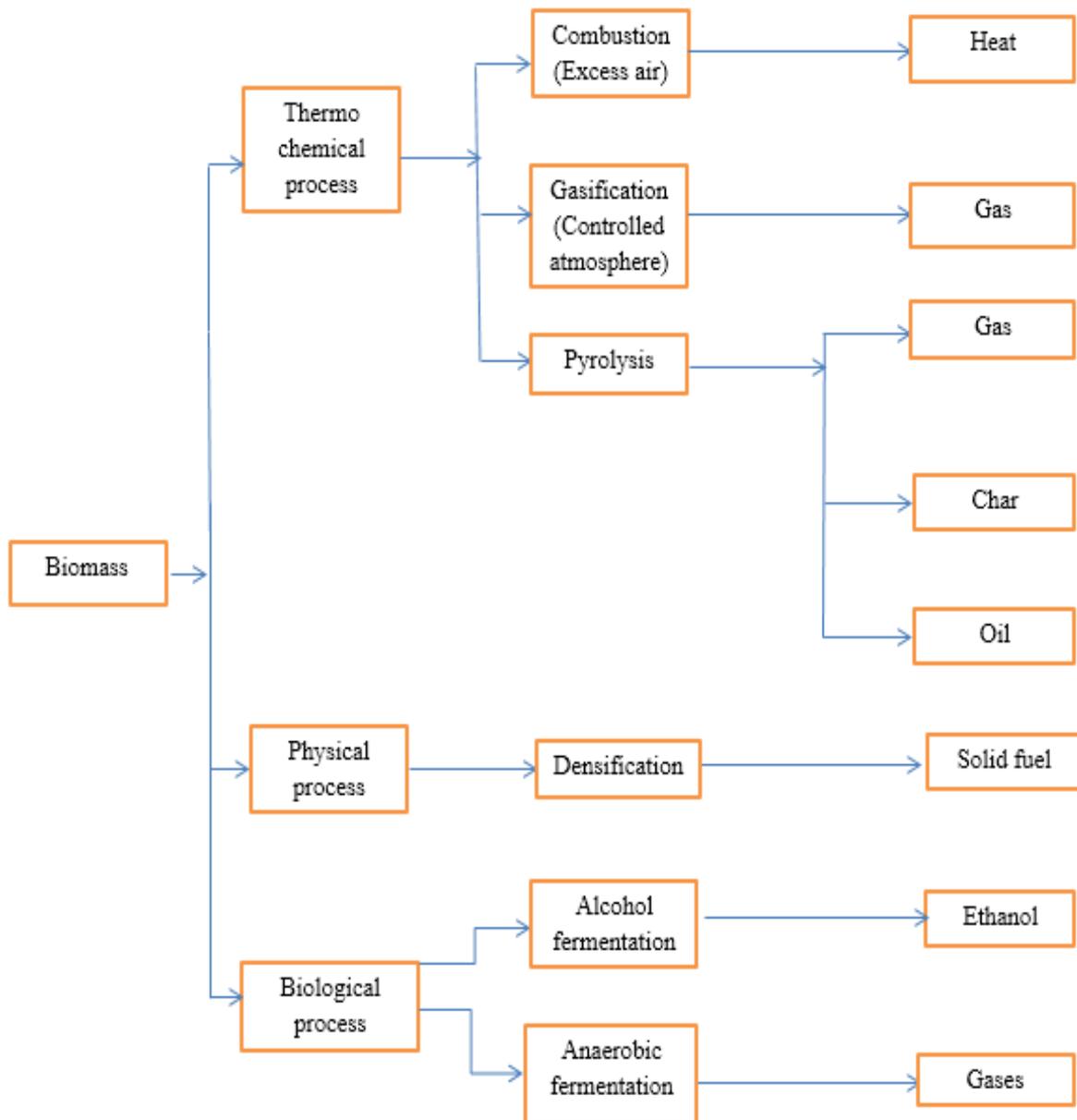


Fig. 1.1: The main process of energy conversion from organic solid waste.

1.3 Thermochemical conversion process

There are four thermochemical methods of converting biomass solid waste: pyrolysis, gasification, direct combustion and liquefaction. Each gives different ranges of products and employs different equipment configurations operating in different modes. These are summarized in Table 1.1.

Table 1.1: Thermochemical conversion technologies, products and applications

Technology	Primary product	Example application
Pyrolysis general	Gas Liquid Char	Fuel gas Liquid fuel and chemical Solid fuel/ fuel slurry
Very slow pyrolysis	Solid charcoal	Solid fuel
Fast pyrolysis (low temperature)	Liquid	Liquid fuel
Fast pyrolysis (high temperature)	Gas	Gaseous fuel and chemical
Gasification	Gas	Fuel gas
Combustion	Heat	Heating
Liquefaction	Liquid	Liquid fuel

1.3.1 Pyrolysis

Pyrolysis is a thermal decomposition process. It decomposes a substance (e.g. an organic material) in completely or partially absence of oxygen. It maintains a moderately high temperature and a high heat transfer rate. It also maintains a short-hot-vapor - residence time in the reaction zone. Several reactor configurations have been shown to assure this condition and to achieve yields of liquid products as high as 75% based on the starting dry biomass weight. Pyrolysis of biomass produces a liquid product, pyrolysis oil

or bio-oil that can be readily stored and transported. Pyrolysis oil is a renewable liquid fuel and can also be used for production of chemicals. Pyrolysis has now achieved a commercial success for production of chemicals and is being actively developed for producing liquid fuels. Pyrolysis oil has been successfully tested in engine, turbines and boilers, and been upgraded to high quality hydrocarbon fuels although at a presently unacceptable energetic and financial cost.

1.3.2 Biomass gasification

Gasification is designed to produce non-condensable gases, usually with the addition of a small amount of oxygen or air (sub-stoichiometric), directly to the reactor to provide the process heat for the gasification reaction

1.3.3 Direct Combustion

Direct combustion of biomass solid waste produces heat energy by direct burning of them.

1.3.4 Liquefaction

Liquefaction of biomass and wastes is accomplished by natural, direct and indirect thermal, and fermentation methods.. Other natural processes that produce liquids suitable as fuels are performed by certain tree species (e.g., the Brazilian *Copaifera langsdorfii* tree that yields sesquiterpenes that can be used as diesel fuels without modification)

1.4 Pyrolysis principles

The word pyrolysis comes from the Greek word “pyro” which means fire and “lysis” which means separating. Pyrolysis is generally described as the thermal decomposition of the organic wastes in the absence of oxygen at mediate temperature about 450° C.

Pyrolysis is presently seemed to be the most promising thermo-chemical conversion technology for the production of liquid fuel. Pyrolysis process is usually conducted in a reactor where heat is applied externally for combustion of feed materials. When organic material is heated in a non-reactive atmosphere, the devolatilization results in vapor, gas and char products. The products are cooled below their dew point in a condenser and the condensed liquids are obtained. The char is a carbon-rich, nonvolatile solid residue. Pyrolysis can be carried out in fixed bed or in fluidized bed. Fixed bed system is considered in this study. The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere.

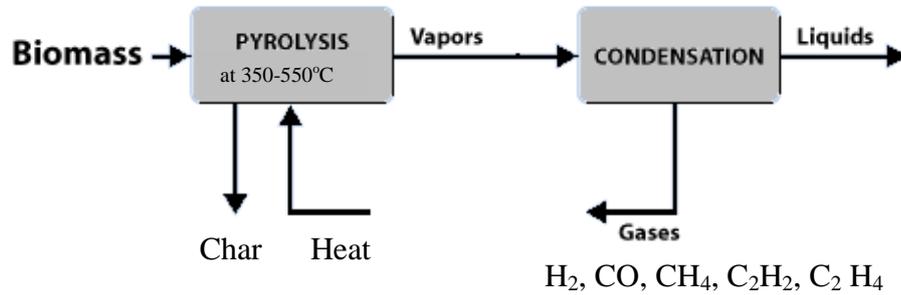
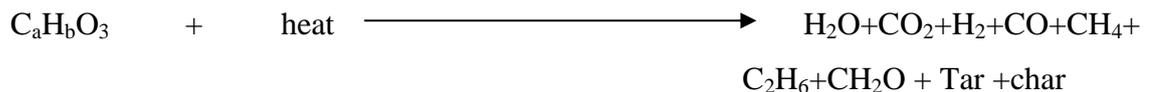


Fig. 1.2: Representation of the reaction paths for biomass pyrolysis

In this process; thermal decomposition of organic components in biomass starts at 350 °C–550 °C and goes up to 700 °C–800 °C in the absence of air/oxygen [31]. The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal under pyrolysis conditions.

1.5 Pyrolysis conversion of biomass solid wastes

Pyrolysis for energy conversion from carbonaceous wastes is defined as the thermal degradation of organic matter either in total absence of air or with a lack of a stoichiometrically needed amount of oxygen to the extent where gasification does not occur. Pyrolysis process is usually conducted in a reactor where heat is applied to the feedstock either externally or by the partial combustion of the feedstock. Three products are usually obtained in a pyrolysis process: liquid, solid char and gases. Pyrolysis is the heating of any fuel particle, droplet or gaseous molecule in the absence of oxygen and for solids it can be presented by the following equation:



There are three classes of products of pyrolysis; they are volatiles, tar and char. The volatiles may or may not be condensable at ambient condition; however, in all practical combustion systems these component remains in the gas phase. The tar is generally a

heavy hydrocarbon substance with an atomic H/C ratio > 1.0 . The char generally is a carbon rich solid with only minor fractions of hydrogen and heteroatom present in the fuel or waste. Although there are exothermic regions associated with some pyrolysis reaction, the overall solid particle pyrolysis is endothermic. This equation presents a summary of pyrolysis; however, it makes fundamental chemical process involved. Pyrolysis involves both chemical and physical changes. The physical changes include the potential for particle shrinkage. Further, pyrolysis changes the thermodynamic and transport properties of the fuel particles resulting in a material which is more isolative.

When the organic matter is heated in an inert atmosphere the primary vapors are first produced, the characteristics of which are most influenced by heating rate. These primary vapors then further degrade to secondary tars and gases if held at high temperature for long enough time for secondary reaction to occur. The proportions and characteristics of the secondary material are a function of temperature and time.

1.6 Availability of the three selected biomass

1.6.1 Tamarind seed

The tamarind plant (*Tamarindus indica*) is one of the sources of renewable energy. It is available mainly in Bangladesh, India, Thailand and Africa. It is also found in Australia, Florida, Malaysia, Oceania, Philippines and Seychelles. The tamarind is a slow heating, long-lived, massive tree reaches under a favorable conditions.

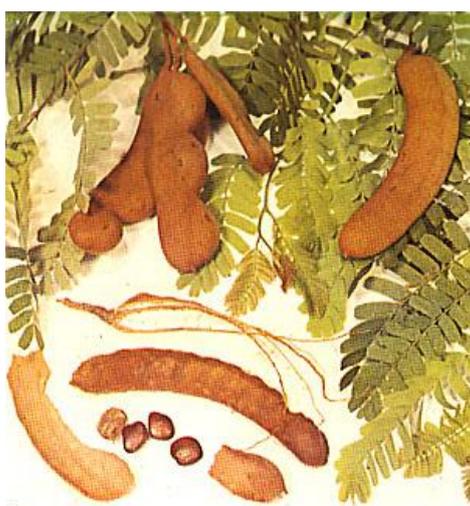


Fig. 1.3: Tamarind fruit



Fig. 1.4: Tamarind seed.

The size of the plant is 35 to 40 feet height with various sections. A single tree contains 9-90 kg seeds. Assuming 100 trees per hector provide 900-9000 kg seeds. The climate of Bangladesh is suitable for growing tamarind plants. The weight percentage of seed is 40-44 of the tamarind fruit. It is estimated that the production of tamarind in Bangladesh is 12000 ton/year and hence the seed production is 5280 ton. The seeds are not used in practice and it is considered as waste biomass. Thus, pyrolysis of tamarind seeds for oil production is promising option. Figs. 1.3 and 1.4 show tamarind fruit and tamarind seed, respectively.

1.6.2 Jute stick

Jute (*Corchorus capsularis*) is a plant (see Fig. 1.5) that mainly grows in India, Bangladesh and China. From a jute plant, one can extract fibers and a residue called jute stick (see Fig. 1.6). Jute fiber is used to produce different products, whereas jute sticks are used as a fuel for cooking and construction material. This means that jute plant has a high economic significance. In particular, Bangladesh (the second largest producer of jute) exports jute fiber and jute fiber based products to other countries to earn foreign currencies [32]. Since jute fiber is an eco-friendly material (*i.e.*, a biodegradable material), its usages is likely to increase in the years to come. On the other hand, due to the advent of urbanization and usages of other fuels (*e.g.*, natural gas), jute sticks have been losing its economic significance. In order to make use of abundantly available jute stick in Bangladesh, pyrolysis treatment of this jute stick was also chosen for this study.



Fig. 1.5: Jute plants



Fig. 1.6: Jute sticks

1.6.3 Japanese cedar wood

Cedar (*Larix sibirica*) is a Japanese wood. Essentially, it is the softwood species with the properties of a hard wood. It is a medium-size to large deciduous coniferous tree. It is about 10-30m tall. The crown is conic when young, becoming broad with age; the main branches are level to upswept, with the side branches often pendulous. The shoots are dimorphic, with growth divided into long shoots (typically 10-50 cm long) and bearing several buds, and short shoots only 1-2 mm long with only a single bud.



Fig. 1.7: Japanese cedar tree

It has biomorphic needles, with needles on new growth borne singly and arranged in a spiral around the branch and needles on older wood borne in clusters of 15-40 needles on short spurs. It is most easily distinguished from the closely related European larch by the shoots being downy (hairless in European larch). The leaves are needle-like, light green, 2-5 cm long, and turn bright yellow before they fall in the autumn, leaving the pale yellow-buff shoots bare until the next spring

Cedar wood is available in the forest though all over Japan. In Japan there is approximately 10% cedar forest [33]. The conventional uses of cedar wood are as fuel for cooking, raw material for building, houses and for paper and pulp industries and apportion has low graded usage. Japanese cedar wood is popular in its native Japan,

China for reforestation, roadside plantation and as an ornamental tree. It grows well in a wide variety of soil types, notably poor ones, and needs a lot of light and usually does not like high water tables.

Japanese cedar wood is a desirable wood to work with are its high dimensional stability, low installation cost, low maintenance, quality of manufacturing, and beautiful appearance. The cedar wood timber is a pale, whitish colored wood with a straight grain, but it can also be silver grey, light brown or reddish. Its characteristics of rot resistance and a very high ignition point ensure the timber's popularity in the world market. Japanese cedar wood grown on plantations generally has widely spaced growth rings and is therefore much less valuable. Cedar wood grows in plenty in Japanese weather all over the country. This wood is also important in China, Korea, and Japan for making the soundboards of stringed musical instruments.

1.7 The objectives of the study

Based on a literature review, the following objectives have been set for this dissertation:

1. To determine the physical, chemical, and thermal characteristics of the three pyrolysis-friendly biomass solid wastes, namely, jute-stick, tamarind seed, and Japanese cedar wood.
2. To perform pyrolysis of the above mentioned biomass solid wastes using a fixed bed reactor under Nitrogen atmosphere.
3. To determine the effects of the pyrolysis conditions (namely, operating temperature, nitrogen flow rate, feed size, and running time) on the yields (liquid, char and gases).
4. To determine the physical and chemical characteristics of pyrolysis oils and chemical substances.
5. To investigate the important uses of the compounds found in biomass derived pyrolysis oils.

Chapter 2

Characterization and pyrolysis kinetics behavior of biomass solid wastes

2.1 Characterization studies

Recently there has been a resurgence of global interest in renewable energy resources from organic solid waste. The heightened awareness is driven by environmental concern and shortage of non-renewable energy resources. The biomass samples that were used for characterization studies include tamarind seed and jute stick are available in Bangladesh, India, Nepal, Pakistan and Bhutan and Japanese cedar wood is available in the forests of Japan. These carbonaceous solid wastes are renewable energy sources and therefore, the potential of converting them into useful energy such as liquid fuel, should be seriously considered. In this way, the wastes would be more readily usable and environmentally more acceptable. Pyrolysis as a multi-product process has shown the potential of recovering hydrocarbon liquid from carbonaceous solid waste, besides char and the gas products. The pyrolytic liquid (pyro-crude oil), which is less bulky and more convenient to handle than the original solid waste, may be used as raw fuel or upgraded to higher quality fuel and chemicals and hence, have potential to conserve depleting petroleum oil reserves. Studies on the characteristics of solid wastes in terms of their physical and chemical properties and thermochemical characteristics are essential in developing a suitable thermal conversion system. The main criteria of feedstock suitability for thermal processing are low moisture and ash content. High volatile matter content is desirable for production of pyro-crude oil by pyrolysis conversion. These information can be obtained by proximate analysis. The TGA gives information about the temperature at which pyrolysis is initiated, when the rate is maximum and the temperature at which the process is completed. In this study investigation were conducted on the characterization of these three selected biomass. This characterization includes proximate analysis and ultimate analysis, calorific value, thermo-gravimetric and differential thermo-gravimetric analysis. All of the selected samples were collected, sun dried and then ground using blender machine. The ground biomass samples were used for the characterization studies.

2.1.1 Proximate analysis

Proximate analysis gives information about feedstock suitability in terms of moisture content, volatile matter content, fixed carbon and ash content. The amount of volatile matter indicates the suitability of waste as the feedstock for pyrolysis conversion to liquid product where high volatile content is desirable. Fixed carbon content gives information about the amount of char formation in the pyrolysis process. However, the carbon content determination through this analysis is not actual content, since some of the carbon present in the feedstock has also escaped along with the volatile during the thermal treatment. The ash content is determined by combustion of the volatile and fixed carbon. Moisture content in the feedstock can vary greatly depending upon the duration of storage and drying methods adopted.

Table 2.1: Proximate analysis of selected biomass

Solid biomass	Moisture content (%wt)	Ash content (%wt)	Volatile matter (%wt)	Fixed carbon (%wt)
Tamarind seed	5.45	2.15	78.59	13.81
Jute stick	9.02	0.78	78.40	11.80
Cedar wood	6.80	0.36	79.72	13.12

Moisture content is important in determining drying cost and energy content of the feed stock. Higher moisture content also presents immediate problem to all thermal processes since more energy is needed to evaporate the water. The moisture content in the feed stock would also reduce calorific value of the pyrolysis liquid product. The proximate analysis has been carried out according to the ASTM D3172-73 test procedure for solid fuel, entitled “standard method of proximate analysis of Coal and Coke”. The proximate analyses of tamarind seed, jute stick and Japanese cedar wood found in this study are presented in Table 2.1. From the information in the Table 2.1, it can be seen that tamarind seed contain small amount of moisture and higher amount of ash than those of jute stick and Japanese cedar wood. However, it has also good potential for pyrolytic liquid production. The variation in the ash content is due to the variation in the inorganic material. Their volatile contents are comparatively higher.

2.1.2 Ultimate analysis

Ultimate analysis in the determination of the percentages of carbon, hydrogen, nitrogen, sulfur and (by difference) oxygen in the gaseous products and ash after the complete combustion of organic materials in a sample of selected biomass. It is essential for their pyrolysis conversion upon which the pyrolysis product quality depends. The test was carried out by an Elemental Analyzer EA 1108 according to the ASTM D3176-84 standard test process in the laboratory of Analytical Research Division, BCSIR, Dhaka, Bangladesh. The technique for the determination of CHNOS was based on the quantitative “Dynamic flash combustion” method. The ultimate analysis results of the selected biomass are presented in Table 2.2.

Table 2.2: Ultimate analysis of selected biomass

Solid biomass	C (%wt)	H (%wt)	N (%wt)	O (%wt)	S (%wt)
Tamarind seed	45.76	9.59	0.02	44.59	0.04
Jute stick	44.94	4.38	0.76	49.90	0.02
Cedar wood	50.64	6.4	0.05	42.88	0.03

2.1.3 Gross calorific value

The gross calorific value of the prepared samples were determined using Plain Oxygen Bomb Calorimeter (model PARR 1341). The test was carried out in the Heat Engine Laboratory of Rajshahi University of Engineering & Technology (RUET), Rajshahi. The relative magnitudes of GCVs of the three selected biomass are considerable for thermochemical conversion and also indicate that tamarind seed, jute stick and Japanese cedar wood are the potential source of energy. The gross calorific values of the selected samples are presented in Table 2.3.

Table 2.3: Gross calorific value of selected biomass

Solid biomass	Gross calorific value (MJ/kg)
Tamarind seed	19.10
Jute stick	20.00
Cedar wood	22.84

Considering these favorable characteristics of tamarind seed, jute stick and Japanese cedar wood, the production of liquids through pyrolysis is an efficient method for the utilization of these selected biomass.

2.2 Pyrolysis kinetics behavior

2.2.1 Apparatus and experimental conditions

The Pyris Diamond Thermo-gravimetric/Differential Thermal Analyzer (TG/DTA) was used to obtain the Thermo-gravimetric Analysis (TGA), Differential Thermo-gravimetric (DTG) and Differential Thermo-analyze (DTA) data for the prepared samples. The 15-20 mg samples were heated over the temperature range of 30 to 800°C at constant heating rates of 10 and 60°C/min in a high purity nitrogen atmosphere with a flow rate of 100 ml/min.

2.2.2 Theoretical

When biomass are subjected to heating or burning conditions, complicated reaction mechanisms such as random-chain scission, end-chain scission, chain stripping, cross-linking and coke formation take place. The approach adopted by many research groups in performing the kinetic analysis of TG and DTG data for biomass and other wastes were to assume a first-order reaction for devolatilization [34]. To determine the apparent kinetic parameters, which are useful for engineering purposes, a two-stage first-order reaction with respect to the amount of decomposed material was assumed in this study. It was also assumed that the sample size is small enough to eliminate heat transfer effects. Thus, the following kinetic equation and reaction scheme (Fig. 2.1) were considered for the thermal degradation process for selected biomass wastes.

$$\frac{dX}{dt} = K_1(1-X_1) + K_2(1-X_2) + \dots \quad (1)$$

Where, $K_1, K_2 \dots K_n$ = reaction rate constants and $X_1, X_2 \dots X_n$ = fractional mass loss (kg)

The Arrhenius Law [7-8] has also been widely used for the one-step decomposition reaction and the reaction rate constants $K_1, K_2 \dots$ can therefore be obtained from the law

$$K_1 = A_1 e^{-\left(\frac{E_1}{RT}\right)} ; K_2 = A_2 e^{-\left(\frac{E_2}{RT}\right)} ; \dots\dots\dots (2)$$

Where, $A_1, A_2 \dots A_n$ = frequency factor (1/min), $E_1, E_2 \dots E_n$ = activation energy (kJ/mol),
 T = temperature ($^{\circ}\text{C}$) and R = universal gas constant (kJ/kg $^{\circ}\text{K}$)

The substitution of the values of the reaction rate constants from Eq. (2) into Eq. (1) yields

$$\frac{dX}{dt} = A_1 e^{-\left(\frac{E_1}{RT}\right)} (1-X_1) + A_2 e^{-\left(\frac{E_2}{RT}\right)} (1-X_2) + \dots\dots\dots (3)$$

Under the condition of a linear heating rate, $\beta = dT/dt$, Eq. (3) can be written as

$$\frac{dX}{dt} = \frac{A_1}{\beta} e^{-\left(\frac{E_1}{RT}\right)} (1-X_1) + \frac{A_2}{\beta} e^{-\left(\frac{E_2}{RT}\right)} (1-X_2) + \dots\dots\dots (4)$$

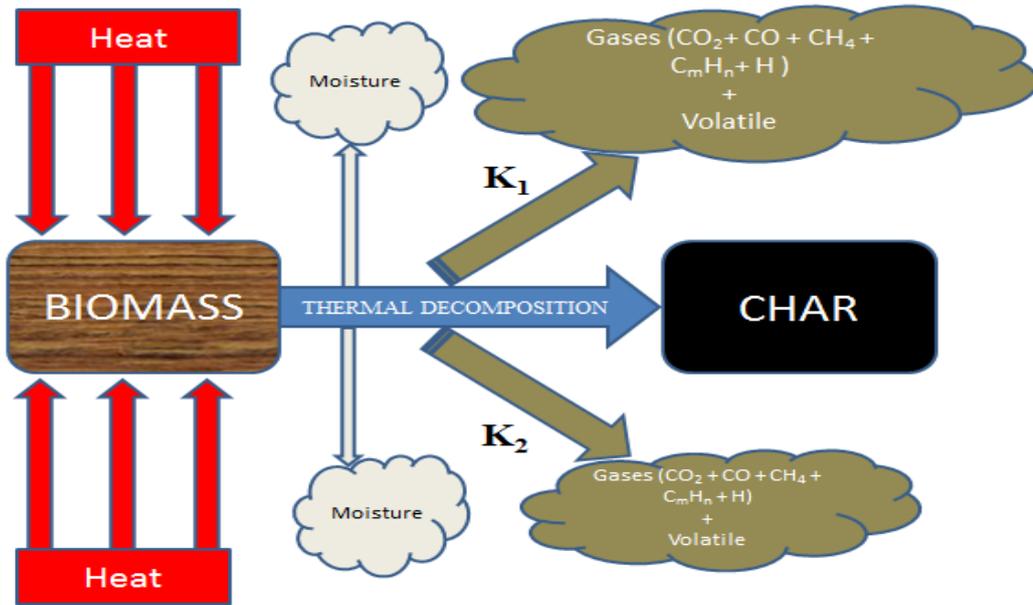


Fig. 2.1: Thermal decomposition scheme for solid biomass

For two individual reactions in two different temperature regions, the kinetic equation can be written as:

$$\frac{dX_1}{dT} = \frac{A_1}{\beta} e^{-\left(\frac{E_1}{RT}\right)} (1-X_1) \quad (5a)$$

$$\frac{dX_2}{dT} = \frac{A_2}{\beta} e^{-\left(\frac{E_2}{RT}\right)} (1-X_2) \quad (5b)$$

The kinetic parameters including E_1 , A_1 , E_2 and A_2 can be determined by using the experimental TG and DTG data. In the presented study, these parameters are evaluated by employing the least-square method, which is briefly described below. Taking the logarithm, Eq. (5a) give

$$\ln \frac{dX_1}{dT} = \ln \left[\frac{A_1}{\beta} (1-X_1) \right] - \frac{E_1}{RT} \quad (6)$$

For fixed values of β and X_1 the first term in the right-hand side of Eq. (6) is constant. Therefore, the equation can be reduced to find a least-square straight line on the $\ln(dX_1/dT)$ versus $1/T$ plane through the experimental data. It is important to note here that the dX/dT data is obtained from the dX/dt data, dividing the respective heating rate. If Eq. (6) is compared to the simple straight line equation $y = a_0 + a_1x$, it is found that $y = \ln(dX_1/dT)$, $x = 1/T$, the interception $a_0 = \ln [A_1/\beta (1-X_1)]$, and the slope, $a_1 = -E_1/R$. The best values of the regression coefficients (coefficients of the linear least-square fit line), a_0 and a_1 , that yield the kinetic parameters for low temperature region, can be calculated from the equations below

$$ma_0 + a_1 \sum_{i=1}^m x_i = \sum_{i=1}^m y_i \quad (7a)$$

$$a_0 \sum_{i=1}^m x_i + a_1 \sum_{i=1}^m x_i^2 = \sum_{i=1}^m x_i y_i \quad (7b)$$

Using the same method, the values of X_2 and the corresponding temperature ranges, Eq. (5b) yield the kinetic parameters for higher temperature regions. The values of the activation energy and the frequency factor for different values of heating rates and conversion factors can also be determined with the above procedure.

2.2.3 Thermo-gravimetric and differential thermo-gravimetric analysis

Figs. 2.2-2.8 show the variations of fractional mass (TG curves) and derivative of mass-lose (DTG curves) with respect to reaction temperature T for two different heating rates 10 and 60 °C/min for tamarind seed, jute stick and cedar wood biomass. The comparisons of the TG and DTG curves for the selected biomass show that they vary with respect to one another. This is due to the compositional differences among the tamarind seed, jute stick and Japanese cedar wood. It shows from the TG and DTG curves for the two different heating rates of a single sample are similar in appearance, but both the TG and DTG curves shift to higher temperature regions when the heating rates are increased.

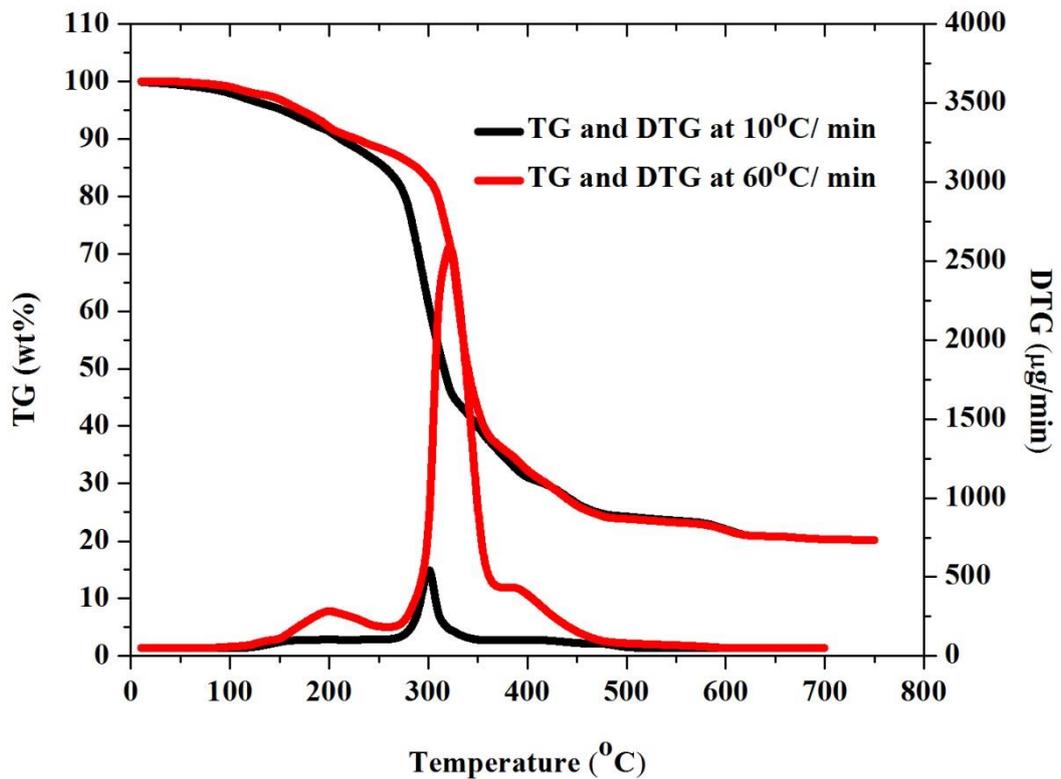


Fig 2.2: TG and DTG plots for tamarind seed at heating rates of 10 and 60°C/min

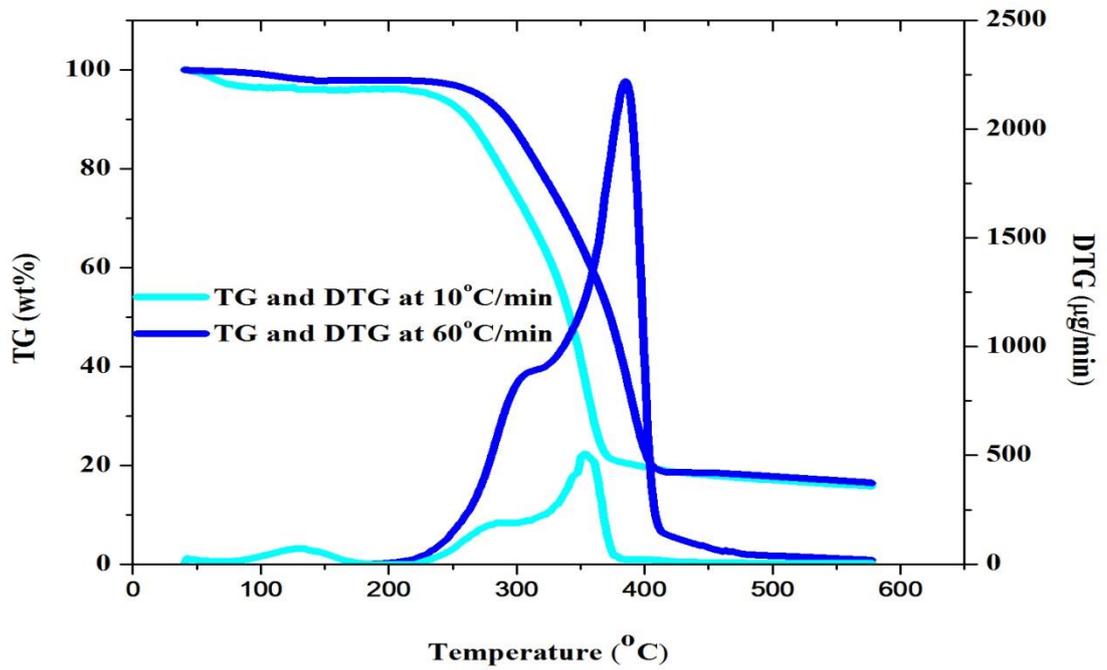


Fig 2.3: TG and DTG plots for jute stick at heating rates of 10 and 60°C/min

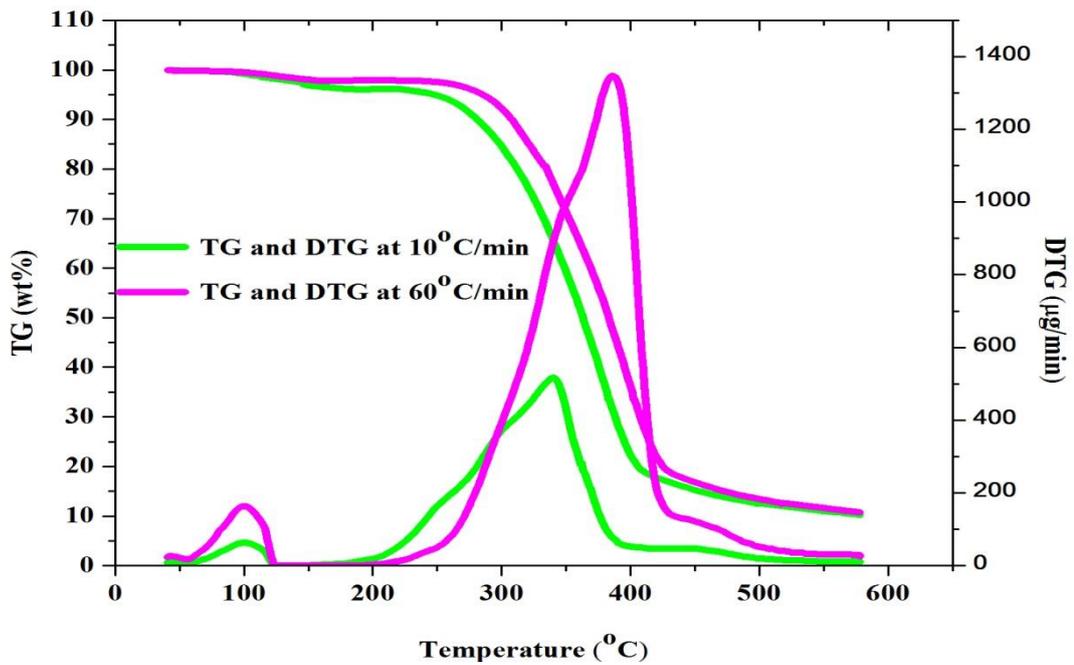


Fig 2.4: TG and DTG plots for cedar wood at heating rates of 10 and 60°C/min

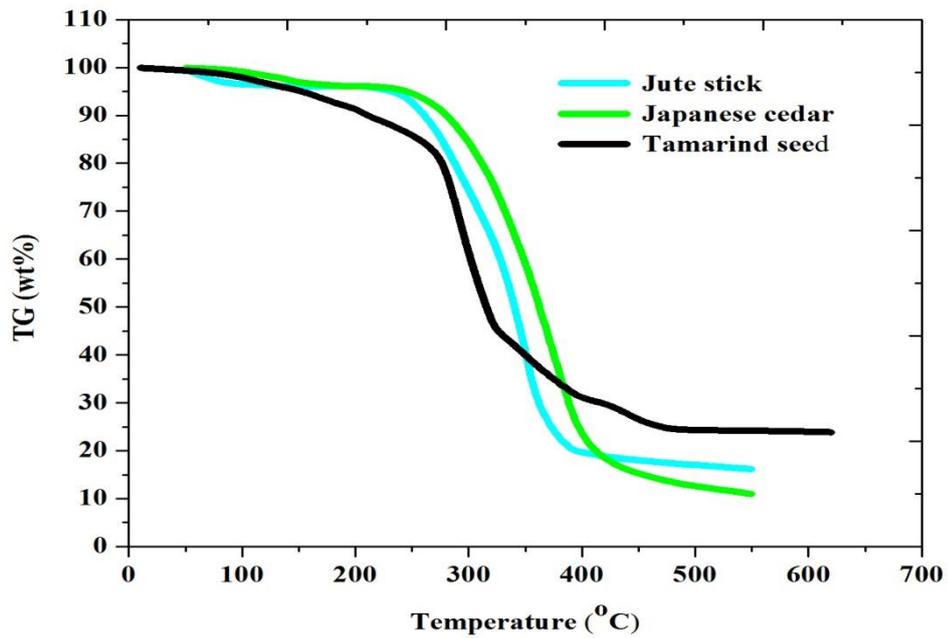


Fig. 2.5: TG plots for jute stick, cedar wood and tamarind seed at heating rate of $10^{\circ}\text{C}/\text{min}$

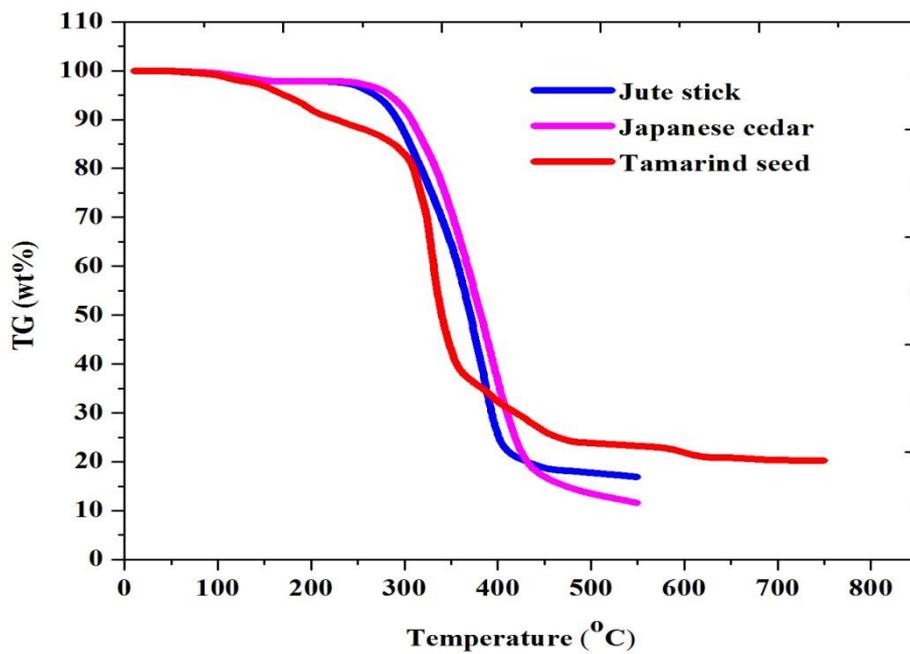


Fig. 2.6: TG plots for jute stick, cedar wood and tamarind seed at heating rate of $60^{\circ}\text{C}/\text{min}$

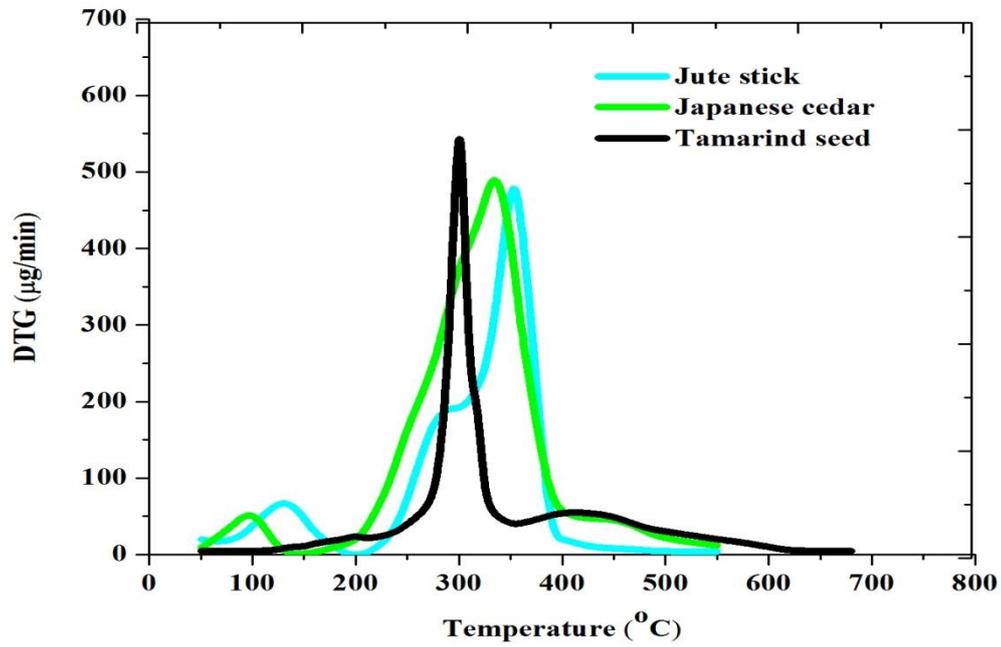


Fig. 2.7: DTG plots for jute stick, Japanese cedar wood and tamarind seed at heating rate of $10^{\circ}\text{C}/\text{min}$

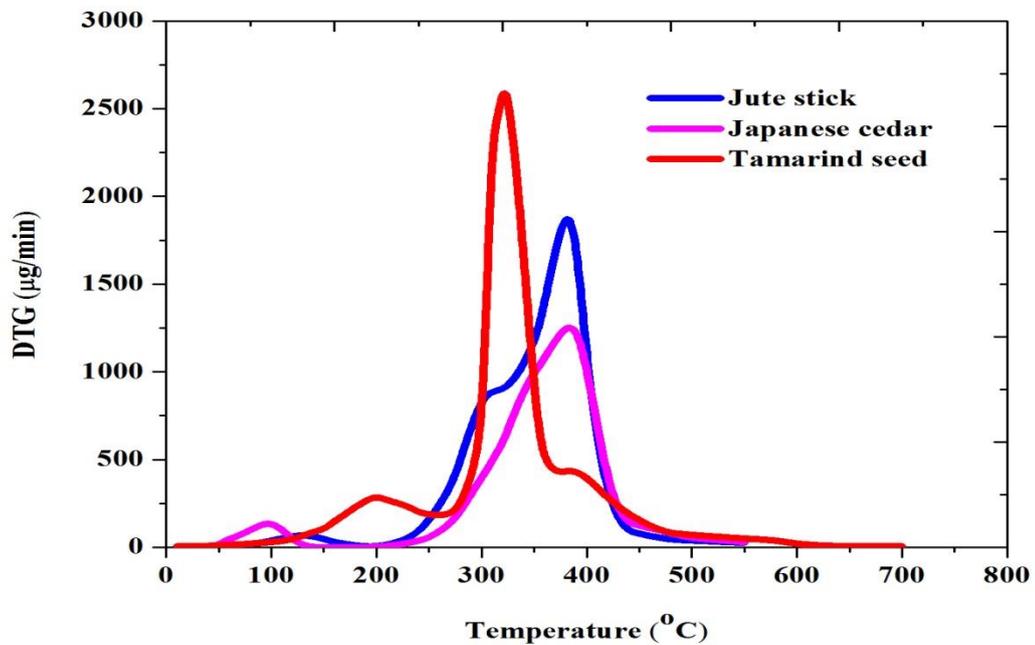


Fig. 2.8: DTG plots for jute stick, Japanese cedar wood and tamarind seed at heating rate of $60^{\circ}\text{C}/\text{min}$

This means that the reaction zones shift to the higher temperature regions and the peak heights increase with the increase of heating rate. The DTG curves for all of the samples show two-step degradation. Each of the DTG curves has one dominant peak. A second lower-value peak appears at lower temperatures for jute stick and cedar wood and at higher temperatures for tamarind seed.

The reaction characteristics of the selected biomass waste samples are summarized in Table 2.4 for three dominant degradation temperature regions. The reaction characteristics show that the initial reaction temperature decreases but the final reaction temperature increase when the heating rate is increased. Thus, the reaction range increases with increasing heating rate.

Table 2.4: Reaction characteristics of the selected biomass

Biomass	Heating rate β ($^{\circ}\text{C}/\text{min}$)	Initial temperature ($^{\circ}\text{C}$)	Peak temperature ($^{\circ}\text{C}$)	Final temperature ($^{\circ}\text{C}$)	Total weight loss (wt %)
Tamarind seed	10	120	300	455	75.5
	60	100	330	500	77.2
Jute stick	10	220	360	390	84.4
	60	200	394	460	85.5
Cedar wood	10	200	330	480	86.5
	60	210	390	520	87.4

Table 2.4 shows that the initial reaction temperature is about 100-120 $^{\circ}\text{C}$ for tamarind seed, 200-220 $^{\circ}\text{C}$ for jute stick and 200 -210 $^{\circ}\text{C}$ for cedar wood, respectively and that the peak temperatures for tamarind seed, jute stick and cedar wood at which the conversion rate is maximized (i.e. $dX/dT = 0$) is at about 300-330 $^{\circ}\text{C}$, 360-394 $^{\circ}\text{C}$ and 330-390 $^{\circ}\text{C}$, respectively. The decomposition temperature is about 180-370 $^{\circ}\text{C}$ for cellulose and hemicelluloses, above 390 $^{\circ}\text{C}$ for lignin. The total weight loss is 75.5-77.2 wt% for tamarind seed, 84.4-85.5 wt% for jute stick and 86.5-87.4 wt% for cedar wood where these values vary slightly with heating rate. The total weight loss for tamarind seed is

comparatively lower than those of jute stick and cedar wood. The conversions of the biomass samples were completed within the temperature ranges of 390– 480 °C for a heating rate of 10 °C/min and 460–520 °C for a heating rate of 60 °C/min.

Biomass mostly consists of three components cellulose, hemicellulose and lignin. Previous research group, Yang et al. [35] reported that the pyrolysis of hemicelluloses started at 220 °C and maximum mass loss rate was at 260 °C. The pyrolysis of celluloses started in the range 315-390°C and maximum mass loss rate was at 355 °C. For lignin maximum mass loss rate was at 750 °C.

Table 2.5: Comparisons of kinetic parameters of selected biomass

Biomass sample	Heating rate (°C/min)	Low temperature region			High temperature region		
		Temp range (°C)	E (kJ/mol)	A (min ⁻¹)	Temp range (°C)	E(kJ/mol)	A (min ⁻¹)
Tamarind Seed	10	150-390	16.02	4.1×10^3	300-500	53.37	6.8×10^4
	60	160-395	16.33	0.42×10^3	290-530	61.96	3.6×10^5
Jute-stick	10	155-400	42.88	3.2×10^5	300-500	104.1	1.9×10^6
	60	180-450	44.19	2.4×10^4	327-555	83.22	7×10^3
Cedar wood	10	180-320	22.02	4.5×10^3	280-480	56.13	5.57×10^4
	60	220-370	25.17	1.3×10^4	350-500	64.37	4.18×10^6

Table 2.5 shows that the values of activation energy of tamarind seed are 16.02 and 16.33 kJ/mol and frequency factor 4.1×10^3 and $0.42 \times 10^3 \text{ min}^{-1}$ for low temperature region at heating rate 10 and 60 °C/min, respectively. For high temperature region the values of activation energy are 53.37 and 61.96 kJ/mol and frequency factor 6.8×10^4 and $3.6 \times 10^5 \text{ min}^{-1}$ at heating rate 10 and 60 °C/min, respectively.

For jute stick the values of activation energy are 22.02 and 25.17 kJ/mol and frequency factor 3.2×10^5 and $2.4 \times 10^4/\text{min}$ for low temperature region at heating rate 10 and 60 °C/min, respectively. For high temperature region the values of activation energy are

83.22 and 104.1 kJ/mol and frequency factor 1.9×10^6 and 7×10^3 /min at heating rate 10 and 60 °C/min, respectively. For both temperature regions the activation energy become high as the heating rate increased.

For Japanese cedar wood the values of activation energy are 42.88 and 44.19 kJ/mol and frequency factor 4.55×10^3 and 1.37×10^4 /min for low temperature region at heating rate 10 and 60 °C/min, respectively. For high temperature region the values of activation energy are 56.13 and 64.37 kJ/mol and frequency factor 5.57×10^4 and 4.18×10^6 /min at heating rate 10 and 60 °C/min, respectively. For both temperature regions the activation energy become high as the heating rate increased.

Previous research group, Fan-fei et al. [36] reported that the values of activation energy of three types of fresh biomass (grass, wheat straw, corn straw) vary in different thermal degradation temperature ranges; the values of activation energy are in the ranges of 35–207 kJ/mol.

Peng et al. [37] found the value of activation energy 4.22 - 5.25×10^4 kJ/mol and frequency factor 3.2×10^3 - 1.11×10^4 /min for chlorella protothecoides and 7.62 – 9.70×10^4 kJ/mol and frequency factor 2.44×10^6 – 9.16×10^7 /min for spirulina platensis.

Sorum et al. [38] found the value of activation energy 47.4-96.7 kJ/mol for newspaper and 46-112.3 kJ/mol for cardboard.

Garcia-Perez et al. [39] reported that the value of activation energy 125.33 kJ/mol and frequency factor 2.12×10^{18} /min for hardwood rich in fibers biomass and for softwood bark the value of activation energy 105.75 kJ/mol and frequency factor 2.18×10^{18} /min at heating rate 10°C/min.

Kim et al. [40] investigated the pyrolysis of chicken litter (flock and broiler) at heating rates 5 °C/min, 10 °C/min and 20 °C/min. They found that the apparent activation energy of flock and broiler were 484 kJ/mol and 464 kJ/mol, respectively.

Caballero et al. [41] obtained the value of activation energy 218.6 kJ/mol and frequency factor 7.014×10^{15} /min for olive stones and 249.2 kJ/mol and frequency factor 1.034×10^{18} /min for almond shells at heating rate 10 °C/min.

From the above discussion the values of the activation energy of tamarind seed, jute stick and cedar wood are lower than those obtained by Peng et al. [37], Garcia-Perez et al.

[39], Peng et. al. [37] and Caballero et al. [41] and in the range those obtained by Fan-fei et al. [36] and Sorum et al. [38].

2.2.4 Pyrolysis rate equation

The apparent kinetic parameters are obtained from the average of the kinetic parameters values listed in Table 2.5 for the two different heating rates and for the two reaction ranges. The value of the apparent activation energy is $E = 32.92$ kJ/mol and the frequency factor is $A = 1.08 \times 10^5$ /min for tamarind seed, $E = 71.09$ kJ/mol and $A = 5.6 \times 10^5$ /min for jute stick, and $E = 39.08$ KJ/mol and $A = 3.08 \times 10^5$ /min for cedar wood for high temperature region. Using the values of the apparent kinetic parameters, a simplified rate equation for selected biomass can be modeled throughout the pyrolysis reaction in nitrogen atmosphere as follows:

$$\frac{dX}{dT} = \frac{3.34 \times 10^5}{\beta} e\left(-\frac{6255.11}{T}\right) (1 - X) \quad (8a)$$

Or

$$\ln K = \ln\left(\frac{3.34 \times 10^5}{\beta}\right) - \frac{6255.11}{T} \quad (8b)$$

Eq. (8a) can be integrated using the fourth order Runge-Kutta numerical integration scheme to obtain the theoretical conversion factor versus temperature for the different heating rates. The comparison of TG data for three selected biomass and computed values for the heating rates of 10 and 60°C/min are presented in Fig. 2.9. From this figure it can be seen that the computed values from numerical integration of rate equations are found to satisfy the measured two sets of TG data fairly well.

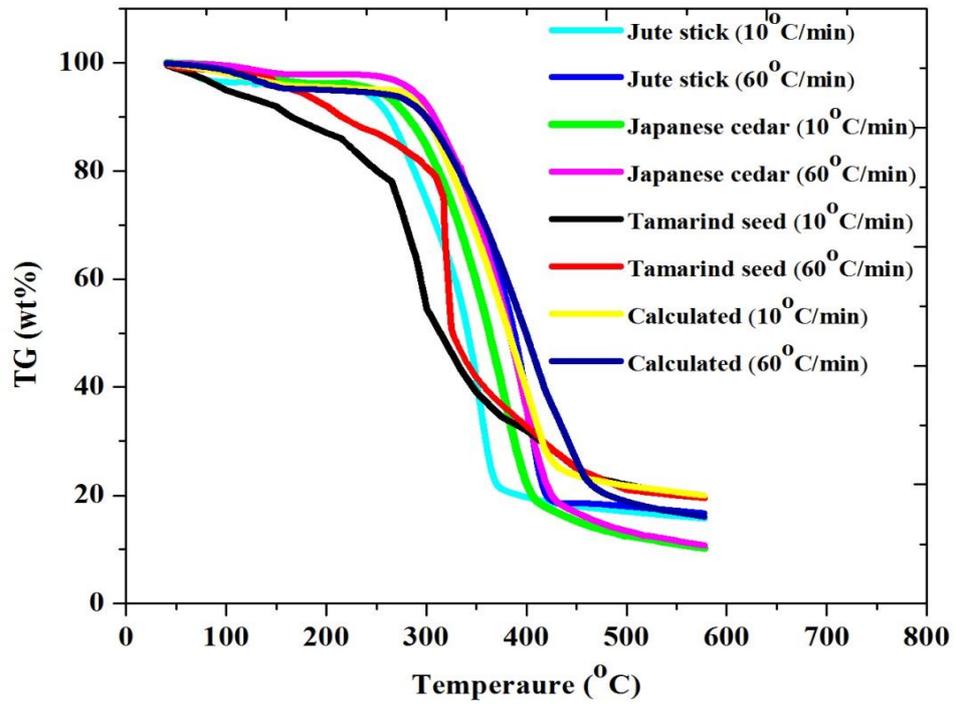


Fig. 2.9: Comparison of TG data and computed values from numerical integration of rate equations

2.2.4.1 Rate equations for heating rate of 10°C/min

For cedar wood,

$$\frac{dX}{dt} = 3.01 \times 10^4 \exp\left(\frac{4699.9}{T}\right) (1 - X) \dots \dots \dots (9)$$

$$\ln K = 10.31 - \left(\frac{4699.9}{T}\right)$$

For jute stick,

$$\frac{dX}{dt} = 6.5 \times 10^5 \exp\left(\frac{8839.3}{T}\right) (1 - X) \dots \dots \dots (10)$$

$$\ln K = 13.38 - \left(\frac{8839.3}{T}\right)$$

For tamarind seed,

$$\frac{dX}{dt} = 2.14 \times 10^6 \exp\left(\frac{10285.06}{T}\right) (1 - X) \dots \dots \dots (11)$$

$$\ln K = 16.86 - \left(\frac{10285.06}{T}\right)$$

2.2.4.2 Rate equations for heating rate of 60°C/min

For cedar wood,

$$\frac{dX}{dt} = 2.09 \times 10^6 \exp\left(\frac{5384.89}{T}\right) (1 - X) \dots\dots\dots(12)$$

$$\ln K = 14.55 - \left(\frac{5384.89}{T}\right)$$

For jute stick,

$$\frac{dX}{dt} = 1.55 \times 10^4 \exp\left(\frac{7662.3}{T}\right) (1 - X) \dots\dots\dots(13)$$

$$\ln K = 9.64 - \left(\frac{7662.3}{T}\right)$$

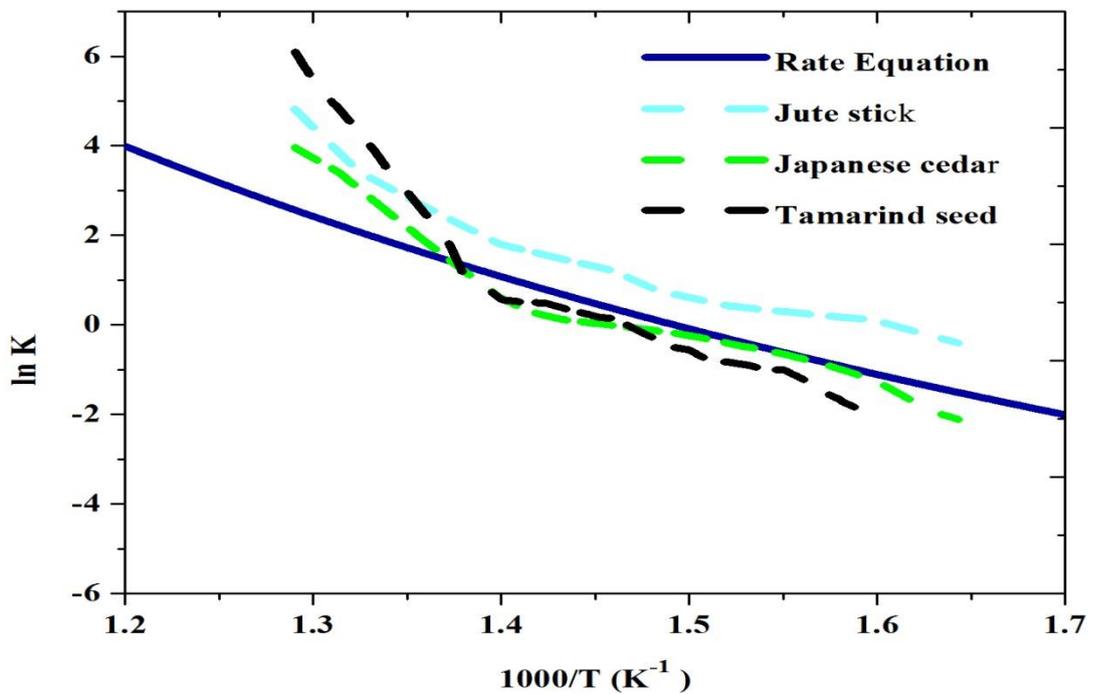


Fig. 2.10: Arrhenius plots of Japanese Jute stick, cedar wood, and tamarind seed in nitrogen at heating rate of 10°C/min

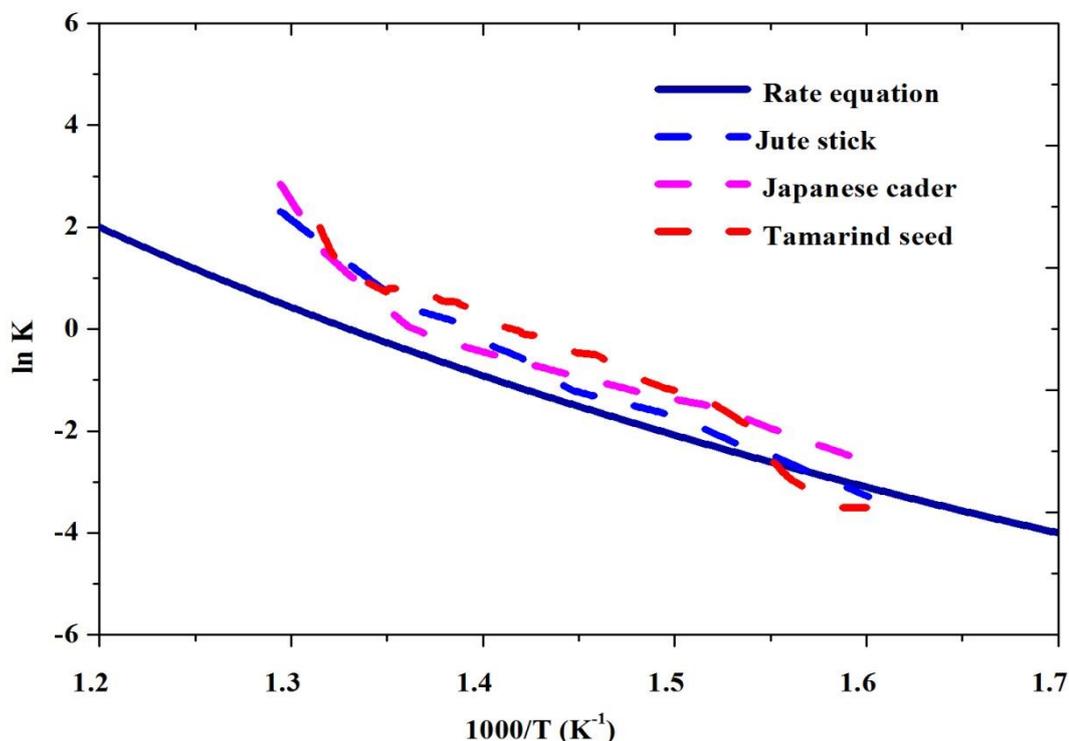


Fig. 2.11: Arrhenius plots of Japanese Jute stick, cedar wood, and tamarind seed in nitrogen at heating rate of 60°C/min.

Figs. 2.10 and 2.11 show the reaction rate versus temperature curve which are the Arrhenius plots of tamarind seed, cedar wood and jute stick at lower and higher heating rates. It means that the reaction rate vary with the temperature and heating rates. When the temperature increases, the reaction rate increases.

The Arrhenius plots of $\ln K$ versus $1000/T$ together with the DTG data for the tamarind seed, cedar wood and jute stick are shown in Figs. 2.10 and 2.11 for heating rates of 10 and 60°C/min, respectively. It can be seen that the derived equation based on the three reactions in the two different temperature regions fit well with the two sets of data for the heating rates of 10 and 60°C/min.

2.3 Conclusions

- Tamarind seed contains small amount of moisture and higher amount of ash than those of jute stick and Japanese cedar wood.
- The percentage carbon is lower for jute stick and higher for Japanese cedar wood.
- The TGA and DTG in this study provide valuable information on the pyrolysis process and reaction mechanism for selected biomass.
- The activation energy and frequency factor also increase with increasing heating rate.
- Among the selected biomass the percentage of total weight loss is higher for cedar wood and lower for tamarind seed.
- The rate equations for the three selected biomass can be modeled satisfactory by a simplified equation, which is found to fit the experimental data fairly well.
- The results of the presented study may be useful for rational design and operation of the pyrolysis system in which waste biomass are involved.

Chapter 3

Experimental set-up and procedure

3.1 The Fixed bed pyrolysis set up

The feed material in the reactor is kept in fixed position and heated at required temperature. As the feed is fixed in the reaction bed (reactor), it is called fixed bed pyrolysis. In this process, the feed material is supplied into the reactor and heat is applied externally. Inert gas is used for making inert conditions inside reactor chamber and for helping the pyrolysis gases to dispose of the reactor. The fixed bed pyrolysis set-up comprises of the following main components:

1. Reactor chamber
2. Condenser
3. Annular shaped electric heater
4. Liquid collector
5. N₂ gas cylinder
6. N₂ gas pre-heater
7. Temperature controller
8. Pyrometer
9. Air compressor

1. Reactor

The reactor is 10 cm diameter and 30 cm high constructed of mild steel with full gas flow and temperature control. Reactor is the enclosure where the biomass feed material are pyrolysed in the absence of oxygen. The annular shaped electrical heater surrounded the reactor to heat the reactor chamber externally. The N₂ gas cylinder provide N₂ gas for creating the inert atmosphere inside the reactor.

2. Condenser

A water cooled glass tube condenser was used for the experimental set-up. The gas and vapor produced from the feed material pass through the condenser tube and water flows surrounding tube. The condenser was positioned vertically and water was supplied from

the lower part and it leaves from the upper part. Thus, the entire condenser remains always full of water and cool by the flow of water.

3. Annular shaped electric heater

An annular shaped electric heater with well insulator was the confinement by which the reactor was surrounded. The capacity of electric heater was 1000 watt and heated the reactor at desired temperatures that were maintained by the controller.

4. Liquid collector

A glass conical shaped liquid collector with two ports was attached at the bottom of the condenser and the liquid is reserved in the collector. The pyrolysis vapor is condensed in the condenser and is collected in the liquid collector. The liquid collector is submerged in the ice bath for better condensation.

5. N₂ gas cylinder

The N₂ gas cylinder is used for supplying N₂ gas in the reactor. The N₂ gas attained O₂ free atmosphere inside the reactor to avoid any combustion reaction. The N₂ gas cylinder was equipped with pressure regulator and gas flow meter for maintaining desired gas flow and pressure from the cylinder.

6. N₂ gas preheater

A 5mm diameter copper tube was wound around the cylindrical reactor chamber for pre-heating the N₂ gas. Cool N₂ gas from the cylinder passed through the copper tube and gained heat and then enter into the reactor with an elevated temperature. The preheated N₂ gas made the pyrolysis reaction faster and created inert atmosphere as well.

7. Temperature controller

A well designed temperature controller was fabricated for operating the pyrolysis reactor at desired temperatures. The controller was enabled to maintain different reactor temperatures within the range 300 to 600°C at an interval 25/50°C \pm 2°C.

8. Pyrometer

The reactor temperature was measured by a digital pyrometer of model Lutron TM-914C with a sensor type of thermocouple K (NiCr-NiAl). Its capacity for measuring temperature range was -40 to 1200°C. The pyrometer probe was inserted the bed of feed in the reactor where the pyrolysis conversion had been taken place.

9. Air compressor

An air compressor is a device that converts power (using an electric motor, diesel or gasoline engine) into potential energy stored in compressed air. The energy contained in the compressed air can be used for a variety of applications, utilizing the kinetic energy of the air as it is released and the tank is depressurized. A compressor euro 30, E3-G100 of capacity 400 liters with a maximum pressure 20 bar was used for this experiment.

3.2 Process flow chart

The process flow chart of the fixed bed pyrolysis of these selected three biomass is given in Fig. 3.1. The prepared feed material is taken into the reactor and heated. The biomass vapor is passed through the condenser to separate the products into liquid and gases.

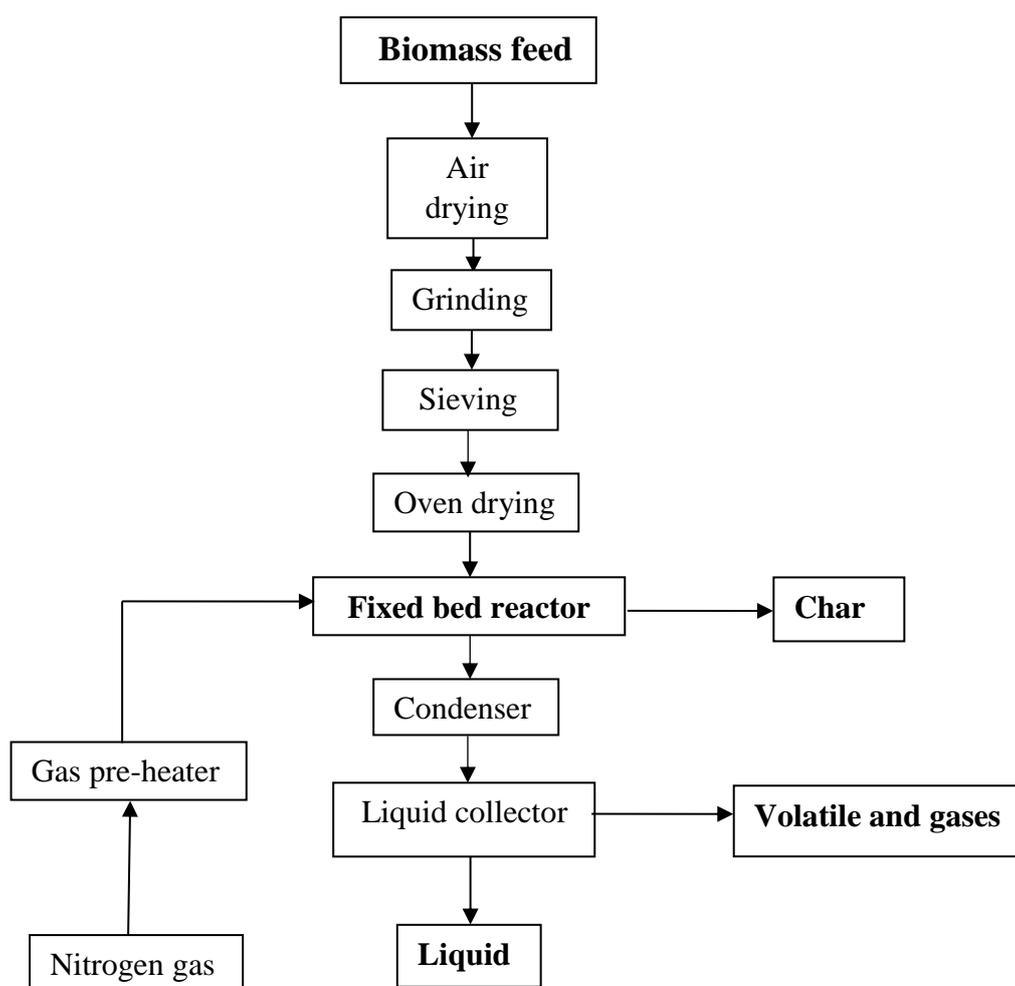


Fig. 3.1: Process flow chart for fixed bed pyrolysis

3.3 Experimental procedure

The following procedures are employed for experimental operation:

1. The experimental set-up was assembled with all accessories and checked carefully.
2. Feed material was weighed and filled into the reactor.
3. The N₂ gas was supplied through copper tube to create inert atmosphere inside the reactor and this flow was controlled by the use of regulating valve.
4. The reactor was heated externally by an electric heater at required temperature and it was measured by pyrometer.
5. Water supply was started into the condenser.
6. The operation time was recorded by means of a hand watch.
7. When the operation was completed a small flow of N₂ gas was allowed to pass through the system to prevent back flow of air which might react with hot char inside the reactor.
8. After cool down the reactor, char was exhausted from the reactor bed by supplying compressed air and weighed.
9. All the parts of the system were cleaned before reassembling for the next run.

3.4 Description of pyrolysis experimental set-up

The experimental system was a fixed-bed batch mode pyrolysis unit. Figs. 3.2 and 3.3 show the schematic diagram and photograph of the pyrolysis conversion system, respectively. The main components of the pyrolysis system are: reactor chamber, condenser, annular shaped electrical heater, liquid collector, N₂ gas cylinder, pyrometer, temperature controller, copper tube gas preheater and air compressor. The reactor chamber was 10 cm diameter and 30 cm high constructed of mild steel with full gas flow and temperature control. The reactor was heated externally by 1000 watt well insulated annular shaped electric heater. The incoming nitrogen gas was preheated before entering into the reactor in a preheating 5mm diameter copper tube wound around the cylindrical reactor chamber. Nitrogen gas was used as carrier gas that made the system inert and pushed away the volatile from the reactor to the condenser. The N₂ gas flow rate was measured and controlled by a gas flow-meter and regulating valve, respectively. A well designed temperature controller controlled the temperature of the reactor. The temperature in the fixed bed reactor was measured by a digital pyrometer. A 300gm of oven dried biomass solid waste sample were fed into the reactor by gravity feed type reactor feeder for every run. The system was maintained at a pressure slightly above atmosphere by a nitrogen gas pressure regulator. The reactor operating temperature was varied at 25/50°C \pm 2°C, interval using the controller in the range 300-550°C at which no visible volatile comes out from the reactor. The vapors and gases produced from biomass waste in the reactor were passed through a water cooled condenser and then ice-cooled collector to trap the derived liquid product. Compressed air was supplied from a compressor to exhaust char particles clearly. The collected liquid and char were weighted and deducted from the weight of feed supply to get weight of non-condensable vapor and gases. The N₂ gas and non-condensable vapor were flared to atmosphere.

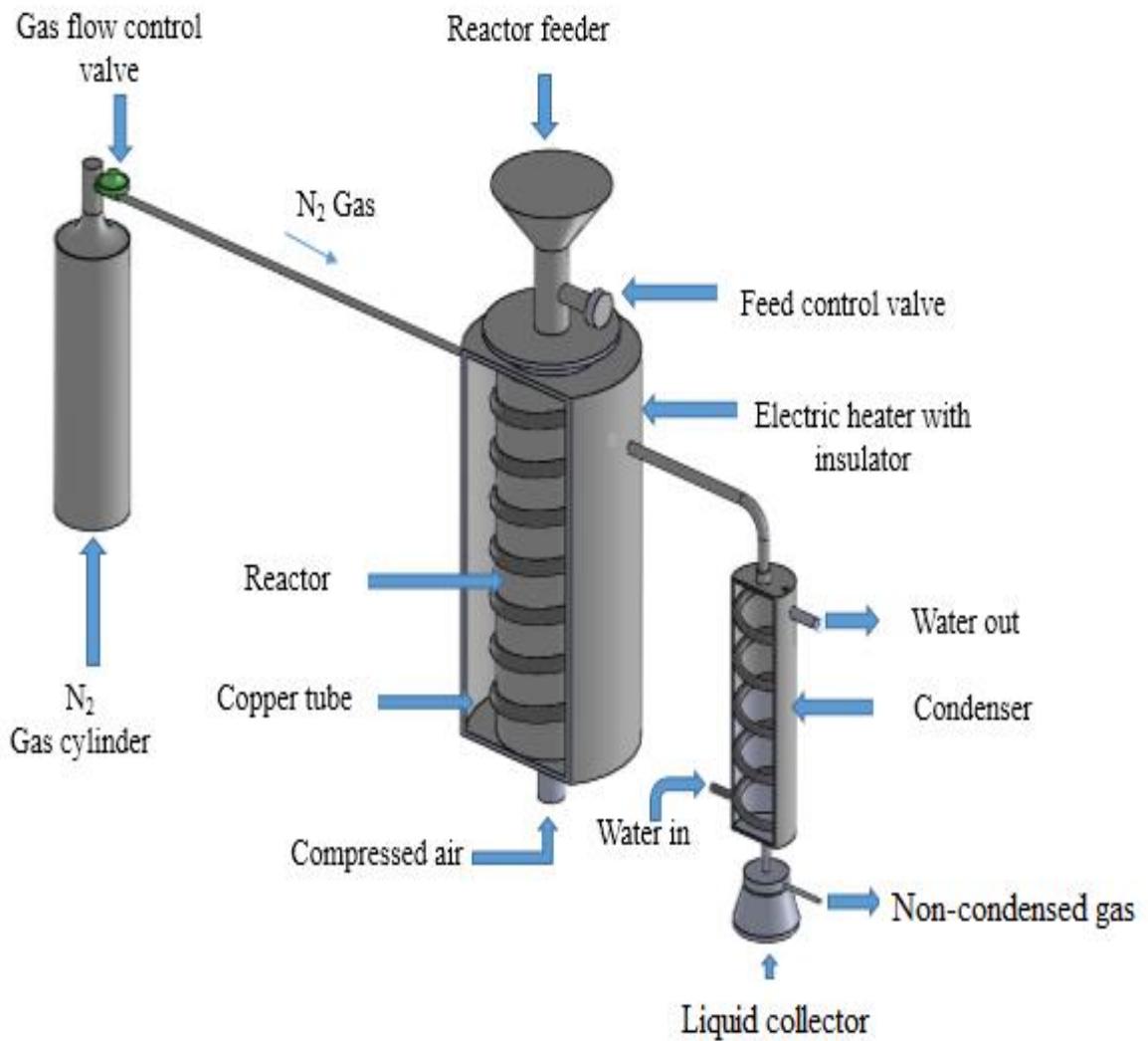


Fig. 3.2: Schematic diagram of the fixed bed pyrolysis system



Fig. 3.3: Photograph of the fixed-bed pyrolysis system

Chapter 4

Pyrolysis of selected biomass solid wastes

4.1 Feed material preparation

Three biomass samples that were used as feed stock for the presented study were tamarind seed, jute-stick and Japanese cedar wood. The ripe tamarind fruits were collected locally in Rajshahi, Bangladesh and seeds were separated manually. Jute-stick was also collected locally from rural areas in Rajshahi, Bangladesh. The Japanese cedar wood was collected from forest near Kitami city, Hokkaido of Japan. All of three samples were sun dried and then ground using blender machine. The grounded samples were then sieved into five different size ranges: 150-300 μm , 300-600 μm , 600-1180 μm , 1180-1700 μm and 1700-2360 μm and the sieved particles were oven dried up to 110°C for 8 hours.

4.2 Pyrolysis of three selected biomass

In general three common products: oil, char and gas were recovered after each pyrolysis experiment of tamarind seed, jute stick and Japanese cedar wood pyrolysis. Higher percentage of liquid collection makes these biomass potential for liquid fuel extraction. The liquid appear dark brownish with a strong acrid smell. Careful handling of the liquid was required since the liquid reacted easily with human skins, leaving permanent yellowish brown marks and an acrid smell for a few days, which can not be removed easily by detergent. Heavy condensate or tar was also formed and adhered to the inner wall of the condenser, liquid collectors and connecting pipes. The tar which was very viscous at room temperature, could be easily removed from the steel surfaces by detergent and hot water. The liquid product was collected in liquid collectors. No phase separation was found to take place. The char was collected from the reactor. The char were expected to be very reactive, and precautions were required to ensure that it would not be exposed to air when still hot. The gas was diluted by flow of nitrogen gas and flared into the atmosphere.

4.3 Results and discussion

The pyrolysis products from each experiment were quantified at different process conditions. The pyrolysis experiments were repeated two/three times for a particular

operating condition. The results of product yields for particular condition were averaged and then presented graphically. The numerical values of the product yield data for three selected biomass are tabulated in appendix of the dissertation book.

4.3.1 Effect of reaction conditions on product yields of tamarind seed

4.3.1.1 Effect of reactor temperature

Fig. 4.1 shows the variation of percentage mass of liquid, char and gas at different reactor bed temperature for tamarind seed pyrolysis with particle size 1180-1700 μm at N_2 gas flow rate 6 l/min. From this figure it is found that the maximum liquid product yield was obtained at a reactor bed temperature of 400°C and this was 45 wt% of total biomass feed. With the decrease of bed temperature at 350°C, the liquid product was decreasing (38 wt% of biomass feed) while with the increase of bed temperature at 450°C the liquid product yield was again decreasing (41 wt% of biomass feed). With the increase of reactor bed temperature, the solid char yield was decreasing over the temperature range of 300 to 550°C.

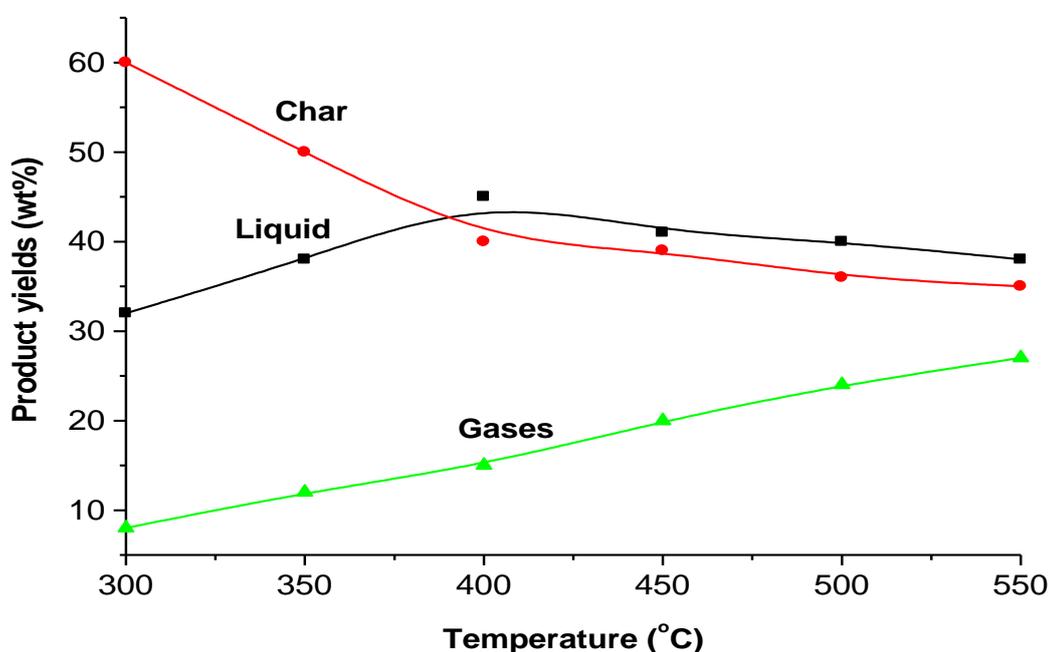


Fig. 4.1: Effect of temperature on product yields of tamarind seed pyrolysis at N_2 gas flow rate 6 l/min with feed particle size 1180-1700 μm

For the feed particle size of 1180-1700 μm at a bed temperature of 300°C yielded the maximum percentage of char 60 wt% of biomass feed.

At a higher temperature of 550°C, the solid char production was lower, it was found to be 35 wt% of biomass feed. Fig. 4.1 also shows that as the reactor bed temperature was increased the gaseous product yield was increasing. A fixed bed temperature of 550°C yielded the maximum percentage of gas yield of 27 wt% of biomass feed.

The reason behind this was that the lower temperature was not sufficiently high enough for the pyrolysis de-volatilization reaction to take place completely rendering reduced amount of liquid and gaseous products. Again the higher temperature was causing secondary cracking reaction of the vapors yielding more gas at the cost of the liquid product yield. However, the intermediate temperature was sufficient enough for complete pyrolysis reaction to take place and at the same time this temperature was not high enough for secondary reaction rendering maximum quantity of liquid product with less amount of char residue and gaseous products. This was found from TGA study of tamarind seed that the de-volatilization was completed at around 400°C.

Onay et al. [42] pyrolyzed rapeseed in a fixed bed reactor and reported that the maximum liquid yield was 41.7 wt% of solid waste at reactor temperature 440°C for particle size 0.6-1.80 mm and gas flow rate 100 cm^3/min .

Acikgoz et al. [43] pyrolyzed linseed in a fixed bed reactor and reported that the maximum liquid product yield 47.7 wt% of solid waste at 440°C for gas flow rate 100 cm^3/min and particle size 0.6-1.80 mm with heating rate 300°C/min.

Kilky et al. [44] pyrolyzed of empty fruit branch (EFB) in a fluidized bed reactor under different pyrolysis condition. They found that the highest bio-oil was 27 wt% at optimum temperature 500 °C with feed particle size 70 mesh.

Some previous research groups [45-53] have been performed their research work for the effect of reactor temperature on the product yields and obtained results that are approximately similar to those of the presented work.

4.3.1.2 Effect of feed particle size

Fig. 4.2 represents the percentage yields of liquid, solid char and gaseous products for different feed size of tamarind seed at optimum temperature of 400°C and N_2 gas flow rate of 6 l/min. It was observed that the percentage yield of liquid product was maximum 45 wt% of total biomass feed for particle size of 1180-1700 μm with a solid char product

of 40 wt% of dry biomass feed. The particle size of 150-300 μm produced a percentage yield of liquid product of 35 wt% of dry biomass feed with a solid char product of 45 wt% of biomass feed. The larger particle size of 1700-2360 μm produced percentage yield of liquid and char products 42 and 41 wt% of biomass feed, respectively.

This may be due to the fact that the smaller particles were overheated or too quick devolatilization occurs producing more gases, on the other hand, the larger size particles were not adequately heated up so rapidly causing incomplete pyrolysis rendering less liquid product yield. With the increase of feed particle size, gas yield was decreasing from 20 to 16 wt% of feed. Smaller feed size provides more reaction surface causes high heating rate and too quick decomposition of crushed tamarind seeds.

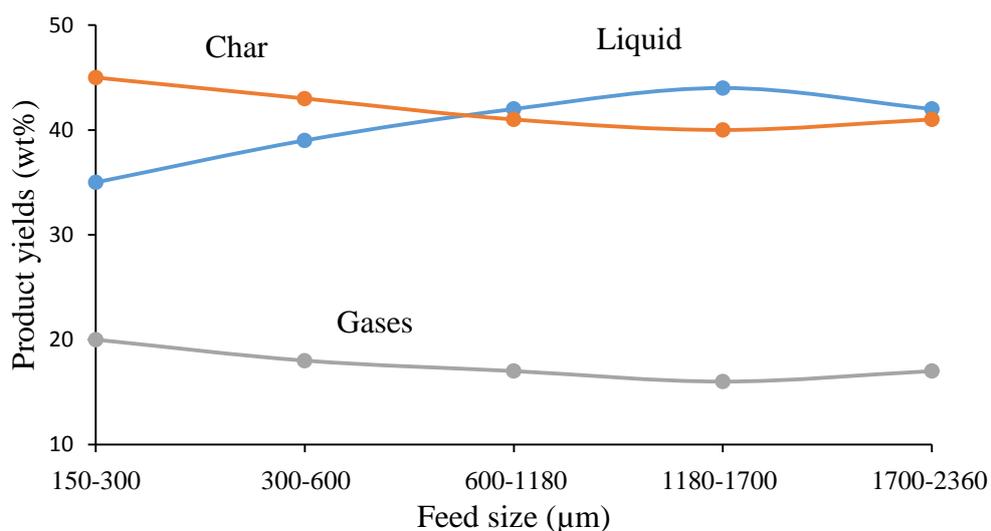


Fig. 4.2: Effect of feed size on product yields for temperature 400°C and N₂ gas flow rate 6 l/min with feed particle 1180-1700 μm

The product oil vapors comparatively get enough time for secondary reaction in the reactor and consequently increase in gas yield and decrease in liquid and char yields. On the other hand, the heating rate in larger feed is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller particles. Thus, the feed of larger pieces becomes carbonized and/or can not be decomposed completely resulting increase

in char yield and decrease in liquid and gas yields. In the presented study it may be concluded that the optimum feed size is 1180-1700 μm for which decomposition of tamarind seed is complete and has less possibility of secondary cracking at the optimum reactor temperature. Previous research groups [42-44] also obtained more or less similar results.

4.3.1.3 Effect of N_2 gas flow rate

Fig. 4.3 represents the variation of percentage yield of liquid, solid char and gaseous product at optimum reactor bed temperature of 400 $^\circ\text{C}$ for optimum feed particle size 1180-1700 μm .

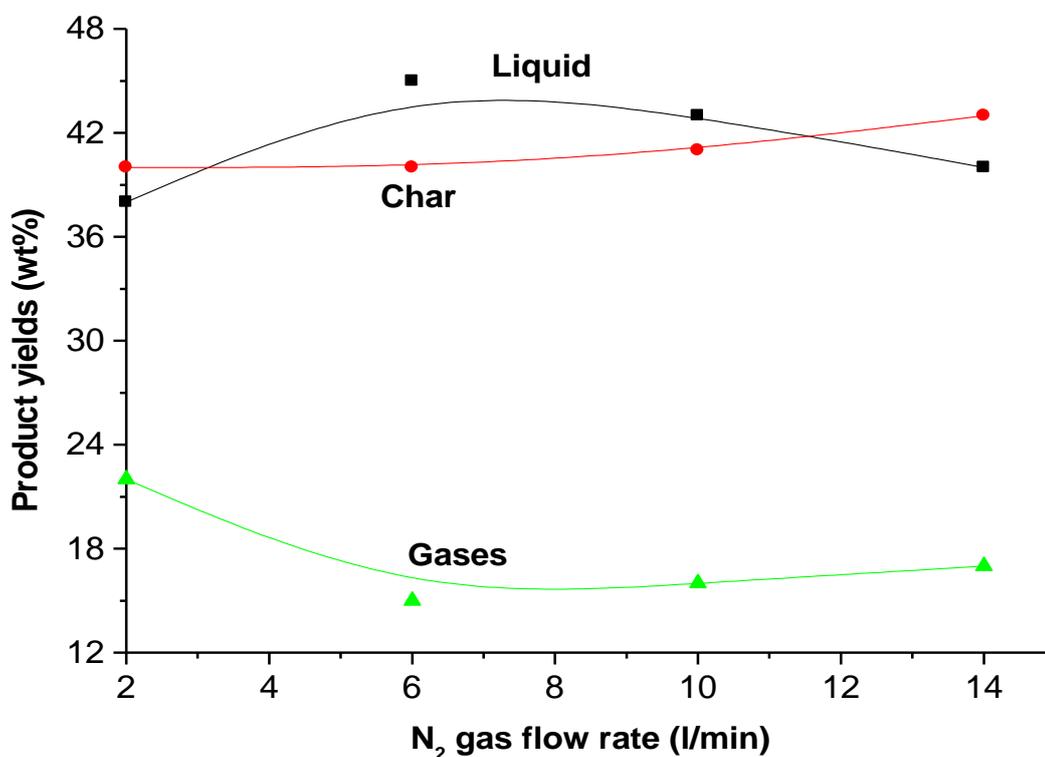


Fig. 4.3: Effect of N_2 gas flow rate on product yields for temperature 400 $^\circ\text{C}$ and feed particle size 1180-1700 μm

The maximum liquid product was 45 wt% of solid biomass feed while the solid char product was 40 wt% of dry feed at N_2 gas flow rate of 6 l/min. It was observed that at the beginning with lower gas flow rate (2 l/min), the liquid product was 38 wt% of biomass feed with char product of 40 wt% and gas yield of 22 wt%. With the increase of N_2 gas

flow rate up to 6 l/min, the liquid product was increasing while gas yield decreasing. The char yield appeared to be more or less constant. When the gas flowrate was increased to values higher than 6 l/min for particle size 1180-1700 μm , liquid products decreases from 45 to 36 wt% of biomass.

The increase in gas yields with decreased N_2 gas flow rate in the present investigation is due to the decomposition of some oil vapor into secondary permanent gases. Primary vapors are first produced from pyrolysis of tamarind seed at optimum reactor temperature and the primary oil vapors then degrade to secondary gases within the period of lower gas flow rate, which leads to less oils and more gaseous products. At a higher N_2 gas flow rate up to 6 l/min, time for decomposition of some oil vapor portion into secondary permanent gases is reduced and causing fast pyrolysis reaction, that results maximum liquid yields with less amount of gases. When the N_2 gas flow rate was increased to a values higher than 6 l/min, char particles were found to be elutriated significantly into the liquid collector with incomplete decomposition resulting less amount of liquid and higher amount of char products.

Rick et al. [54] pyrolyzed biomass waste in a fixed bed reactor and reported that the maximum liquid product yield 48 wt% of solid waste at reactor temperature 450°C with gas flow rate 7 l/min for feed size 1.20 cm^3 . These results are comparable to those of the presented work.

Caglar et al. [55] pyrolysed cotton cocoon shell and the obtained results are also approximately similar to those of the presented work.

4.3.1.4 Effect of running time

Fig. 4.4 shows the variation of product yields with respect to running time at optimum reactor temperature 400°C for feed particle of size 1180-1700 μm. The maximum liquid product is 45 wt% of biomass feed while the solid char product is 37 wt% for running time 30 minutes. It is observed that for running time less than 30 minutes the liquid yield is not optimum that may be due to incomplete pyrolysis reaction of the whole feed. For the running time above 30 minutes the liquid yield is almost constant with slight increase in gases and decreases char yield due to conversion of solid carbon in the char into gaseous products.

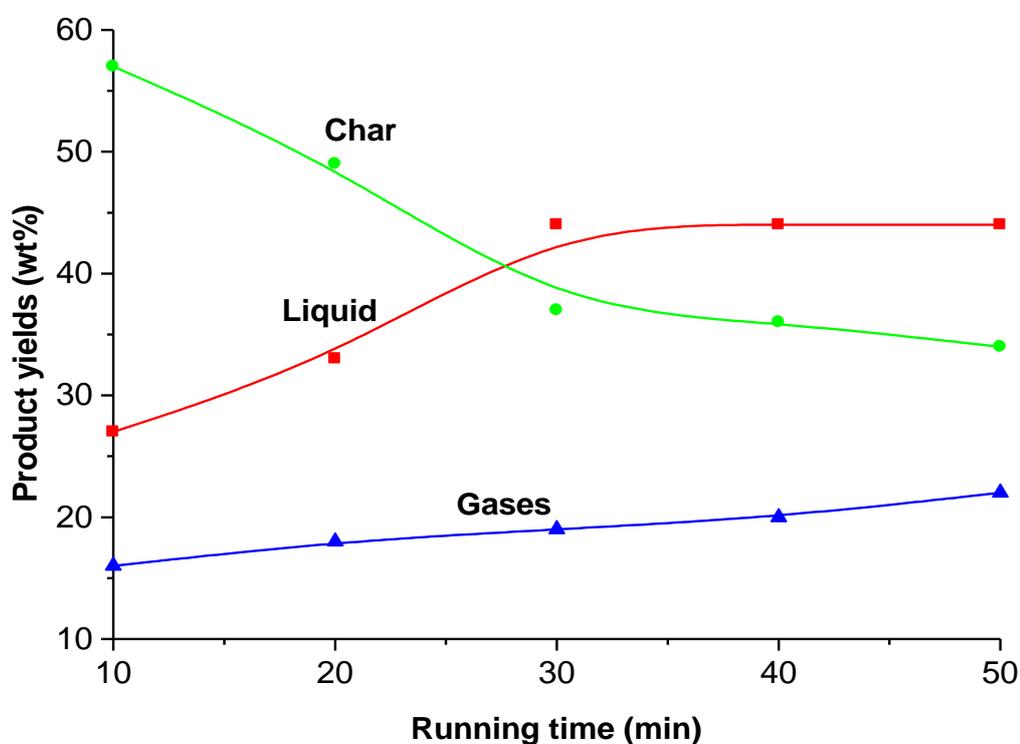


Fig. 4.4: Effect of running time on product yields for N₂ gas flow rate 6 l/min and temperature 400°C and feed particle size 1180-1700 μm

Thus, it may be concluded that the pyrolysis of solid biomass feed is completed within 30 minutes of running time. Through the experimental investigation it is found from paper waste [56] fixed bed pyrolysis for bed temperature 450°C, feedstock size of 2-3 cm with a running time of 45 min, the maximum liquid yield was 44 wt% of solid feedstock

A number of research works [57-64] have been carried out for running time on product yields and their results are approximately similar to those of the presented study.

4.3.2 Effect of reaction conditions on product yields of jute stick

4.3.2.1 Effect of reaction temperature

The relationship between the variations of percentage mass of liquid, char and gaseous products from jute-stick pyrolysis with particle size of 1180-1700 μm at different reactor temperature are presented in Fig. 4.5.

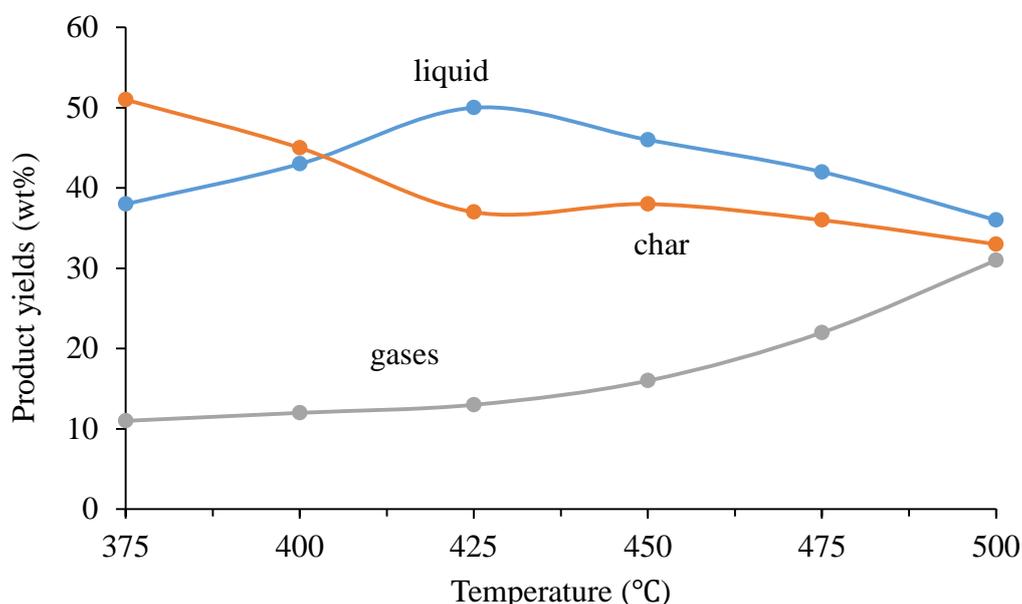


Fig. 4.5: Effect of reaction temperature on product yields of pyrolysis of jute stick for particle size 1180-1700 μm and N_2 gas flow rate 6 l/min

The results showed that as the reactor temperature increased, the liquid yield was increasing up to 425°C. After this temperature the liquid product yield was decreasing. The maximum liquid product yield was obtained at a reactor temperature of 425 °C and this was found to be 50 wt% of total biomass feed. With the decrease of reactor temperature at 375°C, the liquid product yield was decreasing up to 38 wt% of biomass feed while with the increase of reactor temperature at 500°C the liquid product yield was again decreasing up to 36 wt% of biomass feed.

Fig. 4.5 shows that with increase of reactor temperature the solid char yield was decreasing for the temperature range of 375°C to 500°C. A reactor temperature of 375°C yielded the maximum percentage mass of char 51 wt% of jute-stick biomass feed. At a

higher temperature of 425°C, the solid char product was lower, it was found to be 37 wt% of biomass feed. This is supported by the TGA study of jute-stick pyrolysis that at higher reactor temperature there was a possibility of further decomposition reactions to take place in the fixed bed reactor, thus cracking both char and liquid products rendering lower yields of both char and liquid. On the other hand the complete vaporization of jute stick particle did not take place at temperature below 425°C leaving more residual char.

In Fig. 4.5 the results showed that as the reactor temperature was increased the gaseous product yield was increasing. A reactor temperature of 500°C yielded the percentage mass of char 31wt% of jute-stick biomass feed. The gas yield was increasing near to minimum at the condition of maximum oil production. This may be due to the fact that at this temperature the rate of pyrolysis de-volatilisation reaction was higher and the rate of secondary cracking reaction was lower yielding lesser amount of gaseous product.

Islam et al. [65] pyrolyzed jute-stick in a fluidized bed reactor and reported that the yield of liquid was maximum up to 40 wt% at 425°C with 300-600 µm feed particle size and 30 l/min fluidized gas flow rate.

Putun et al. [66] pyrolyzed olive residue in a fixed bed reactor under different pyrolysis condition. They found that the maximum oil yield 32.7 wt% of solid waste at temperature 400°C with gas flow rate 200 cm³/min.

Guanyi et al. [67] co-pyrolyzed corn-cob with waste cooking oil in a fixed bed reactor under different pyrolysis conditions. They found the highest bio-oil was 70.62 wt% at optimum temperature 550°C and feed particle size 8-10 mm.

Peng et al. [68] pyrolyzed rice straw in a fixed bed reactor and found the highest bio-oil mass fraction in the product is around 30% when the rice husk feeding rate and the fluidizing nitrogen gas flow rate are 10 g/min and 40 l/min, respectively.

Caglar et al. [69] pyrolysed cotton cocoon shell and the obtained results are approximately similar to those of the presented work.

4.3.2.2 Effect of feed particle size

Fig. 4.6 represents the percentage mass of liquid, solid char and gaseous products for different particle size at a reactor temperature of 425°C.

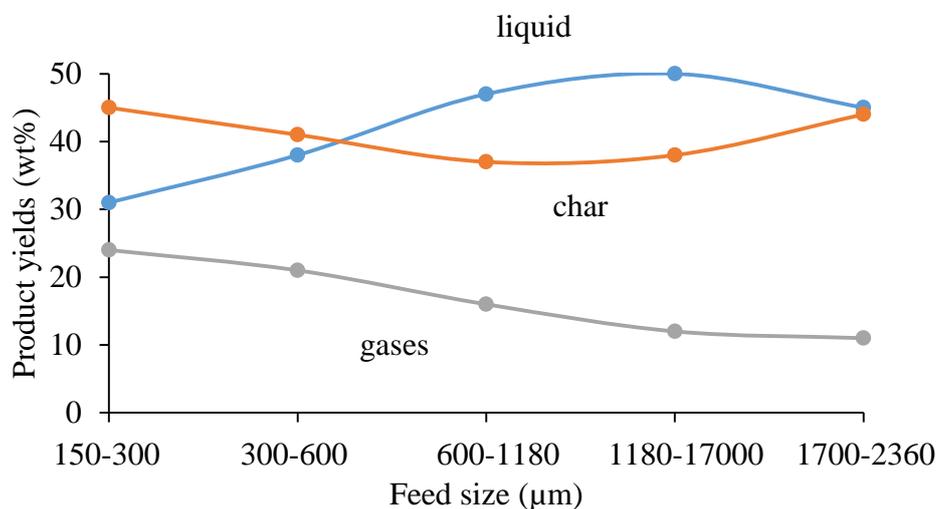


Fig. 4.6: Effect of feed particle size on product yields from pyrolysis of jute stick at reactor temperature 425°C with N₂ gas flow rate 6 l/min

It was observed that at N₂ gas flow rate of 6 l/min, the percentage mass of liquid product was maximum (50 wt% of total biomass feed) for feed particle size of 1180-1700 μm with a solid char product 38 wt% of dry biomass feed. The particle size 150-300 μm produced percentage mass of liquid product 31 wt% of dry biomass feed with a solid char product 45wt% of biomass feed. The larger particle size of 1700-2360 μm produced percentage mass of liquid and char products of 44 and 44 wt% of biomass feed, respectively.

This may be due to the fact that the smaller size particles were either overheated, or too quickly blown from the reactor before commencing pyrolysis completely producing more char, on the other hand, the larger size particles were not adequately heated up so rapidly causing incomplete pyrolysis rendering reduced liquid product yield. With the increase of feed particle size gas decreasing from 24 to 11 wt% biomass feed. Smaller feed size provides more reaction surface causes high heating rate and too quick decomposition of crushed jute stick. The product oil vapors comparatively get enough time for secondary reaction in the reactor and consequently increase in gas yield and

decrease in liquid and char yields. On the other hand, the heating rate in larger feed is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller particles. Thus, the feed of larger pieces becomes carbonized and/or can not be decomposed completely resulting increase in char yield and decrease in liquid and gas yields. In the presented study it may be concluded that the optimum feed size is 1180-1700 μm for which decomposition of jute stick is complete and has less possibility of secondary cracking at the optimum reactor temperature. Previous research groups [65-69] also obtained more or less similar results.

4.3.2.3 Effect of N_2 gas flow rate

Fig. 4.7 shows the variation of the mass percentage of liquid, solid char and gaseous products for different N_2 gas flow rate and at a reactor bed temperature of 425°C for feed particle size of 1180-1700 μm .

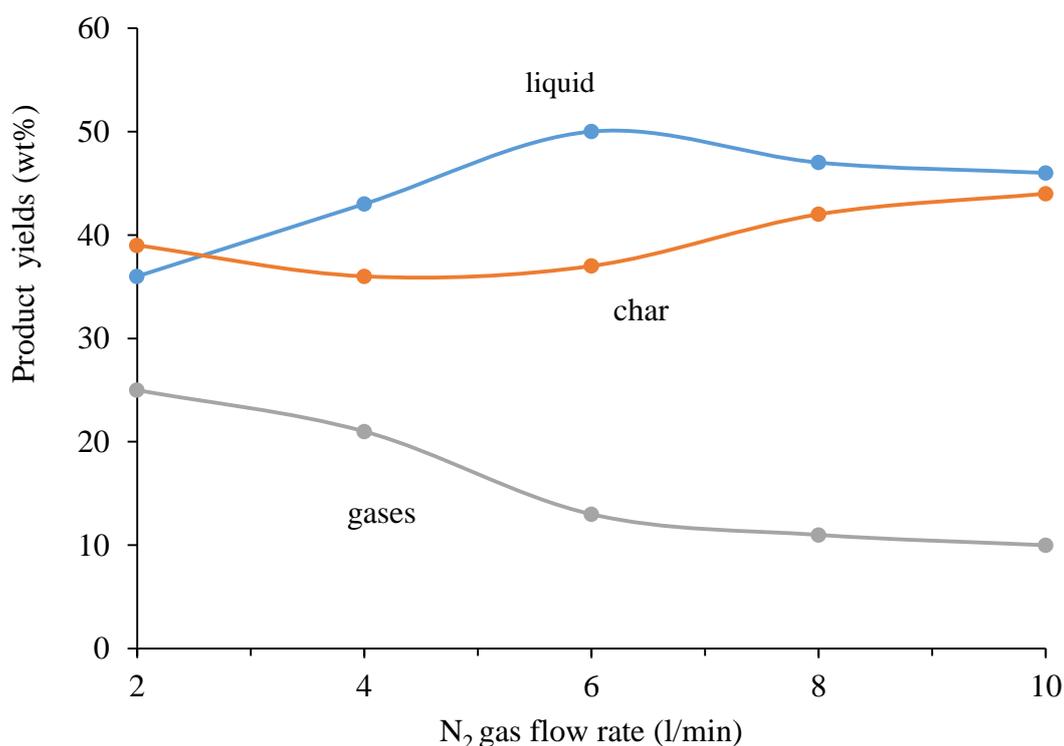


Fig. 4.7: Effect of N_2 gas flow rate on product yields from pyrolysis of jute stick at reactor temperature 425°C for particle size 1180-1700 μm

The maximum liquid product was 50 wt% of biomass fed while the solid char product was 37 wt% of dry feed at N₂ gas rate of 6 l/min. It was observed that at the beginning with lower N₂ gas flow rate of 2 l/min, the liquid product was 36 wt% of biomass fed with a char product of 39 wt% of biomass feed and a gas yield of 25 wt%. With the increase of N₂ gas flow rate up to optimum value the liquid product was increasing with a decreasing trend of gas yield. The char yield appeared to be more or less constant. When the gas flowrate was increased to values higher than 6 l/min for particle size 1180-1700 μm, liquid products decreases from 50 to 46 wt% of biomass.

The increase in gas yields with decreased N₂ gas flow rate in the present investigation is due to the decomposition of some oil vapor into secondary permanent gases. Primary vapors are first produced from pyrolysis of jute stick at optimum reactor temperature and the primary oil vapors then degrade to secondary gases within the period of lower gas flow rate, which leads to less oils and more gaseous products. At a higher N₂ gas flow rate up to 6 l/min, time for decomposition of some oil vapor portion into secondary permanent gases is reduced and causing fast pyrolysis reaction, that results maximum liquid yields with less amount of gases. When the N₂ gas flow rate was increased to a values higher than 6 l/min, char particles were found to be elutriated significantly into the liquid collector with incomplete decomposition resulting less amount of liquid and higher amount of char products. Previous research groups [65-69] also obtained more or less similar product yields distributions for variety of agricultural wastes.

4.3.2.4 Effect of running time

Fig. 4.8 shows the variation of product yields with respect to running time at optimum reactor temperature 425°C for feed particle of size 1180-1700 μm . The maximum liquid product is 46 wt% of biomass feed while the solid char product is 40 wt% and gaseous product yield is 14 wt% for running time 30 minutes.

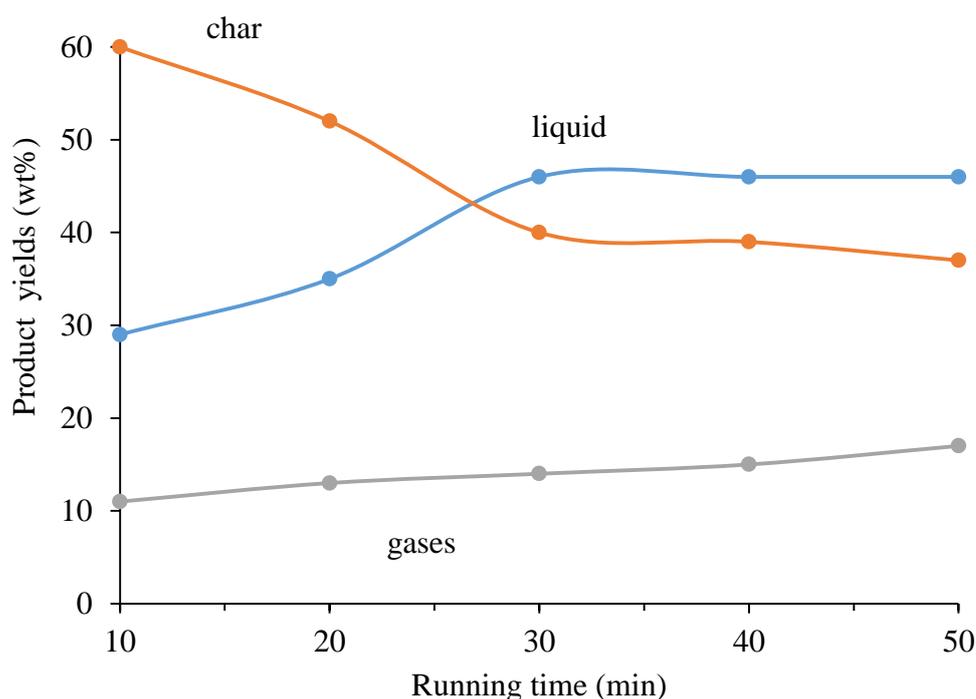


Fig. 4.8: Effect of running time on product yields at temperature 425°C for particle size 1180-1700 μm with N_2 gas flow rate 6 l/min

It is observed that for decreasing running time at 10 minutes the liquid yield is 29 wt%, solid char product is 60 wt% and gas yield is 11 wt% of biomass feed. For the running time above 30 minutes the liquid yield is almost constant with slight increase in gases and decreases char yield due to conversion of solid carbon in the char into gaseous products. Thus, it may be concluded that the pyrolysis of solid biomass feed is completed within 30 minutes of running time. Previous research groups [65-69] also obtained more or less similar results for pyrolysis of different agricultural wastes.

4.3.3 Effect of reaction conditions on product yields of Japanese cedar wood

4.3.3.1 Effect of reactor temperature

The relationship between the variations of percentage mass of liquid, char and gaseous products from cedar wood pyrolysis with particle size of 1180-1700 μm at different reactor temperature are presented in Fig. 4.9. The result shows that as the reactor temperature increased, the liquid yield was increasing up to 450°C, after this temperature the liquid product yield was decreasing.

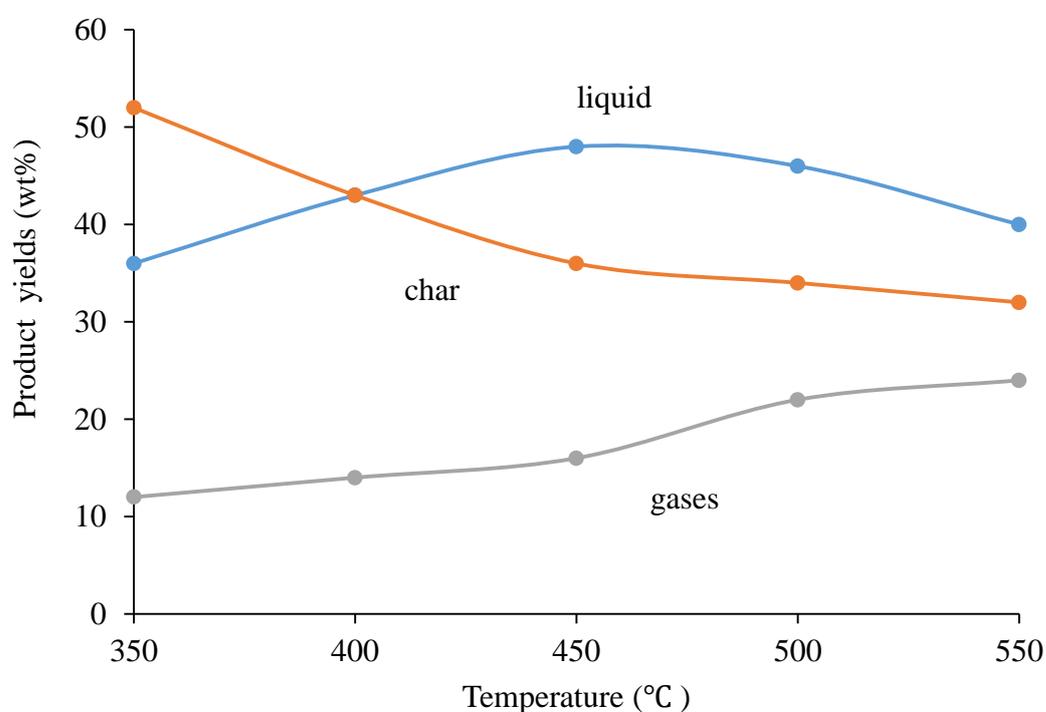


Fig. 4.9: Effect of reaction temperature on product yields from pyrolysis of cedar wood for particle size 1180-1700 μm and N_2 gas flow rate 6 l/min

The maximum liquid product yield was obtained at a reactor temperature of 450°C and this was found to be 48 wt% of total biomass feed. With the decrease of reactor temperature at 350°C, the liquid product yield was decreasing up to 36 wt% of biomass feed while with the increase of reactor temperature at 550°C the liquid product yield was again decreasing up to 40 wt% of biomass feed.

Fig. 4.9 shows that with increase of reactor temperature the solid char yield was decreasing for the temperature range of 350°C to 550°C. A reactor temperature of 350°C yielded the maximum percentage mass of char 52 wt% of cedar wood biomass feed. At a higher temperature of 550°C, the solid char product was lower, it was found to be 32 wt% of biomass feed. In Fig. 4.9 the results showed that as the reactor temperature was increased the gaseous product yield was increasing. At a reactor temperature of 550°C yielded the maximum percentage mass of gas 24 wt% of cedar wood biomass feed. The gas yield was increasing near to minimum at the condition of maximum oil production. This may be due to the fact that at this temperature the rate of pyrolysis devolatilisation reaction was higher and the rate of secondary cracking reaction was lower yielding lesser amount of gaseous product.

Sait et al. [70] pyrolyzed paulownia wood in a fixed bed reactor under different pyrolysis condition. They found that the maximum oil yield 54 wt% of solid waste at temperature 773 K with gas flow rate 100 ml/min and optimum feed particle size 0.425-1 mm.

Barbary et al. [71] pyrolyzed torrefied wood and polystyrene with catalytic fast pyrolysis under different conditions. They found optimum phenolic yield is 53.2 wt% at 550 °C and more than 60 wt% yield of aromatic hydrocarbons were produced from the pyrolysis of torrefied wood and polystyrene.

Evan et al. [72] pyrolyzed wood waste in a fixed bed reactor and showed maximum liquid product 54 wt% of biomass waste was obtained for temperature 440°C with 0.8 to 1.2 mm feed size. The feedstock size of 0.25 to 1 cm and 1 to 2 cm produced a maximum percentage of liquid of 45 wt% and 52 wt%, respectively.

Islam et al. [73] pyrolyzed municipal solid waste in a fixed bed reactor and reported that the maximum liquid yield 55 wt% of solid waste at temperature 450°C for feed size 1-2 cm.

Jeong et al. [74] pyrolyzed construction waste wood reported that the maximum oil yield 56.9 wt% at 500°C with 0.2-2 mm feed particle size and 60 ml/min fluidized gas flow rate.

Charles et al. [75] Pyrolyzed of energy cane bagasse and invasive Chinese tallow tree (*Triadica sebifera* L.) biomass in an inductively heated reactor and they found maximum oil yield 48.9 wt% at 500°C.

4.3.3.2 Effect of feed particle size

Fig. 4.10 represents the percentage yields of liquid, solid char and gaseous products for different feed size of cedar wood at optimum temperature of 450°C and N₂ gas flow rate of 6 l/min.

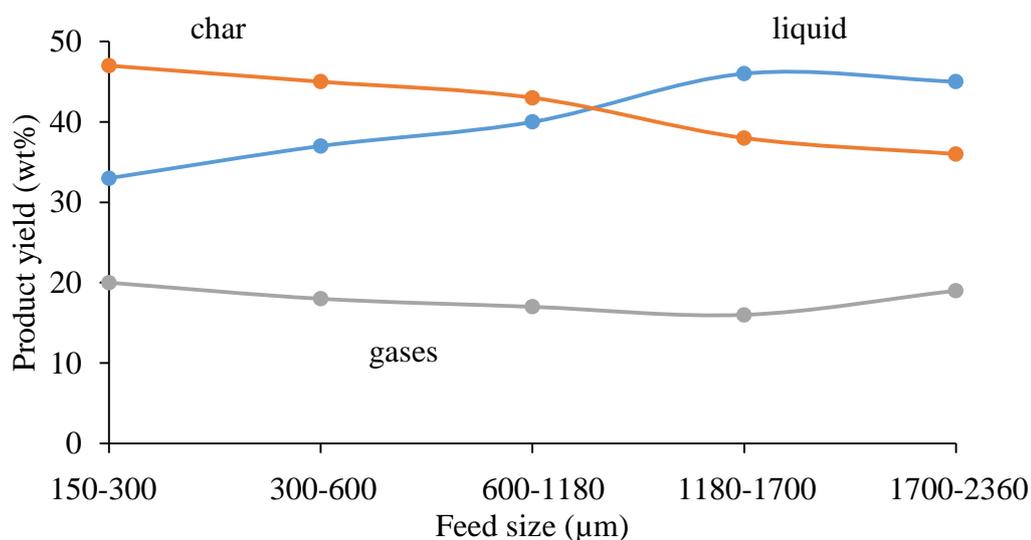


Fig. 4.10: Effect of feed particle size on product yields from pyrolysis of cedar wood at reactor temperature 450°C at N₂ gas flow rate 6 l/min

It was observed that the percentage yield of liquid product was maximum 48 wt% of total biomass feed for particle size of 1180-1700 µm with solid char product of 38 wt% of dry biomass feed. The particle size of 150- 300 µm produced a percentage yield of liquid product of 33 wt% with a solid char product of 47 wt% of biomass feed. The larger particle size of 1700-2360 µm produced percentage yield of liquid and char products 45 and 36 wt% of biomass feed, respectively.

With the increase of feed particle size, gas yield was decreasing from 20 to 18 wt% of feed. Smaller feed size provides more reaction surface causes high heating rate and too quick decomposition of crushed cedar wood. The oil vapors comparatively get enough time for secondary reaction in the reactor and increase in gas yield and decrease in liquid and char yields. On the other hand, the heating rate in larger feed is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller particles. Thus, the feed of larger pieces becomes carbonized and/or cannot be decomposed completely

resulting increase in char yield and decrease in liquid and gas yields. In the presented study it may be concluded that the optimum feed size is 1180-1700 μm for which decomposition of cedar wood is complete and has less possibility of secondary cracking at the optimum reactor temperature. Previous research groups [70-75] also obtained more or less similar result for pyrolysis of woody biomass.

4.3.3.3 Effect of N_2 gas flow rate

Fig. 4.11 shows the variation of the mass percentage of liquid, solid char and gaseous products for different N_2 gas flow rate at a reactor bed temperature of 450°C for feed particle size of 1180-1700 μm .

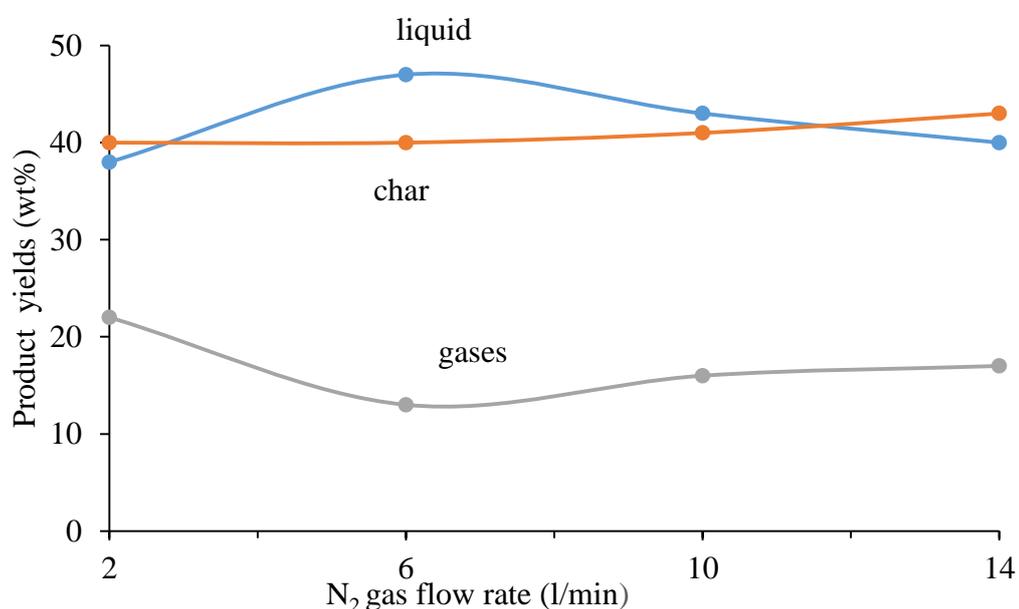


Fig. 4.11: Effect of N_2 gas flow rate on product yields from pyrolysis of cedar wood at reactor temperature 450°C for particle size 1180-1700 μm

The maximum liquid product was 47 wt% of biomass feed while the solid char product was 40 wt% and a gas yield of 13 wt% of dry biomass feed at a N_2 gas rate of 6 l/min. It was observed that at the beginning with lower N_2 gas flow rate of 2 l/min, the liquid product was 38 wt% of biomass feed with a char product of 40 wt% of biomass feed and a gas yield of 22 wt%. With the increase of N_2 gas flow rate up to optimum value the liquid product was increasing with a decreasing trend of gas yield. The char yield appeared to be more or less constant. When the gas flowrate was increased to values higher than 6 l/min for particle size 1180-1700 μm , liquid products decreases from 47 to

40 wt% of biomass. The increase in gas yields with decreased N_2 gas flow rate in the present investigation is due to the decomposition of some oil vapor into secondary permanent gases. Primary vapors are first produced from pyrolysis of cedar wood at optimum reactor temperature and the primary oil vapors then degrade to secondary gases within the period of lower gas flow rate, which leads to less oils and more gaseous products. At a higher N_2 gas flow rate up to 6 l/min, time for decomposition of some oil vapor portion into secondary permanent gases is reduced and causing fast pyrolysis reaction, that results maximum liquid yields with less amount of gases. When the N_2 gas flow rate was increased to a values higher than 6 l/min, char particles were found to be elutriated significantly into the liquid collector with incomplete decomposition resulting less amount of liquid and higher amount of char products. Previous research groups [70-75] also obtained more or less similar trend of product yields distribution from different wood wastes.

4.3.3.4 Effect of running time

Fig. 4.12 shows the variation of product yields with respect to running time at optimum reactor temperature 450°C for feed particle of size $1180\text{-}1700\ \mu\text{m}$. The maximum liquid product is 48 wt% of biomass feed while the solid char product is 40 wt% for running time 30 minutes.

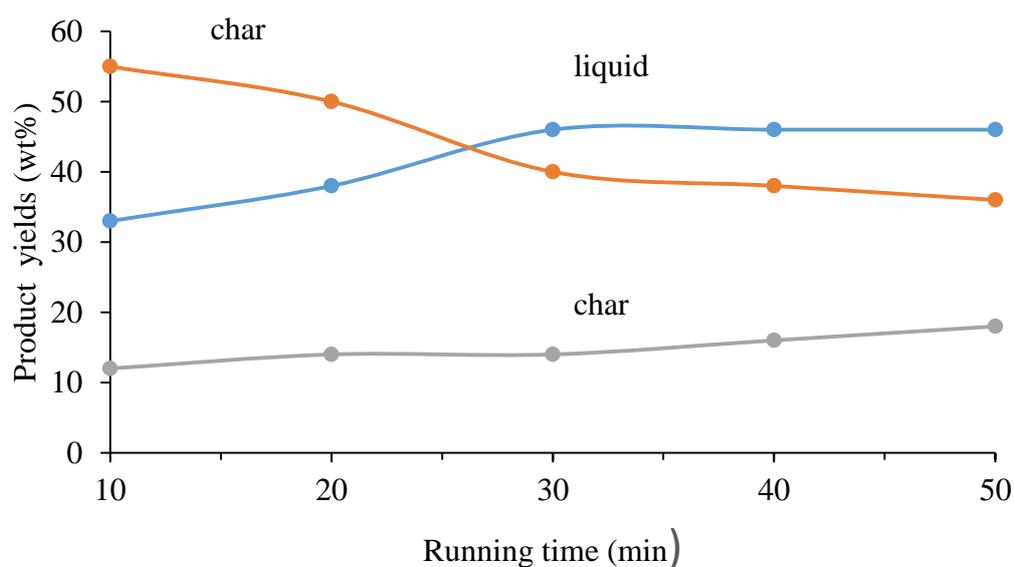


Fig. 4.12: Effect of running time on product yields of cedar wood at temperature 450°C at N_2 gas flow rate 6 l/min for particle size $1180\text{-}1700\ \mu\text{m}$

It is observed that for running time that of 30 minutes the liquid yield is not optimum that may be due to incomplete pyrolysis reaction of the whole feed. For the running time above 30 minutes the liquid yield is almost constant with slight increase in gases and decreases char yield. Thus, it may be concluded that the pyrolysis of Japanese cedar wood is completed within running time 30 minutes. Previous research groups [70-75] also obtained more or less similar result for various wood wastes.

4.4 Conclusions

- All the selected parameters for reactor operation were found to be influenced the product yields distribution significantly.
- The maximum liquid yields were 50, 45 and 48 wt% of biomass feed for jute stick, tamarind seed and Japanese cedar wood at reactor temperatures 425, 400 and 450°C for feed stock particle size 1180-1700 μm and running time 30 minutes.
- The maximum char yields were 51, 60 and 52 wt% of biomass feed for jute stick, tamarind seed and Japanese cedar wood at reactor temperature 375, 300 and 350°C, respectively.
- The maximum gas yields were 31, 32 and 24 wt% of biomass feed for jute stick, tamarind seed and Japanese cedar wood at reactor temperature 500, 550 and 550°C, respectively.

Chapter 5

Physical and chemical properties of pyrolysis oils

5.1 Physical properties

The pyrolytic oils obtained at the maximum liquid yield condition were characterized for their physical properties. These properties were determined according to the standard formulated by the American Society for Testing of Materials (ASTM) and Institute of Petroleum (IP) test methods. The properties determined were: kinematic viscosity, density, ash content, pH value, flash point, pour point and gross calorific value.

5.1.1 Kinematic viscosity

Kinematic viscosity is a measure of the resistance to flow of a fluid. Viscosity of a liquid is an important property since it affects the flow of the liquid through pipelines. The lower the viscosity of the oil, the easier it is to pump and to atomize and achieve finer droplets. The pyrolytic liquid viscosity is highly variable from one liquid to another depending on the water content, production conditions. This is the major criterion upon which the oils are graded.

5.1.2 Density

The density of oil is a measure of its aromaticity in hydrocarbon oils, but not in biomass derived oils. It is a necessary parameters used to calculate the volumetric output of pumps and injectors needed to supply a given rate of delivered energy, because the heat of combustion is determined on a weight basis. The density of the oxygenated bio-oils is much higher i.e. 1050 to 1300 kg/m³, than petroleum derived hydrocarbon oils. Pyrolysis liquid density varies with time, temperature and water content. The bio-oils having relatively higher densities typically have lower water contents. Wood derived pyrolysis liquid has density of typically 1200 kg/m³ for a water content of 25 wt% at 20°C.

5.1.3 Ash content

Ash is the incombustible material, which remains when fuel is burned. Ash is detrimental in combustion processes in which it lowers the calorific value of the fuel. Excessive amounts of ash can cause high wear in pumps and injectors and lead to deposits in combustion equipment. The ash content of the derived liquids was determined according to ASTM D482/IP 4 test methods. The liquid sample was burned in an open crucible and the carbonaceous residue was reduced to ash at high temperature of 732°C.

5.1.4 Flash point

Flash point is a measure of the liquid temperature necessary for the vapors above a pool of the fuel to ignite by passing a flame through the vapors. This is also a measure of the volatility of the oil, as well as its ease of ignition. The higher this number, the safer the oil is to handle because the risk of accidental vapor ignition is reduced. The flash point of the liquids was determined using Cleveland Open Cup tester, according to ASTM D92/IP 36 test method. Pyrolysis oil often has a reported flash point of between 50°C and over 100°C, reflecting a wide variation in the content of volatiles. However, above temperatures of 70 to 75° C, water vapors from the pyrolysis oils start to disturb the analysis and a reproducible value is difficult to obtain. No other suitable alternative method has been devised . To get a reasonable result, the test was carried out three times for each sample.

5.1.5 Pour point

The pour point is the lowest temperature at which the liquid is observed to flow under prescribed conditions. This parameter is an indication of the minimum temperature at which the oil can be pumped without heating the storage tank. The typical values for the pour point are –10 to –20°C. The standard test method for determination of the pour point are ASTM D97/IP 15.

5.1.6 Gross calorific value

The gross calorific value is a measure of the quantity of heat released in total combustion and therefore, measures the energy content of a fuel. It is the most important fuel property of any liquid fuel. The gross calorific value of the derived oils was determined using a PARR adiabatic bomb calorimeter according to the test method of DIN 51900. The high water content pyrolysis liquids can lead to poor ignition and a fine cotton thread is often used as a wick. The heat content of the thread is subtracted from the result. The lower heating value is calculated from the gross calorific value knowing the hydrogen content in the liquids. The typical lower heating value for the fast pyrolysis liquids are in the range of 12.8 to 17.8 MJ/kg.

5.1.7 pH Value

The pH value measures the acidity of the derived oil and therefore, indicates the corrosiveness of the oil. Biomass-derived oils are known to be highly acidic. The unusual aspect of bio-oils is their carboxylic acid content, e.g. formic and acetic acids, which causes the oils to have a pH of between 2 and 5. This acidity causes the pyrolysis oils to be corrosive to mild steel, aluminum, etc. Aldehydes also contribute to the low pH. A pH probe with digital meter, of model 3051, JENWAY was used to determine the pH value.

5.2 Fuel properties of the pyrolytic liquids

Bio-crude oils obtained from pyrolysis of tamarind seed, jute stick and cedar wood were homogeneous and no phase separation took place in the storage bottles. The derived liquids were characterized in terms of fuel properties and chemical compositions and compared to commercial diesel (Table 5.1). The water contents were 11.60, 12.80 and 10.80 wt% for tamarind seed, jute stick and cedar wood, respectively while that reported in the literature varied from 15 to 30 wt%, depending on the initial moisture in feed stocks and pyrolysis conditions [76]. The presence of water has both negative and positive effects on the storage and utilization of bio-oils. On the one hand, it lowers heating values, can cause phase separation, increases ignition delay and reduces combustion rates and adiabatic flame temperatures during the combustion process. In addition, it leads to premature evaporation and subsequent injection difficulties during the preheating process. On the other hand, it reduces viscosity, facilitates atomization, and reduces pollutant emissions during combustion [77]. Water lowers and evens the temperature profiles in chambers that are important for suppressing NO_x formation. It also contributes to micro explosion of droplets, which is beneficial to sufficient combustion. In addition, OH radicals from water can inhibit the formation of soot and can also accelerate its oxidation.

Table 5.1 shows that the density of pyrolytic liquids was higher than that of commercial diesel fuel, which corresponds to a higher energy content. Viscosity plays an important role in design and operation of the fuel injection system as well as in atomization quality and subsequent combustion properties of the fuel. The viscosity of liquid products from tamarind seed, jute stick and cedar wood samples were higher than commercial diesel but considerably lower than that of heavy fuel oil. A low viscosity of 21.50 cSt at 30°C is a favorable feature in the handling and transportation. The viscosity of bio-oils usually vary over a wide range depending on the feedstock and process conditions and especially on the efficiency of collection of low boiling components [78]. The flash point of a liquid fuel is the temperature at which the oil begins to involve vapors in sufficient quantity to form a flammable mixture with air. The temperature is an indirect measure of volatility and serves as an indication of the hazards associated with storage and application of the fuel. The flash point of the selected biomass-derived liquids was $\leq 75^{\circ}\text{C}$. The flash is high when compare with petroleum-refined fuels; for example, kerosene has a required minimum flash point of 23°C, diesel fuel of 55°C. The high flash points of biomass-derived liquids are not surprising since the product liquids represent un-refined liquids with a mixture of components having a wide distillation range. The flash points of bio-oils usually vary in the range of 40–70°C or above 100°C, depending

on the contents of light organic volatiles [79]. The pour point of the selected biomass derived liquid is comparatively low compared to the commercial diesel fuel but the laboratory experience of the author's present study shows that it is not problematic even at 7°C.

Table 5.1: Comparison of tamarind seed, jute stick and cedar wood pyrolysis oil with petroleum fuels

Properties	Tamarind Seed oil	Jute Stick oil	Cedar wood oil	Diesel [81]	Heavy Fuel oil [81]
Elemental (wt%)					
C	45.70	47.18	45.73	86.58	85.86
H	6.32	8.36	7.12	13.29	11-11.50
C/H	7.23	5.64	6.42	6.51	7.50-7.70
N	0.20	10.9	0.45	39.01	0.07
S	0.00	0.00	0.00	0.11	1-2.60
Ash	0.25	0.33	0.44	0.00	0.10
O	47.53	44.13	45.84	0.01	-
Water content (wt%)	11.60	12.80	10.80	9.75	-
Viscosity at 30°C (cSt)	6.51	5.56	5.30	2.61	200 [#]
Density (kg/m ³)	1150	1200	1050	827.10 [*]	980 [*]
pH value	4.02	4.15	3.56	-	-
Pour point (°C)	-16	-14	-20	-	25-30
Flash point (°C)	75	72	73	53	90-180
GCV (MJ/kg)	19.10	21.00	23.86	45.18	42.00

N.B: [#] @ 50°C ^{*}@ 20°C

The pH value of the pyrolytic liquids is 4-5 which is in weak acidic nature. It is found that there is very little contamination of the liquids with metals (V, Mn, Mg, Ba, Ni, Ti, Cu, Cr, Cd, Co, Fe, Al and Zn) and does not contaminated with glass and PET plastic and/or other plastics. The pH value of soft drinks like Coca Cola Company is 2.5 and they use PET plastics bottle for its storage and handlings. Thus, storage and handling of the liquids are not problematic in industrial usage.

5.3 Chemical properties analysis

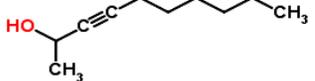
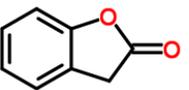
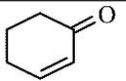
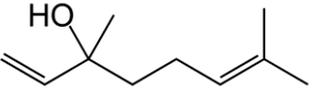
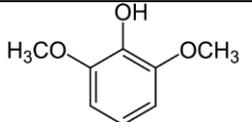
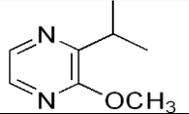
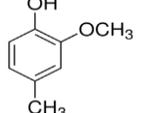
Condensable liquids are the major products of the solid biomass pyrolysis. Since, the liquids consist of numerous and diverse components, it is difficult to quantify them. Almost all of the researchers have been using elemental analysis and GC/MS analytical technics to identify and to quantify possible compounds in the pyrolytic liquids derived from different types of organic solid wastes.

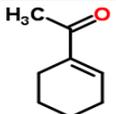
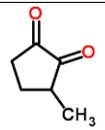
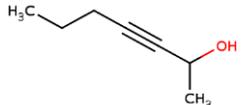
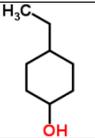
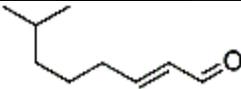
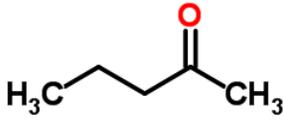
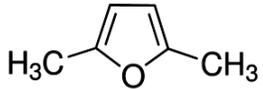
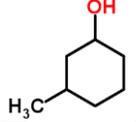
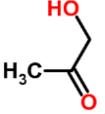
Ultimate analysis in the determination of the percentages of carbon, hydrogen, nitrogen, sulfur and (by difference) oxygen in the gaseous products and ash after the complete combustion of organic materials in a sample of selected biomass. It is essential for their pyrolysis conversion upon which the pyrolysis product quality depends. The test was carried out by an Elemental Analyzer EA 1108 according to the ASTM D3176-84 standard test process in the laboratory of Analytical Research Division, BCSIR, Dhaka, Bangladesh. The technique for the determination of CHNOS was based on the quantitative “Dynamic flash combustion” method

Elemental analysis, C/H ratio and gross calorific values for the liquids are presented in Table 5.1. The elemental analysis shows that the carbon content of the derived oils is lower than the petroleum products. The pyrolysis oils of tamarind seed, jute stick and Japanese cedar wood are highly oxygenated. The hydrogen content of the derived oils are lower than the petroleum fuels. Obviously, the product liquids contain large amount of oxygen with a lower ratio of C/H. The C/H ratio of the pyrolytic liquids indicate that such oils are a mixture of aliphatic and aromatic compounds [4]. The nitrogen and sulfur content of the oils are significantly lower than the petroleum fuels and ash content is always higher than the petroleum fuels. The calorific value of the biomass derived oils is lower, about 40-47% of energy content of petroleum due to the presence of high fraction of moisture and other oxygenated compounds. The heating value of biomass pyrolysis oils is usually about 44-50% of the heating value of heavy fuel oil.

GC/MS analysis was carried out with the pyrolysis liquids obtained from tamarind seed, jute stick and cedar wood at temperature 400, 425 and 450°C, respectively at N₂ gas flowrate 6 l/min for feed size 1180-1700 µm and running time 30 min to get an idea about the nature and type of compounds in such liquids. The NIST search software was used to analyze the peaks provided by the chromatogram, from which more than the half was not identified. The peaks whose identification results of match quality $\geq 90\%$ were considered valid and their tentative assignment were confirmed where in agreement the published GC/MS data for similar products. The GC/MS results from the pyrolytic oils of tamarind seed, jute stick and cedar wood are presented from Table 5.3.1-5.3.6.

Table 5.3.1: Possible identified compounds in jute stick pyrolysis oil by GC/MS analysis with their structural formula and applications

Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
01	3-Decyn-2-ol	C ₁₀ H ₁₈ O			Aliphatic compound
02	Hexadecan-1-ol	C ₁₆ H ₃₄ O		Cosmetic industry, in the manufacture of skin creams and lotions and as a lubricant for nuts and bolts	Aliphatic compound
03	2(3H)-Benzofuranone	C ₈ H ₆ O ₂		Synthesis of indolinones, antitumor bis-indole derivatives and cancers treatment	Heterocyclic compound
04	1-Cyclohex-2-enone	C ₆ H ₈ O		Synthesis of pharmaceuticals and fragrances	Alicyclic compound
05	3,7-dimethylocta-1,6-dien-3-ol	C ₁₀ H ₁₈ O		Perfumed hygiene products and cleaning agents including soaps, detergents, shampoos, and lotions	Aliphatic compound
06	1,3-Dimethoxy-2-hydroxybenzene	C ₈ H ₁₀ O ₃		Food Preparation and Chemical feedstock	Aromatic compound
07	2-methoxy-3-propan-2-ylpyrazine	C ₈ H ₁₂ N ₂ O		Produces odor in wine grapes, coffee	Heterocyclic compound
08	2-Methoxy-4-methylphenol	C ₈ H ₁₀ O ₂		Antiseptic and is an active part of creosote	Aromatic compound

Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
09	1-(1-cyclohexen-1-yl)-ethanone	$C_8H_{12}O$			Alicyclic compound
10	3-methylcyclopentane-1,2-dione	$C_6H_8O_2$		Food Production, beverage, pharmaceutical, cosmetics and agriculture/animal feed.	Alicyclic compound
11	3-heptyn-2-ol	$C_7H_{12}O$			Aliphatic compound
12	4-ethylcyclohexan-1-ol	$C_8H_{16}O$			Alicyclic compound
13	2-isononenal	$C_9H_{16}O$			Aliphatic compound
14	2-pentanone	$C_5H_{10}O$		Metal degreasing, ink remover, industrial cleaning fluids, paint and coatings formulations, printing inks and vinyl-coated fabrics.	Aliphatic compound
15	2,5-dimethylfuran	C_6H_8O		Serves as a scavenger for singlet oxygen	Heterocyclic compound
16	3-methylcyclohexan-1-ol	$C_7H_{14}O$		Used as nutrient	Alicyclic compound
17	1-hydroxy-2-propanone	$C_3H_6O_2$		Manufacture drugs, spices, dyes, organic intermediates	Aliphatic compound

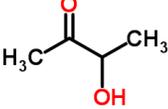
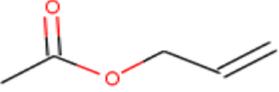
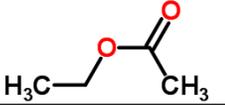
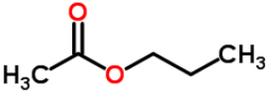
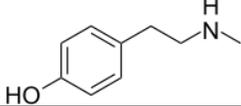
Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
18	3-hydroxybutan-2-one	$C_4H_8O_2$		Used to make other chemicals	Aliphatic compound
19	2-Propenyl acetate	$C_5H_8O_2$		Synthetic flavoring agent, glycerol and precursor for drying oils	Aliphatic compound
20	Ethyl acetate	$C_4H_8O_2$		Glues, nail polish removers, decaffeinating tea and coffee, and cigarettes	Aliphatic compound
21	Propyl ethanoate	$C_5H_{10}O_2$		Fragrances and flavor additive	Aliphatic compound
22	4-[2-(Methylamino) ethyl] phenol	$C_9H_{13}NO$			Aromatic compound

Table 5.3.2: Possible identified compounds in jute stick pyrolysis gas by GC/MS analysis with their structural formula and applications

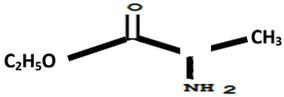
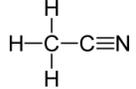
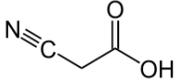
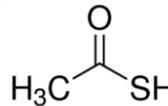
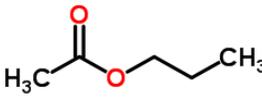
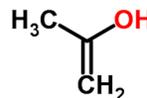
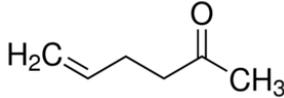
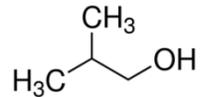
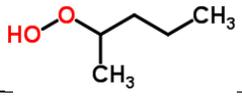
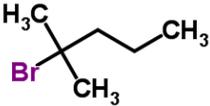
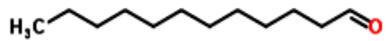
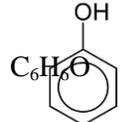
Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
01	Propyne	C ₃ H ₄	CH ₃ -C≡CH	Rocket fuel & gas welding	Aliphatic compound
02	L-Alanine, ethyl ester	C ₅ H ₁₁ NO ₂		Produce N-Boc-L-Phe-L-Ala-OEt with N-tert-butoxycarbonyl-L-phenylalanine at ambient temperature	Aliphatic compound
03	Acetonitrile	C ₂ H ₃ N		Used as a solvent in the purification of butadiene in refineries and in battery applications	Aliphatic compound
04	2-cyanoacetic acid	C ₃ H ₃ NO ₂		Used in the preparation of chemicals and drugs	Aliphatic compound

Table 5.3.3: Possible identified compounds in tamarind seed pyrolysis oil by GC/MS analysis with their structural formula and applications

Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
01	Thioacetic acid	C ₂ H ₄ OS		Used in organic synthesis & as a reagent for introduction of the thiol group into organic molecules	Aliphatic compound
02	Propyl ethanoate	C ₅ H ₁₀ O ₂		Fragrances and flavor additive	Aliphatic compound
03	Prop-1-en-2-ol	C ₃ H ₆ O			Aliphatic compound
04	Hex-5-en-2-one	C ₆ H ₁₀ O		Synthesize spices, pesticides and medicines.	Aliphatic compound
05	2-methylpropan-1-ol	C ₄ H ₁₀ O		Used as a solvent, varnish remover, ink ingredient etc.	Aliphatic compound
06	2-hydroperoxy-pentane	C ₅ H ₁₂ O ₂			Aliphatic compound
07	2-bromo-2-methylpentane	C ₆ H ₁₃ Br			Aliphatic compound
08	Dodecanal	C ₁₂ H ₂₄ O		Flavoring agent, fragrance ingredient, masking	Aliphatic compound
09	Phenol	C ₆ H ₆ O		Synthesize plastic, polycarbonates, epoxies, Bakelite, nylon, detergents, and numerous pharmaceutical drugs	Aromatic compound

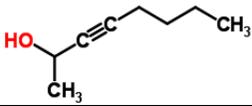
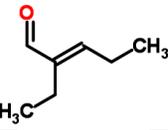
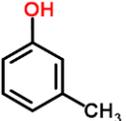
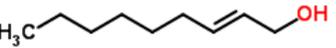
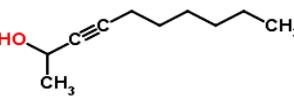
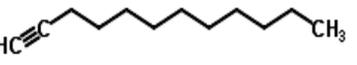
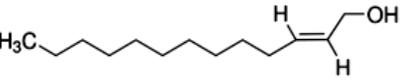
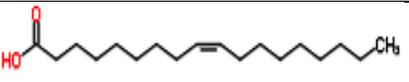
Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
10	Oct-3-yn-2-ol	$C_8H_{14}O$			Aliphatic compound
11	(E)-2-ethylpent-2-enal	$C_7H_{12}O$			Aliphatic compound
12	3-Methylphenol	C_7H_8O		Synthetic intermediates to plastics, pesticides, pharmaceuticals, and dyes	Aromatic compound
13	(E)-non-2-en-1-ol	$C_9H_{18}O$			Aliphatic compound
14	3-Decyn-2-ol	$C_{10}H_{18}O$			Aliphatic compound
15	Dodec-1-yne	$C_{12}H_{22}$		Synthesis of stable ruthenium nano particles	Aliphatic compound
16	(E)-tridec-2-en-1-ol	$C_{13}H_{26}O$		Flavor and fragrance agents	Aliphatic compound
17	Oleic acid			Used as an emulsifying agent in soap, aerosol products and induce lung damage in certain types of animals	Aliphatic compound

Table 5.3.4: Possible identified compounds in tamarind seed pyrolysis gas by GC/MS analysis with their structural formula and applications

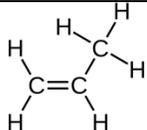
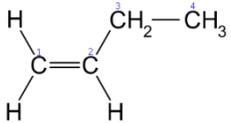
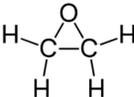
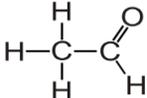
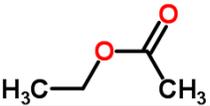
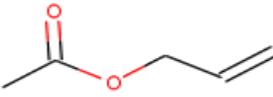
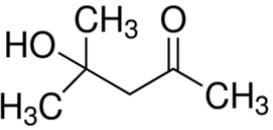
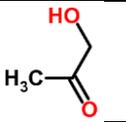
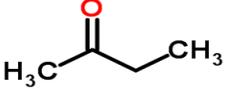
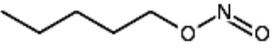
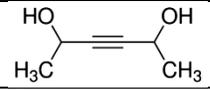
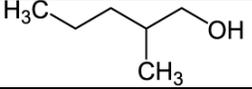
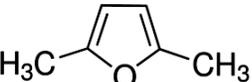
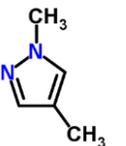
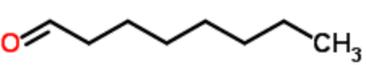
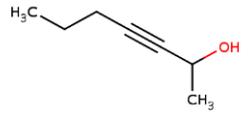
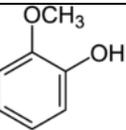
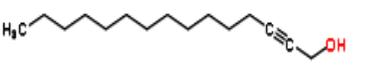
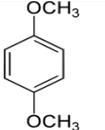
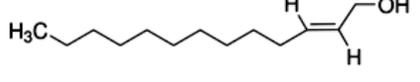
Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
01	Propene	C ₃ H ₆		Production of propylene oxide, acrylonitrile, cumene, butyraldehyde, and acrylic acid	Aliphatic compound
02	But-1-ene	C ₄ H ₈		Production of polyethylene, and as a precursor to polypropylene resins, butylene oxide, and butanone	Aliphatic compound
03	Ethylene oxide	C ₂ H ₄ O		Synthesis of ethylene glycols, including diethylene glycol and triethylene glycol	Heterocyclic compound
04	Propane	C ₃ H ₈		Fuel for engines, oxy-gas torches, portable stoves, and residential central heating	Aliphatic compound
05	Acetaldehyde	C ₂ H ₄ O		Used as a precursor to acetic acid.	Aliphatic compound

Table 5.3.5: Possible identified compounds in Japanese cedar wood pyrolysis oil by GC/MS analysis with their structural formula and applications

Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
01	Ethyl acetate	$C_4H_8O_2$		Glues, nail polish removers, decaffeinating tea and coffee, and cigarettes	Aliphatic compound
02	2-Propenyl acetate	$C_5H_8O_2$		Synthetic flavoring agent, glycerol and precursor for drying oils	Aliphatic compound
03	4-Hydroxy-4-methylpentan-2-one	$C_6H_{12}O_2$		Used as a solvent, lacquer thinners, printing pastes, permanent markers; in making artificial silk and leather, in metal cleaning compounds and in the manufacture of photographic film	Aliphatic compound
04	1-hydroxy-2-propanone	$C_3H_6O_2$		Manufacture drugs, spices, dyes, organic intermediates	Aliphatic compound
05	Butan-2-one	C_4H_8O		Used as an industrial solvent & as a plastic welding	Aliphatic compound
06	1-nitropentane	$C_5H_{11}NO_2$		used as organic nitrogen (ON) standard in quantitative method for the speciation of ON within ambient atmospheric aerosol	Aliphatic compound
07	3-Hexyne-2,5-diol	$C_6H_{10}O_2$		Used in chemical intermediate	Aliphatic compound
08	2-Methyl-1-pentanol	$C_6H_{14}O$		Used as a solvent and an intermediate in the manufacture of other chemicals	Aliphatic compound

Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
09	2-isononenal	$C_9H_{16}O$			Aliphatic compound
10	2,5-dimethylfuran	C_6H_8O		Serves as a scavenger for singlet oxygen	Heterocyclic compound
11	1,4-dimethylpyrazole	$C_5H_8N_2$		Manufacturing of basic chemicals, pesticide, fertilizer, pharmaceuticals	Aromatic compound
12	Octanal	$C_8H_{16}O$		Perfumes and in flavor production for the food industry	Aliphatic compound
13	3-heptyn-2-ol	$C_7H_{12}O$			Aliphatic compound
14	2-methoxyphenol	$C_7H_8O_2$		Flavorants, such as eugenol and vanillin, antiseptic, and local anesthetic; and as an indicator in chemical reactions that produce oxygen	Aromatic compound
15	pentadec-2-yn-1-ol	$C_{15}H_{28}O$		Employed as starting reagent for the synthesis of (-)-muricatacin and in the preparation of (2Z)-3-tributylstannyl-2-penten-1-ol	Aliphatic compound
16	1,4-Dimethoxybenzene	$C_8H_{10}O_2$		perfumes and soaps	Aromatic compound
17	(E)-tridec-2-en-1-ol	$C_{13}H_{26}O$		Flavor and fragrance agents	Aliphatic compound

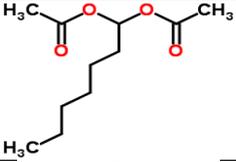
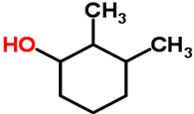
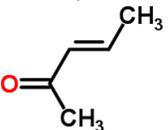
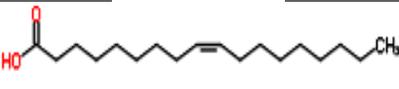
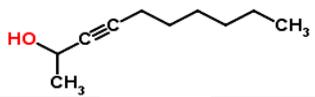
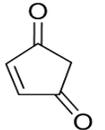
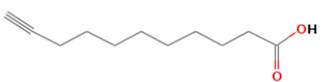
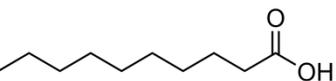
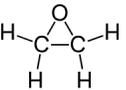
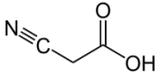
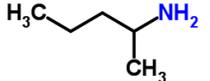
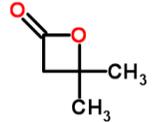
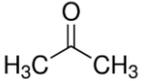
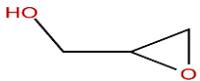
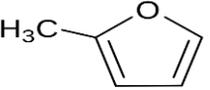
Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
18	1-acetyloxyheptyl acetate	$C_{11}H_{20}O_4$			Aliphatic compound
19	2,3-dimethylcyclohexan-1-ol	$C_8H_{16}O$		natural substances and extractives	Alicyclic compound
20	3-Penten-2-one	C_5H_8O		Used in the synthesis of the alkaloids	Aliphatic compound
21	Oleic acid	$C_{18}H_{34}O_2$		Used as an emulsifying agent in soap, aerosol products and induce lung damage in certain types of animals	Aliphatic compound
22	3-Decyn-2-ol	$C_{10}H_{18}O$			Aliphatic compound
23	cyclopent-4-ene-1,3-dione	$C_5H_4O_2$		Synthesis of 2-methoxymethylene-4-cyclopentene-1,3-dione	Homocyclic compound
24	Undec-10-ynoic acid	$C_{11}H_{18}O_2$		Form molecular layers & in synthesis process	Aliphatic compound
25	Decanoic acid	$C_{10}H_{20}O_2$		Used in the manufacture of esters for artificial fruit flavors and perfumes, lubricants, greases, rubber, dyes, plastics, food additives, pharmaceuticals and in synthesis process	Aliphatic compound
26	Tetradecanal	$C_{14}H_{28}O$		Food spice, fragrance, flavor milk, incense and so on	Aliphatic compound

Table 5.3.6: Possible identified compounds in Japanese cedar wood pyrolysis gas by GC/MS analysis with their structural formula

Serial No.	Possible identified compounds	Chemical formula	Structural formula	Possible uses	Classification
01	Ethylene oxide	C ₂ H ₄ O		Synthesis of ethylene glycols, including diethylene glycol and triethylene glycol	Heterocyclic compound
02	2-cyanoacetic acid	C ₃ H ₃ NO ₂		Used in the preparation of chemicals and drugs	Aliphatic compound
03	Pentan-2-amine	C ₅ H ₁₃ N		Used as a solvent, as a raw material in the manufacture of dyes, emulsifiers, and pharmaceutical products and as a flavoring agent	Aliphatic compound
04	4,4-Dimethyl-2-oxetanone	C ₅ H ₈ O ₂			Aliphatic compound
05	Acetone	C ₃ H ₆ O		Used as a solvent, medical and cosmetic uses & domestic and other niche uses	Aliphatic compound
06	Glycidol	C ₃ H ₆ O ₂		Natural oil, vinyl polymers, surface coatings, chemical synthesis, pharmaceuticals, sanitary chemicals and sterilizing milk of magnesia, and in synthesis process	Aliphatic compound
07	2-Methylfuran	C ₅ H ₆ O		Flavoring substance, with the potential for use in alternative fuels	Heterocyclic compound

5.4 Classification of identified compounds present in selected biomass derived pyrolysis oils

The identified compounds presented in the selected biomass derived pyrolysis oil have been classified into three major groups: aliphatic, aromatic and alcohol.

Aliphatic: An aliphatic compound is a hydrocarbon compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings. The aliphatic compounds are three types such as alkanes containing single bonds, alkenes formed with double bonds and alkynes containing one carbon-carbon triple bonds.

Aromatic: A hydrocarbon that contains one or more benzene rings that is characteristic of the benzene series of organic compounds. The ring structure is very stable and accommodates additional $-\text{CH}_2$ groups in side chains and not by ring expansion.

Alcohol: A substance containing an OH group attached to a hydrocarbon group. In these organic compounds, one hydroxyl ($-\text{OH}$) group is substituted for one hydrogen atom.

5.4.1 (a) Jute sticks oil

Aliphatic:

SL. No.:	Possible identified compounds	Area (%)
03	2(3H)-benzofuranone	0.400
06	2,6-dimethoxy Phenol	0.621
13	2-isononenal	1.405
14	2-pentanone	5.082
15	2,5-dimethyl-furan	3.80
17	1-hydroxy-2-propanone	17.324
18	3-hydroxy-2-butanone	8.104
19	2-propenyl ester acetic acid	12.920
20	Ethyl acetate	4.940
21	n-propyl acetate	3.930
TOTAL		58.526

$$\% \text{ of Aliphatic} = \frac{58.526}{75.95} \times 100 = 77.07\%$$

Aromatic:

SL. No.:	Possible identified compounds	Area (%)
04	2-Cyclohexen-1-one	0.506
07	2-methoxy-3-(1-methylethyl)-pyrazine	1.133
08	2-methoxy -4-methyl – Phenol	0.929
09	1-(1-cyclohexen-1-yl)- ethanone	0.737
10	3-methyl 1,2-cyclopentanedione	0.757
11	3-heptyn-2-ol	0.797
16	3-methyl -cyclohexano	2.440
22	4-2-(methylamino)ethyl- phenol	7.150
TOTAL		14.631

$$\% \text{ of Aromatic} = \frac{14.631}{75.95} \times 100 = 19.26 \%$$

Alcohol:

SL. No.:	Possible identified compounds	Area (%)
01	3-Decyn-2-ol	0.308
02	Hexadecanol	0.639
05	1-hydroxilinalool	0.694
12	4-Ethylcyclohexanol	1.330
TOTAL		2.789

$$\% \text{ of Alcohol} = \frac{2.789}{75.95} \times 100 = 3.67\%$$

5.4.1 (b) Jute sticks gas

SL. No.:	Possible identified compounds	Area (%)
01	1-Propane Allyene	5.33
02	L-Alanine, ethyl ester	32.17
03	Acetonitrile	5.33
04	Acetic acid cyano	32.17
TOTAL		75.00

5.4.2 (a) Tamarind seed oil**Aliphatic:**

SL No.:	Possible identified compounds	Area (%)
01	Ethanethioic acid	2.68
02	N-Propyl Acetate	2.97
04	5-Hexen-2-one	10.19
06	1-Methylbutyl Hydroperoxide	13.95
07	2-Bromo-2-Methyl-Pentane	2.57
08	Dodecanal	2.04
11	2-Ethyl-2-Pentenal	1.31
17	Oleic Acid	0.98
TOTAL		36.69

$$\% \text{ of Aliphatic} = \frac{36.69}{75.009} \times 100 = 48.91\%$$

Aromatic:

SL. No.:	Possible identified compounds	Area (%)
09	Phenol	2.04
12	3-Methyl Phenol	1.72
14	3-Decyn-2-ol	0.85
15	1-Dodecyne	1.04
TOTAL		5.65

$$\% \text{ of Aromatic} = \frac{5.65}{75.009} \times 100 = 7.53\%$$

Alcohol:

SL. No.:	Possible identified compounds	Area (%)
03	1-Propen-2-ol	25.92
05	2-Methyl-1-propanol	2.54
10	3-Octyn-2-ol	1.52
13	2-Nonen-1-ol	0.91
16	2-Tridecen-1-ol	1.23
TOTAL		32.12

$$\% \text{ of Alcohol} = \frac{32.12}{75.009} \times 100 = 42.82\%$$

5.4.2 (b) Tamarind seed gas

SL. No.:	Possible identified compounds	Area (%)
01	Propene	45.42
02	1-Butane	19.97
03	Ethylene Oxide	3.44
04	Dimethyl methane	3.07
05	Acetaldehyde	3.07
TOTAL		74.97

5.4.3 (a) Japanese cedar wood oil**Aliphatic:**

SL. No.:	Possible identified compounds	Area (%)
01	Ethyl Acetate	2.60
02	2-Propeneyl ester, acetic acid	10.40
04	1-Hydroxy-2-propanone	12.00
05	2-Butanone	14.4
06	1-Nitro-Pentane	3.40
09	2-Isononenal	1.90
19	2,3-Dimethyl cyclohexanol	0.32
21	Oleic acid	0.28
26	Tetradecanal	0.22
TOTAL		45.52

$$\% \text{ of Aliphatic} = \frac{45.52}{73.32} \times 100 = 62.08 \%$$

Aromatic:

SL. No.:	Possible identified compounds	Area (%)
10	2,5-Dimethyl-Furan	1.90
11	1,4-Dimethyl Pyrazole	3.80
12	Octanal	1.30
14	2-Methoxy- Phenol	2.23
16	1,4-Dimethoxy-Benzene	1.60
20	3-Pentane-2-one	0.35
22	3-Decyn-2-ol	0.43
23	4-Cyclopentene-1,3-dione	0.34
TOTAL		11.95

$$\% \text{ of Aromatic} = \frac{11.95}{73.32} \times 100 = 16.30\%$$

Alcohol:

SL. No.:	Possible identified compounds	Area (%)
03	4-Hydroxy-4-methyl-2-Pentanone	10.39
07	3-Hexyne-2,5-diol	2.60
08	2-Methyl-1-Pentanol	2.10
15	2-Pentadecyn-1-ol	0.28
17	2-Tridecen-1-ol	0.23
18	1,1-Heptanediol,diacetate	0.55
24	Undec-10-ynoic acid	0.40
25	Decanoic acid	0.55
TOTAL		17.10

$$\% \text{ of Alcohol} = \frac{17.10}{73.32} \times 100 = 23.32\%$$

5.4.3 (b) Japanese cedar wood gas

SL. No.:	Possible identified compounds	Area (%)
01	Ethylene oxide	63.33
02	Acetic acid,cyano	1.01
03	2-Pentamine	0.04
04	4,4-dimethyl-2-Oxetanone	0.42
05	Acetone	3.49
06	2,3-Epoxy-1-Propa	0.30
07	2-methyl -Furan	0.24
TOTAL		68.83

The major identified compounds in jute stick derived pyrolysis oils are 2,5-dimethyl-furan, 1-hydroxy-2-propanone, 3-hydroxy-2-butanone, 2-propenyl ester acetic acid, 4-(2-methyl)ethyl-phenol and their respective uses are blue light, flavor and fragrance agents and absorbent paper [80]. The dominating compounds in the jute stick pyro-gas are L-alanine-ethyl ester and acetic acid cyano that are widely used in Catalyzed reaction and biomedical applications and water spray, dye-sensitized solar cells and eye ointment.

The remarkable identified compounds in tamarind seed derived pyrolysis oils 5-hexen-2-one, 1-methylbutyl hydro-peroxide, oleic acid and their respective uses are evaporative light-scattering detection, covalently to silica gel, reduction of polyphonic and photo catalytic applications, sunlight and dispensing of high-purity acids [80]. The dominating compounds in the tamarind seed pyro-gas are propane, 1-butane that are widely used in polyethylene and thermoplastics, paint coating and pharmaceuticals.

The major identified compounds in Japanese wood oil derived pyrolysis oils are 2-propenyl ester-acetic acid, 1-hydroxy-2-propanone, 2-butanone and their respective uses are oxidizing agent and solvents, water spray to keep fire-exposed containers cool, flavor and fragrance agents, paints and coatings [69,77]. The dominating compounds in Japanese cedar wood pyro-gas are ethylene oxide, acetone that is widely used in industrial chemicals, biological research.

In the chemical compositional analysis of jute stick oil, it is found that among the identified compounds total alcohol originated 3.67%, aromatic 19.26%, and aliphatic 77.07% while these percentage in tamarind seed oil are alcohol 42.82%, aromatic 7.53%, and aliphatic 48.91% and is Japanese cedar wood oil are alcohol 23.32%, aromatic 16.30%, and aliphatic 62.08%.

Previous research group [82] worked with two energy crops: switchgrass, alfalfa and found aromatic compounds: toluene, styrene, and methyl naphthalene etc. The identified aliphatic compounds are acetic acid, propionic acid and the alcoholic compounds are ethylene glycol and hydroquinone etc. A huge amount of aromatic hydrocarbon work found in their study.

Salleh et al. [83] studied GC/MS for bio-fuel source from combination feed of sewage sludge, rice waste and identified aromatic compounds are 1-dodecane, benzofuran, toluene; the aliphatic compounds are 1-decene, octamethyl, 1-hexadecane etc. The alcoholic compounds are present in small amount.

Previous research group [84] worked with “analytical pyrolysis characteristics of enzymatic/mild acidolysis lignin from sugarcane bagasse” and found that aromatic compounds are 2-methyl-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol etc. The aliphatic compounds are Furfural, 4-methyl-2, 6-dimethoxybenzaldehyde and the alcohol compounds are eugenol, 2-allylphenol etc.

Rui lou et al. [85] studied GC/MS for “pyrolytic products from rice straw and enzymatic/mild acidolysis lignin (emal)” and identified aromatic compounds are 2-methoxy-phenol, 4-ethyl-phenol, 2-methoxy-4-(1-propenyl)-phenol etc.; the aliphatic compounds are acetic acid, propanoic acid, 1-hydroxy-2-propanone etc. The alcoholic compounds are tetrahydro-2-furan methanol, 2-furan methanol etc.

Another research group [81] worked with “heterogeneous and homogeneous reactions of pyrolysis vapors from pine wood” and found that aromatic compounds are 2-hydroxy benzaldehyde, 2-hydroxy-4-methylbenzaldehyde, cresol, phenol etc.; the aliphatic compounds are hydroxy-acetaldehyde, 3-hydroxy-Propionaldehyde, croton aldehyde etc. and the alcoholic compounds are coniferyl alcohol, 4-methyl-guaiacol, 4-ethyl-guaiacol

5.5 Conclusions:

- The aliphatic, aromatic and alcoholic compounds present in jute stick pyrolysis oil are 77.07, 19.26 and 3.67 wt% respectively, while these for tamarind seed 48.91, 7.53 and 42.82 wt%, and for cedar wood 62.08, 16.30, and 23.32 wt%, respectively.
- The major identified compounds are 2,5-dimethyl-furan, 1-hydroxy-2-propanone, 3-hydroxy-2-butanone, 2-propenyl ester acetic acid, 4-(methyl)ethyl-phenol in jute stick derived pyrolysis oils; 5-hexen-2-one, 1-methylbutyl hydro-peroxide, oleic acid in tamarind seed derived pyrolysis oils; and 2-propenyl ester-acetic acid, 1-hydroxy-2-propanone, 2-butanone in cedar wood derived pyrolysis oils.

Recommendations**6.1 Recommendations**

This study is hoped to fill some of the gapes existing between research and applications on pyrolysis conversion of biomass solid wastes to liquid fuels and chemicals, and to compliment the vast existing data on pyrolysis technologies for the production of liquid fuel. Based on this study, several recommendations which is hoped to pave the way for other researchers in this area are suggested.

6.1.1 On the current experimental set-up

The liquid yield of jute stick, cedar wood and tamarind seed from the fixed bed reactor quite satisfactory. However, the performance of the system could be improved further, to produce more reliable and better results. The following recommendations are suggested for such improvement.

- The effect of other possible process parameters such as the presence of catalyst, and different pyrolysis atmosphere may be studied.
- The study on the energy and full material balances, and the optimization of the operating conditions, should be conducted with a view of scaling up the system.
- The char products from pyrolysis of jute stick, cedar wood and tamarind seed were reasonably high. The high char yield has a potential value as a solid fuel or as activated carbon and further characterization of the char is suggested. The energy content of the char could be utilized through combustion to pre-heat the N₂ gas. The gaseous product may also be taken into consideration.

Recommendations

- The consumption of expensive inert N₂ gas was high. The gas product could be recycled as inert gas. However, the effect of the use of recycling gas of the pyrolysis product yield and characteristics should be studied first.

6.1.2 On the future work

Jute-stick, tamarind seed and cedar wood solid wastes pyrolysis is a new concept and unique to Japan and Bangladesh, and have not been studied extensively elsewhere. With the availability of large amount of solid waste, more research on pyrolysis process technologies and product utilization should be conducted, which would finally provide a way to maximize their utilization. The research may include the improvement of liquid yield through basic and applied researches, a pilot-plant performance study, environmental aspects and detailed techno-economic assessment of the process. The comparison of liquid yield and characteristics from fixed bed pyrolysis process may be studied. The study can be extended further to other types of organic solid wastes which are found in abundance locally, such as other agricultural residues, rubber and plastic wastes, municipal wastes etc.

Further characterization studies on pyrolysis liquid products on solid wastes such as Jute-stick, tamarind seed and cedar wood should be conducted to provide ways of utilizing the liquid as fuels in boiler, internal combustion engine etc. or as value added chemicals. The data on the stability and consistency of the liquid, the combustion characteristic etc. are important for the direct utilization of the liquid as fuel. Catalytic upgrading of the liquid products to higher utility fuels, using various types of catalyst may also be studied. Catalytic upgrading of liquid products may be conducted in two possible ways:

- The pyrolysis liquid is collected and later it is subjected to the upgrading process.
- The pyrolysis vapor is passed directly to the catalytic reactor without prior condensation.

The advantages of each routes in terms of liquid fuel yield, fuel quality etc. may be studied. Finally the fuel may be tested in an internal combustion engine.

References

- [1] Sayigh. A, Comprehensive Renewable Energy, 1st Edition, 17th June, 2012.
- [2] Gassi. M, Relationship between environmental factors, tapping dates, tapping intensity and gum arabic yield of an Acacia senegal plantation in western Sudan, 2005, 63(2): 379-389.
- [3] Rodriguez. I.M, laresgoitti. M.F, Cabrero. M.A, Torres. A, Chommon. M.J, Caballero. B.M, Pyrolysis of scrap tyres. Fuel and Process Tech, 2001, 72: 9-22.
- [4] Laresgoiti. M.F, Caballero. B.M, Marco I. de, Torres. A, Cabrero. M,A, Characterization of the liquid products obtained in tyre pyrolysis, J. Anal. Appl. Pyrolysis, 2004, 71: 917-934.
- [5] Gonzalez. J.F, Enchinar. J.M, Canito. J.L, Rodriguez. J.J, Pyrolysis of automobile tyre waste. Influence of operating variables and kinetics study. J. Anal. Appl. Pyrolysis, 2001, 58-59: 667-683.
- [6] Diebold. JP and Bridgwater. AV, Overview of fast pyrolysis of biomass for the production of liquid fuels. In : Bridgwater AV and Boocock DGB (eds).Development of thermochemical biomass conversion London: Blackie. Academic and professional, 1997, 5-23.
- [7] Ferdous. D, Dalari. AK, Bej. SK , Pyrolysis of lignin's : experimental and kinetic studies. Energy & Fuels, 2002, 16: 1405-1412.
- [8] Capart. R, khezami. L, Burnham. AK, Assessment of various kinetic models for the pyrolysis of microgranular cellulose. Thermo-chemacaActal, 2004, 417 – 7989.
- [9] McKendry. P, Energy production from biomass wastes. Renewable energy, 2002, 83: 37.
- [10] Ebeling. J.M, Jenkins. B.M, Physical and chemical properties of biomass fuels. Bio-resource Technology, 1958, 28: 898.
- [11] Diebold. JP., Bridgwater. A.V, Overview of fast pyrolysis of biomass for the production of liquid fuels. Fuel, 1997, 5: 23.
- [12] Lukáš. G, Zuzana. K, L'udovít J, Kinetic study of wood chips decomposition by TGA. Renewable energy, 2012, 64(2): 174-181.
- [13] Birch. C, Purpose in the Universe: A search for wholeness, 1971, 1: 4-27.

- [14] Williams. PT and Besler. S, Thermo-gravimetric analysis of the components biomass, in Bridgwater AV, Advances thermochemical biomass conversion, Blackie academic Professional, London, 1994, 771-783.
- [15] Antar. JR. MJ, Vahgyi. G, Cellulose pyrolysis kinetics, the current state of knowledge. In. Eng. Chem. 1995, 34(3): 703-717.
- [16] Diebold. JP and Bridgwater. AV, Overview of fast pyrolysis of biomass for the production of liquid fuels. In: Bridgwater AV and Boocock DGB. (eds.) Development of thermochemical biomass conversion London: Blackie. Academic and professional, 1997, 5-23.
- [17] Aysu. T, Kucuk. M, Biomass pyrolysis in a fixed –bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. Energy 2014, 64: 1002-1025.
- [18] Chido. V, Maisano. G, Freny. S, Urbani. F, Pyrolysis of different biomass: Direct comparison among Posidonia Oceanica, Lacustrine Alga and White-Pine. Fuel, 2016, 164: 220-227.
- [19] Cepeliogullar. O, Putun. A.E, Products characterization study of a slow pyrolysis of biomass-plastic mixtures in a fixed –bed reactor. J. Anal. App. Pyrolysis, 2014, 110: 363-374.
- [20] Islam. MR, Thermal Decomposition behavior study of two Agricultural solid wastes for production of bio-fuels by Pyrolysis Technology. Thermal Science & Technology, 2011, 6 (1): 132-138.
- [21] Chen, Andries G, Spliethoff J, and Leung H, DYC, Experimental investigation of biomass waste (rice straw, cotton stalk and pine sawdust) pyrolysis characteristic. Energy Source, 2003, 25: 331-337.
- [22] Williams. PT and Besler S, Thermo-gravimetric analysis of the components biomass, in Bridgwater AV. Advances thermochemical biomass conversion, Blackie academic Professional, London, 1994, 771-783
- [23] Antar. JR. MJ, Vahgyi G, Cellulose pyrolysis kinetics, the current state of knowledge. In. Eng. Chem. 1995, 34(3): 703-717.
- [24] Cunliffe. A.M, Wiliams P.T, Composition of oils derived from the batch pyrolysis of tyres J. Anal. Appl. Pyrolysis, 1998, 44: 131-52.

- [25] Barbooti. M.M, Mohammamd. T, Hussain. A.A, Abas. F.O, Optimization of pyrolysis conditions of scrap tires under inert gas atmosphere. *J. Anal. Appl. Pyrolysis*, 2004, 72: 165-170.
- [26] Ollero. P, Serrera. A, Arjona. R, Diffusional effect in TGA gasification experiments for kinetic determination. *Fuel*, 2002, 81: 1898-2000.
- [27] Putun. A.P, Luzon. B.B, Putun. E, Bio-oil from olive oil industry wastes: Pyrolysis of olive residue under different condition. *Fuel processing technology*, 2005, 87: 25-32.
- [28] Onay. O and O.M, Fixed bed pyrolysis of rape seed (*Brassica napus L.*), *Biomass and Bio energy*, 2004, 26: 289-299.
- [29] Yaman. S, Pyrolysis of biomass to produce fuels and chemicals feed stocks. *Energy conversion and management*, 2004, 45: 651-671.
- [30] Zahang. S, Yan. Y, Li. T and Ren. Z, Upgrading of liquid fuel from the pyrolysis of biomass. *Bio-resource technology*, 2005, 96: 545-550.
- [31] Web Links
- a. <http://www.frtr.gov/matrix2/section4/4-25.html>
 - b. <http://www.llnl.gov/IPandC/op96/03/3h-mol.html>
 - c. <http://www.bestenergies.com/companies/bestpyrolysis.html>
 - d. <http://www.DirectScience.com>
 - e. <http://www.en.wikipedia.org>
- [32] 2014 Statistical Yearbook of Bangladesh, Government of Bangladesh, June, 2015.
- [33] Chubinski. A.N, Sosna. L.M. and Tsoy J.I, Cedar a good material for laminated veneer lumber reduction. *International timber engineer conference*, Tokyo, Japan, 1990, 227-230.
- [34] Jenkins. B.M, Baxter. L.L. and Miles. JR, Characterization of MIS structures and PTFTs using TiOx deposited by spin-coating *Fuel Process Technol. Fuel* 1998, 54: 898.
- [35] Yang. H, Yan. R, Chen. H, Zheng. C, HoLee. D, and David. T.L, In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy & Fuels*, 2006, 20: 388-393.
- [36] Fan-fei. MIN, ZHANG. M, Chen. Q, Non-isothermal kinetics of pyrolysis three kinds of fresh biomass. *J China University Mining & Technology* 2007, 17(1): 0105-0111.

- [37] Peng. QW, Tu. P, Zhao. N, Pyrolytic characteristics of microalgae as renewable energy source determined by thermos-gravimetric analysis. *Bio-resource technology*, 2001, 80: 1-7.
- [38] Sorum, L, Groni. MG, Hustad. JE, Pyrolysis characteristics and kinetics of municipal solid wastes. *Fuel*, 2001, 27: 135-140.
- [39] Garica-Perez. M, Chaala. A, Pakdel. H, Kretschmer. D, Roy C, Vacuum Pyrolysis of softwood and hard wood biomass: Comparison between product yields and bio-oil properties. *Anal J. Appl. Appl. Pyrolysis*, 2007, 78: 104-116.
- [40] Kim. SS, Foster. A. Agblevor, Pyrolysis characteristics and kinetics of chichen litter. *Waste Management*, 2007, 27: 135-140.
- [41] Caballero. J.A, Conesa. J.A, Font R, Marcilla A, Pyrolysis kinetics of almond shells and olives stones considering their organic fractions. *Journal of Analytical and Applied Pyrolysis*, 1997, 42: 159-175.
- [42] Onay. O and Kockar. O.M, Fixed bed pyrolysis of rapeseed (*Brassica Napus L.*). *Biomass and Bioenergy*, 2004, 26: 651-671.
- [43] Acikgoz. C, Onay. O and Kockar. O.M, Fast pyrolysis of linseed: product yields and compositions. *J Anal App. Pyrolysis*, 2004, 71: 417-429.
- [44] Kilky. C.S, Rinaldi N and Simanungkalit S.P, "Bio-oil from fast pyrolysis of empty fruit bunch at various temperature. *J. Renewable energy and Energy Conservation*, 2015, 65: 162-169.
- [45] Horne. P.A, Willium. P.T, Influence of temperature on the products from the flash pyrolysis of biomass. *Fuel*, 1997, 75: 1051-1059.
- [46] Islam. M.N, Zailani.R, Ani. F.N., Pyrolysis oil from fluidized bed pyrolysis of oil palm shell and its characterization. *Renewable Energy*, 1999, 17: 73-84.
- [47] Mansaray. K.G, Ghaly. A.E, Thermal degradation of rice husks in nitrogen atmosphere. *Bio-source Technology*, 1938, 65: 13-20.
- [48] Karaosmanoglu. F, Culcuoglu. E, Pyrolysis of rapeseed cake. *Energy Sources*, 2001, 23: 377-382.
- [49] Demirbas. A, Caglas. A, Akdeniz. F, Gullu. F, Conversion of olive husk to liquid fuel by pyrolysis catalytic liquefaction. *Energy Sources*, 2000, 22: 411-420.
- [50] Willium. P.T, Besler. S, The influence of temperature and heating rate on pyrolysis biomass. *Renewable Energy*, 1998, 7: 233-250.

- [51] Putun. A.E, Ozbay. N, Kockar. OM, Putun. E, Fixed bed pyrolysis of cotton seed cake: product yields and compositions. *Energy Sources*, 1997, 19: 905-915.
- [52] Yorgun. S, Sensoz. S, Kockar. O.M, Flash pyrolysis of sun flower oil cake for production of liquid fuels. *J. Anal Appl. Pyrolysis*, 2001, 60: 1-12.
- [53] Drummond. A.R.F, Drummond. I.W, Pyrolysis of sugar cane bagasse in a wire-mesh reactor. *Ind. Eng. Chem. Res*, 1997, 35: 1263-1268.
- [54] Rick. F, Product standards for pyrolysis products for use as fuel in industrial firing plants. In: A.V. Bridgwater, G. Grassi, editor. *Biomass pyrolysis liquids upgrading and utilization*, London: Elsevier Science, 1991, 177- 218.
- [55] Caglar. A, Demirbas. A, Conversion of cotton cocoon shell to liquid products by pyrolysis. *Energy Conversion & Management*, 2000, 41: 1749-1756.
- [56] Islam. M.N, Zailani. R, Ani. F.N, Pyrolysis oil from fluidized bed pyrolysis of oil palm shell and its characterization. *Renewable Energy*, 1997, 17: 73-84.
- [57] Horne. P.A, Willium. P.T, Influence of temperature on the products from the flash pyrolysis of biomass. *Fuel*, 1997, 75: 1051-1059.
- [58] Islam. M.N, Zailani. R, Ani. F.N, Pyrolysis oil from fluidized bed pyrolysis of oil palm shell and its characterization. *Renewable Energy*, 1999, 17: 73-84.
- [59] Mansaray. K.G, Ghaly. A.E, Thermal degradation of rice husks in nitrogen atmosphere. *Bio-source Technology*, 1998, 65: 13-20.
- [60] Karaosmanoglu. F, E. Culcuoglu. E, Pyrolysis of rapeseed cake. *Energy Sources*, 2001, 23: 377-382.
- [61] Demirbas. A, Caglas. A, Akdeniz. F, Gullu. D, Conversion of olive husk to liquid fuel by pyrolysis catalytic liquefaction. *Energy Sources*, 2000, 22: 411-420.
- [62] Willium. PT, Besler. S, The influence of temperature and heating rate on pyrolysis biomass. *Renewable Energy*, 1998, 7: 233-250.
- [63] Putun. A.E, Ozbay. N, Kockar. O.M, Putun. E, Fixed bed pyrolysis of cotton seed cake: product yields and compositions. *Energy Sources*, 1997, 19: 905-915.
- [64] Yorgun. S, Sensoz. S, Kockar. O.M, Flash pyrolysis of sun flower oil cake for production of liquid fuels. *J. Anal Appl. Pyrolysis*, 2001, 60: 1-12.
- [65] Islam. MR, Fluidized bed pyrolysis of biomass solid wastes for alternative liquid fuel production. M.Sc thesis. Dept. of Mechanical Engineering, Rajshahi University of Engineering and Technology, Sept. 2002.

- [66] Putun. A.P, Luzon B.B.E, Putun. A.E, Bio-oil from olive oil industry wastes: Pyrolysis of olive residue under different condition. *Fuel processing technology*, 2005, 87: 25-32.
- [67] Guanyi.C, Zahang. X, Ma. W, Yan B and Yanbin Li, Co-pyrolysis of corn-cob and waste cooking-oil in a fixed bed reactor with HY upgrading process. The 6th International Conference on Applied Energy-ICAE, 2014, 61: 2363-2366.
- [68] Peng. W.Q, Pingguan Tu, Naming. Z, Pyrolytic characteristics of microalgae as renewable energy source determined by thermos-gravimetric analysis. *Bio-resource technology*, 2001, 80: 1-7.
- [69] Caglar. A, Demirbas. A, Conversion of cotton cocoon shell to liquid products by pyrolysis. *Energy Conversion & Management*, 2000, 41: 1749-1756.
- [70] Sait. Y, Yildiz S, Slow pyrolysis of paulownia wood: Effect of pyrolysis parameters on product yields and bio-oil characterization. *J. Anal Appl. Pyrolysis*, 2015, 114: 68-78.
- [71] Barbarry. H.El., Elsayed. I, Eseyin. A, Production high yields of aromatic hydrocarbons through fast pyrolysis of torrefied wood and polystyrene. *Fuel*, 2016, 174: 317-324.
- [72] Evans. R.J, Milne. T, Molecular-beam, mass-spectrometric studies of wood vapor and model compounds over an hzsm-5 catalyst. In: Soltes, E.J. and Milne, T.A. (Eds.). *Pyrolysis oils from biomass producing analyzing, and upgrading*. Washington: America Chemical Society, 1988, 311-327.
- [73] Islam. M.N, Beg. M.R.A, and Islam. MR, Pyrolytic oil from fixed bed pyrolysis of municipal solid waste and its characterization, *Renewable Energy* , 2005, 30: 413-420.
- [74] Jeong. K.W, Lee, W.H, Jeon. J, Ryu. C, Park. S.H, Park. Y.K, Influence of reaction condition on bio-oil production from pyrolysis of construction waste wood. *Renewable Energy*, 2014, 65: 41-48.
- [75] Charles. H, Muley. P.D, Abdollahi. K,K, Marculescu. C, Boldor. D, Pyrolysis of energy cane bagasse and invasive Chinese tallow tree (*Triadica sebifera* L.) biomass in an inductively heated reactor. *Energy Conversion and Management*, 2016, 109: 175-183.
- [76] Lu. Q, Li, Wen-Zhi, Zhu, Feng. X, Overview of fuel properties of biomass fast pyrolysis oils. *Energy Conversion and Management*, 2009, 50: 1376–1383.

- [77] Meier D, New methods for chemical and physical characterization and round robin testing. In: *Fast Pyrolysis of Biomass: A Handbook*. CPL Press, Newbury, 1999.
- [78] Piskorz. J, Mejerski. P, Radlein, D, Scott. D.S, Bridgwater A.V, Fast pyrolysis of sweet sorghum and sweet sorghum bagasse. *Journal of Analytical and Applied Pyrolysis*, 1998, 46: 15–29.
- [79] Parihar. M.F, Kamil. M, An experimental study on pyrolysis of biomass. *Process Safety and Environmental Protection*; Trans IChemE Part B, September, 2007.
- [80] Aysu. T, M. Kucuk. M, Biomass pyrolysis in a fixed –bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. *Energy*, 2014, 64: 1002-1025.
- [81] Chido. V, Maisano. G, Freny. S, Urbani. F, Pyrolysis of different biomass: Direct comparison among *Posidonia Oceanica*, *Lacustrine Alga* and *White-Pine*. *Fuel*, 2016, 164: 220-227.
- [82] Charles. A.M, Akashi. A, Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. *Energy and Fuels*, 2008, 22: 2104-2109.
- [83] Salleh. F.R, Samsuddin, Husin. M, Biofuels source from combination feed of sewage sludge and rice waste. 2011 International Conference on Environment Science and Engineering ipcbee vol.8 (2001) © (2011) iacsit Singapore.
- [84] Lv. G, Wu. S, Yang. Q, Analytical pyrolysis characteristics of enzymatic/mild acidolysis lignin from sugarcane bagasse. *Cellulose chemistry and technology*.
- [85] Rui. L, Wu. S, Lv. G, Guo. D, Pyrolytic products from rice straw and enzymatic/mild acidolysis lignin (emal). Guangzhou, Guangdong 510640, PR Chin.
- [86] Hoekstra. E, Roel, Westerhofa. J.M, Windtb. M, Brilmana. W, Swaaija, W.P.M, Sascha. R.A, Kerstena, Kees. J.A, Hogendoorna, Heterogeneous and homogeneous reactions of pyrolysis vapors from pine wood.

ACKNOWLEDGEMENTS

It is the author's immense pleasure to express her praiser and gratitude to the Merciful Allah, who makes him capable to successfully complete this study.

The author is profoundly indebted to her supervisor Prof Dr. Hiroyuki HANIU of Mechanical Engineering Department, Kitami Institute of Technology, Japan for his proper guidance, inspiration, suggestion and all kinds of support in performing and completing the dissertation works. The author also wish to express her heart felt gratitude to her supervisor who tolerated her shortcomings, showed patience in author all kind of activities relevant to thesis works, remove intricacy in research and made her confidence enough in the research field.

The author would like to express her sincere gratitude to her local supervisor Prof. Dr. Md. Shahidur Rahman, Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Bangladesh for his cooperation to carry out part of the research works in this University and potential encouragement for completing the PhD dissertation works.

The author would like to express her appreciation to the thesis examination committee members: Prof. Dr. Takanobu YAMADA, Dr. Hirotugu MINAMI, Dr. Sharif ULLAH and Dr. Kazuhiro HAYASHIDA of Kitami Institute of Technology for their valuable comments and suggestions to improve the quality of the dissertation book.

The author is also grateful to Dr. Kazunori Takai, Department Mechanical Engineering, Kitami Institute of Technology, Japan for his helping in GC/MS analysis and providing study material in her research work. Warmest and sincere thanks are extended to Mr. Yoshiro Obata, Technical Officer of Fluid Mechanics Laboratory, for his support and expertise in precise fabrication of pyrolysis reactor chamber.

The technical assistance for all of the chemical analyses supported by the technical staffs of Instrumental Analysis Center, Kitami Institute of Technology is gratefully acknowledged.

Also, the patience, understanding, moral support and cooperation of the author's parents and family are deeply acknowledged.

May Allah bless and reward all of them.

Momtaz Parveen

Completed Graduate Course of Manufacturing Engineering
of Kitami Institute of Technology, Japan

Appendix**Data tables for experimental studies of biomass pyrolysis****Table A.1: Effect of temperature on product yields of tamarind seed**

Experiment No.	Temperature (°C)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	300	32	60	8
02	350	38	50	12
03	400	45	40	15
04	450	41	39	20
05	500	40	36	24
06	550	38	35	27

Table A.2: Effect of feed particle size on product yields of tamarind seed

Experiment No	Feed Size (µm)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	150-300	35	45	20
02	300-600	39	43	18
03	600-1180	42	41	17
04	1180-1700	44	40	16
05	1700-2360	42	41	17

Table A.3: Effect of gas flow rate on product yields of tamarind seed

Experiment No.	N ₂ Gas flow rate (l/min)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	2	38	40	22
02	6	45	40	15
03	10	43	41	16
04	14	40	43	17

Table A.4: Effect of running time on product yields of tamarind seed

Experiment No	Running Time (minute)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	10	27	57	16
02	20	33	49	18
03	30	44	37	19
04	40	44	36	20
05	50	44	34	22

Table B.1: Effect of temperature on product yields of jute stick

Experiment No.	Temperature (°C)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	375	38	51	11
02	400	43	45	12
03	425	50	37	14
04	450	46	38	26
05	475	42	36	22
06	500	36	33	31

Table B.2: Effect of feed particle size on product yields of jute stick

Experiment No	Feed Size (µm)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	150-300	31	45	24
02	300-600	38	41	21
03	600-1180	47	37	16
04	1180-1700	50	38	12
05	1700-2360	45	44	11

Table B.3: Effect of gas flow rate on product yields of jute stick

Experiment No.	N ₂ gas flow rate	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	2	40	38	22
02	6	47	40	13
03	10	43	31	16
04	14	40	43	17

Table B.4: Effect of running time on product yields of jute stick

Experiment No	Running Time (minute)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	10	33	55	12
02	20	38	50	114
03	30	46	40	14
04	40	46	38	16
05	50	46	36	18

Table C.1: Effect temperature on product yields of cedar wood

Experiment No	Temperature (°C)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	400	36	52	12
02	450	43	43	14
03	500	48	36	16
04	550	46	34	22
05	600	40	32	24

Table C.2: Effect of feed particle size on product yields of cedar wood

Experiment No	Feed Size (cm ³)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	150-300	33	47	20
02	300-600	37	45	18
03	600-1180	40	43	17
04	1180-1700	46	38	16
05	1700-2360	45	36	19

Table C.3: Effect of gas flow rate on product yields of cedar wood.

Experiment No.	N ₂ gas flow rate	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	2	34	43	23
02	4	41	39	20
03	6	48	37	15
04	8	46	40	14
05	10	44	40	16

Table C.4: Effect of running time on product yields of cedar wood.

Experiment No	Running Time (minute)	Liquid (wt%)	Char (wt%)	Gas (wt%)
01	10	28	58	14
02	20	31	51	18
03	30	41	39	20
04	40	41	37	22
05	50	43	33	24